



55TH INTERNATIONAL CONFERENCE "COAL CITY 2025"



THE NIGERIAN SOCIETY OF CHEMICAL ENGINEERS (NSChE)
(A Division of Nigerian Society of Engineers)

55TH

**INTERNATIONAL CONFERENCE
EXHIBITION & ANNUAL GENERAL MEETING**

Conference Proceedings



Theme:

**The Role & Contribution of SMEs to
National Industrial Development & Growth**

**13th - 15th November, 2025 @ Multi Purpose Hall
International Conference Centre, Enugu.**





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FORWARD

It is with great pleasure that I present this Book of Abstracts for the 55th International Conference, Exhibition and Annual General Meeting of the Nigerian Society of Chemical Engineers, with the theme “The Role and Contribution of Small and Medium Enterprises to National Industrial Development and Growth.” This theme underscores the indispensable role of innovation-driven entrepreneurship and small-scale industrial initiatives in advancing national development, particularly within the chemical and process industries.

Small and Medium Enterprises (SMEs) continue to serve as a bridge between academic research and industrial application. They play a pivotal role in translating scientific discoveries into practical solutions that drive productivity, sustainability, and technological advancement. In the chemical engineering sector, SMEs are crucial in promoting local production, value addition, and resource optimization—thereby enhancing national self-reliance and industrial diversification.

This conference brings together professionals, researchers, policymakers, and industry leaders to exchange ideas, share experiences, and explore strategies for strengthening the SME ecosystem. The papers and abstracts compiled in this volume reflect a broad range of topics, including innovative processing technologies, environmental sustainability, industrial chemistry, entrepreneurship, and policy frameworks that support SME growth.

The synergy between academia and industry—embodied in this gathering—remains central to achieving sustainable industrial development. It is our belief that the insights and findings presented herein will not only enrich scholarly discourse but also inspire actionable pathways toward strengthening SMEs as catalysts for national and regional industrial progress.

On behalf of the Local Organizing Committee, I extend heartfelt appreciation to all contributors, reviewers, and participants for their invaluable input and commitment. May this collection serve as a valuable reference and inspiration for continued collaboration between academia, industry, and government in pursuit of sustainable industrial growth.

Prof. E. O. Ekumankama
LOC Chairman



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CONTENTS

Cover page.....	1
National Executives.....	3
Local Organizing Committee.....	4-6
Foreword.....	7
Content.....	8
Lead Paper One :Roles of Chemical Engineers in Food Security and National Development of Nigeria.....	9-13
Lead Paper Two: “The Role of SMEs in the Industrialisation of Nigeria.....	14-16
Guest Speaker: Sustainable National Energy Supply in Nigeria: A Panacea To Stable Industrial Development and Growth.....	17-20
Lead Paper Three: The Role and Contribution of SMEs to National Industrial Development and Growth: Focusing on Raw Materials Development and Utilization.....	21-31
Lead Paper Four: Solid Minerals Development and Growth in Nigeria.....	32-41
Lead Paper Five: Driving Industrial Growth through Sustainable Waste Management: The Pivotal Role of SMEs.....	42-46
Articles on: Raw Materials and Solid Minerals Development, Utilization and growth....	47-209
Articles on: Sustainable National Energy Supply: A Panacea to Stable Industrial Development and Growth.....	210-346
Articles on: Waste, Environmental Management and Sustainability, Biomaterials and Biosynthesis.....	347-516
Articles on: Food Security for Sustainable Development, Quality Management and Support to SMEs, The Role of AI in Process Industry.....	517-669

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Lead Paper One

ROLES OF CHEMICAL ENGINEERS IN FOOD SECURITY AND NATIONAL DEVELOPMENT OF NIGERIA

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Abstract

Food security remains a major concern in Nigeria despite the nation's abundant agricultural and natural resources. Challenges such as rapid population growth, post-harvest losses, energy shortages, and reduced youth participation in farming continue to threaten sustainable food production. This presentation highlights the critical role of chemical engineers in addressing these challenges and promoting national development. Chemical engineers drive industrialization through agro-processing, renewable energy solutions, waste-to-wealth initiatives, and technologies that add value to local raw materials. Their expertise in process design, resource optimization, and environmental sustainability supports economic diversification and improved food systems. However, issues such as weak infrastructure, inadequate research funding, limited industry-academia collaboration, and inconsistent policy implementation hinder their impact. The presentation calls for stronger government support, policy consistency, and professional empowerment to enable chemical engineers to fully contribute to a food-secure and industrially developed Nigeria.

FOOD SECURITY ISSUES IN NIGERIA

Food security refers to a situation where all people, at all times, have physical, social, and economic access to sufficient, safe, and nutritious food to meet their dietary needs for an active and healthy life. In Nigeria, achieving food security remains a major challenge despite vast agricultural potential and natural resources

FOOD SECURITY CHALLENGES IN NIGERIA

- ❖ Population growth
- ❖ Reduction in basic food production activities
- ❖ Post -harvest losses
- ❖ Energy /water shortages
- ❖ Food safety issues
- ❖ Reduced access to farm
- ❖ Reduced interest in food production by youths

STRATEGIES FOR POSSIBLE IMPROVEMENT

- ❖ Modernize agriculture through mechanization, irrigation, and improved seed varieties.
- ❖ Develop rural infrastructure such as roads, storage, and markets.
- ❖ Invest in agricultural research and extension services.
- ❖ Promote climate-smart and sustainable farming.
- ❖ Strengthening rural security and conflict resolution.
- ❖ Encourage private-sector investment and Agro-processing.
- ❖ Provide access to credit, land, and insurance for farmers.
- ❖ Incentivize investments in Agro processing activities

COMPONENTS OF NATIONAL DEVELOPMENT

National development refers to the comprehensive, sustained improvement in the economic, social, technological, political, and cultural well-being of a nation's citizens. For a country like Nigeria—diverse, resource-rich, and strategically positioned in Africa and awaiting appropriate development—national development requires a balanced approach across multiple interdependent components.

COMPONENTS OF NATIONAL DEVELOPMENT

COMPONENTS	DESCRIPTION
❖ Economic development	Growth in GDP, diversification beyond oil, industrialization, SME promotion, and infrastructure expansion
❖ Human capital development	Quality education, healthcare, technical skills youth empowerment, and gender equality
❖ Political & institutional development	Good governance, transparency, rule of law, democratic participation, anti corruption reforms
❖ Social & cultural development	Poverty reduction, unity and tolerance, expanded welfare programs
❖ Technological & industrial advancement	Research, innovation, local manufacturing digital transformation
❖ Environmental & sustainable development	Environmental protection, renewable energy, sustainable agriculture, urban planning
❖ Infrastructure development	Reliable roads, railways, power supply, water systems, and affordable housing

NATIONAL DEVELOPMENT

National development is a multidimensional process integrating economic, human, political, and environmental progress. It demands visionary leadership, effective policy implementation, citizen participation, technological growth and commitment to inclusive growth.

In Nigeria, there is hardly any other profession that is as equipped as The Chemical Engineer for the task of National Development



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ROLES OF CHEMICAL ENGINEERS

1. Role in Industrial and Economic Development

Chemical engineers are instrumental in driving industrialization, they lead in establishing agro-allied industries, petrochemical plants, biofuel refineries, and manufacturing systems that add value to Nigeria's raw materials and create employment. Their ability to design production plants and optimize resource utilization supports economic diversification

2. Technological Innovation and Environmental Sustainability

Chemical engineers lead innovators in renewable energy, waste-to-wealth conversion, and green processing technologies which promote environmental protection and ensure energy availability for industrial and agricultural applications. These help achieve Nigeria's environmental and developmental goals.

3. Policy, Research, and Capacity Building

Chemical engineers contribute to policy formulation, research, and capacity building through systems thinking and data-driven analysis. Their interdisciplinary approach enables them to advise on energy balance, production efficiency, and technological adaptation — all essential for effective national planning and sustainable food systems.

CROSS DISCIPLINARY VALUE

Chemical engineers stand at the crossroads of science, technology, agriculture, and industry. Generally, in the course of their training, they acquire problem-solving skills, innovation mindset, and process optimization expertise which make them indispensable in any country's quest for food security and national development. By harnessing their capabilities, Nigeria can build a self-reliant, technologically advanced, and food-secure future.

OBSTACLES IMPENDING CHEMICAL ENGINEERS IN NIGERIA IN THEIR BID TO AID FOOD SECURITY AND NATIONAL DEVELOPMENT

The effectiveness of Chemical Engineers in Nigeria is often undermined by systemic, institutional, and infrastructural challenges that limit innovation, industrial application, and professional impact.

1. Poor Industrial Infrastructure

Many manufacturing and processing plants operate with obsolete or inadequate equipment, while industrial parks and technology hubs are nearly absent in our country. Without access to pilot plants,



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testing facilities, and reliable utilities such as electricity, water, and gas, chemical engineers struggle to implement large-scale process designs or pilot new technologies.

2. **Severely Limited Research and Development (R&D) Support**

Research is known to be fundamental to innovation, yet funding for scientific and industrial research in Nigeria remains extremely low. Universities and research institutions lack modern laboratories and equipment.

3. **Weak Link Between Academia and Industry**

There is a persistent disconnect between universities, research institutions, and industries. Many chemical engineering graduates are trained with outdated curricula that emphasize theory over practice, resulting in limited industry-ready graduate engineers.

4. **Inadequate Government Policies and Implementation**

Policies supporting industrialization, agricultural processing, and renewable energy are rare or poorly implemented or inconsistent, Bureaucratic bottlenecks.

5. Weak regulatory frameworks, and lack of incentives for local manufacturing hinder chemical engineers from setting up innovative enterprises that could address national food and energy needs.

6. **Financial Constraints and Investment Challenges**

The high cost of industrial start-ups and limited access to credit deter chemical engineers from commercializing innovations or establishing agro-processing ventures. Banks and investors often view such ventures as high-risk due to long payback periods and uncertain policy environments.

7. **Brain Drain and Professional Underutilization**

Many skilled chemical engineers migrate abroad in search of better opportunities, resulting in a domestic shortage of experienced professionals. Those who remain are often underemployed in unrelated fields, wasting technical potential that could contribute to national projects.

8. **Environmental and Energy Challenges**

Frequent power outages, environmental degradation, and poor waste management affect process industries. Sustainable operations remain difficult under current infrastructural limitations.

9. **Lack of Patriotic support.**

Developments made in Nigeria usually struggle for acceptance by Nigerians. Unfortunately, some of our societal problems are so peculiar to us that solutions from the more developed economies do not work. A very worrisome example is our nation-wide problem with waste management.



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Therefore, in order to maximise the contribution of chemical engineers to food security and national development, Nigeria must address the systematic barriers through investment in infrastructure, research, policy consistency and professional engagement. Empowering chemical engineers with enabling environments and resources will accelerate industrial growth, technological innovation and economic self-sufficiency.

SOME AREAS OF INTEREST

- v Agro-processing facilities
- v Mineral processing facilities
- v Agricultural equipment & chemicals
- v Biochar production
- v Down-stream oil & gas processing
- v Renewable energy generation
- v Chemicals & paints production
- v Palm oil derivatives
- v Smelting of various metals
- v Hvac systems
- v Special solvents for industries
- v Waste management systems & processes

Note: *In an economy like ours, a trained chemical engineer should be an employer of labour*

CONCLUSION

To maximize the contribution of Chemical Engineers to food security and national development, Nigeria must address the systemic barriers through investment in infrastructure, research, policy consistency & implementation, and professional engagement. Empowering chemical engineers with enabling environments and resources and incentives will accelerate industrial growth, technological innovation, and economic self-sufficiency.

At the risk of sounding controversial, I will Boldly state that, in Nigeria, no other professional is equipped like the Chemical Engineer in positively impacting the food security and National development of this resource-rich country. We just need to be supported and encouraged.

THANK YOU

'KELUO B. CHUKWUOGO

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Lead Paper Two

“THE ROLE OF SMEs IN THE INDUSTRIALISATION OF NIGERIA”:

By
Engr. Ben Okah
Managing Director Green and Trees Farms and Machines Ltd.

Abstract

Small and Medium Enterprises (SMEs) play a pivotal role in driving industrialisation and economic diversification in developing nations such as Nigeria. This paper examines the contribution of SMEs to Nigeria's industrial development, focusing on their role in job creation, innovation, value addition, and regional economic integration. Using both secondary data and relevant case studies, the study highlights how SMEs serve as vital links between the agricultural, manufacturing, and service sectors, thereby promoting inclusive industrial growth. Despite their contributions, SMEs face challenges such as inadequate financing, weak infrastructure, limited access to technology, and policy inconsistencies that hinder their full potential. The paper underscores the need for targeted policy interventions, improved access to credit, and enhanced capacity-building programmes to strengthen SME competitiveness. It concludes that sustainable industrialisation in Nigeria depends largely on a supportive ecosystem that empowers SMEs to innovate, expand, and integrate into global value chains. Strengthening SME performance is therefore not only crucial for industrial transformation but also for achieving broader socio-economic goals such as employment generation and poverty reduction.

1. Introduction: Understanding SMEs and Their Relevance

Small and Medium Enterprises (SMEs) are the engine of Nigeria's economic growth. They provide employment, innovation, and industrial linkages, serving as a bridge between raw production and large-scale industrialization. According to the National Bureau of Statistics (NBS): SMEs make up approximately 96% of all Nigerian businesses, provide around 84% of total employment, and contribute about 48% to Nigeria's GDP. Without SMEs, Nigeria's dream of industrialisation cannot be realised.

2. The Connection Between SMEs and Industrialisation

SMEs play a central role in pushing Nigeria from a consumption-based economy to a production-driven industrial system.

- Key Roles:
Manufacturing Backbone: SMEs provide components, spare parts, and intermediate goods for larger industries.

Innovation Drivers: Small enterprises adapt quickly and introduce new products and production techniques.

Employment Creation: They absorb the bulk of Nigeria's workforce, curbing unemployment and reducing poverty.

Rural Industrialisation: Many SMEs operate outside major cities, spreading industrial activity to rural areas.

Examples include fintech SMEs like Paystack and Flutterwave, which transformed financial services, and agro-processing SMEs like Green and Tree Farms and Machines Ltd, which push sustainability and local production.

3. Case Insight: Green and Tree Farms and Machines Ltd

Green and Tree Farms and Machines Ltd is a manufacturing, agricultural, and trading company with a focus on sustainability and agro innovation.

- Core Operations:
 - Converts waste paper into toilet rolls.
 - Produces briquettes from waste palm kernel shells and charcoal for paper mill boilers.
 - Manufactures pellets from rice husk and sawdust for energy.
 - Produces cement blocks and kerbs for construction.
 - Operates pig and cassava farms, integrating agriculture with manufacturing.
 - Involved in machinery and equipment sales, including tractors and agro-machine parts.
 - The company demonstrates how an SME can link agriculture with manufacturing, drive local value addition, and serve as a model for green industrial growth in Nigeria.

4. Challenges Confronting Nigerian SMEs

Despite their importance, over 70% of Nigerian SMEs fail within 3–5 years, largely due to harsh operating conditions.

- Major Challenges:
 - Power and Infrastructure Deficits: Unreliable electricity increases manufacturing costs.
 - Limited Access to Finance: High interest rates and strict collateral requirements make loans difficult.
 - Taxation and Policy Inconsistency: Multiple taxation reduces business viability and planning confidence.
 - Market Instability: Fluctuations in material costs and currency depreciation affect production and pricing.
 - Low Technical Support: SMEs often lack access to training and industrial partnerships.

5. The Government's Role: What's Working and What Needs Improvement

- What the Government Is Doing Right:
 - SMEDAN offers training, business development, and SME registration support.
 - CBN intervention funds such as the MSME Development Fund and Anchor Borrowers' Programme.
 - Bank of Industry provides structured loans to SMEs.
 - Efforts to create industrial parks and shared manufacturing facilities.
- Areas for Improvement:
 - Subsidies and Tax Incentives: Support SMEs with energy subsidies or tax reliefs, especially sustainable ones.
 - Stable Power Supply and Infrastructure: Investment in reliable grid and rural electrification.
 - Simplified Regulation: Streamlining tax collection and reducing bureaucracy.
 - SME-focused Financial Institutions: Specialized micro-industrial banks with realistic loan structures.



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6. The Case for Subsidies and Government Support

Manufacturing SMEs consume high energy and raw materials but operate on thin margins. Subsidies in power, fuel, or input materials can help reduce production costs and extend business survival beyond the critical 3–5-year mark. For green-focused firms like Green and Tree Farms and Machines Ltd, subsidies could lower energy costs, support sustainable sourcing, and encourage clustering.

7. Policy Recommendations Area

Recommendation Access to Finance Create state-level industrial credit schemes for SMEs with flexible collateral systems.
Power Supply Prioritize small manufacturers in renewable energy support programs.
Taxation Introduce five-year startup tax relief and harmonize local levies.
Industrial Clusters Establish agro-industrial parks for SMEs to share resources.
Skills Development Strengthen partnerships between polytechnics, BOI, and private SMEs for training.

8. Conclusion

SMEs are not just participants in Nigeria's economy—they are the foundation of its industrial future. Through innovation, adaptability, and community impact, enterprises like Green and Tree Farms and Machines Ltd showcase how local manufacturing can thrive sustainably. However, for the sector to fully drive Nigeria's industrialisation, government must provide enabling policies, infrastructure, and subsidies, while SMEs embrace innovation and digital transformation. With the right support, SMEs can move Nigeria from import dependence to true industrial independence.

Guest Speaker

SUSTAINABLE NATIONAL ENERGY SUPPLY IN NIGERIA: A PANACEA TO STABLE INDUSTRIAL DEVELOPMENT AND GROWTH

By:

Prof. Chinedu Ositadinma Nebo, CON
Former Minister of Power, Federal Republic of Nigeria
Former Vice Chancellor, Federal University Oye-Ekiti (FUOYE)
Presently, Vice Chancellor, University on the Niger, Umunya

Delivered at the Nigeria Society of Chemical Engineers (NSChE) National Conference

Abstract

Energy remains the lifeblood of industrial growth and national prosperity. In Nigeria, persistent energy deficits have constrained productivity, hindered industrial expansion, and stifled economic transformation. This paper examines the nexus between sustainable national energy supply and industrial development, explores the underlying causes of energy instability, and proposes an integrated pathway anchored on diversification, technological innovation, regulatory reform, and local content development. The central thesis is that a sustainable energy ecosystem is indispensable for achieving stable, inclusive, and globally competitive industrial growth in Nigeria.

1. INTRODUCTION

The progress of any modern economy is closely tied to the adequacy, reliability, and affordability of its energy supply. Nations that have achieved industrial breakthroughs—such as China, South Korea, and Malaysia—did so through deliberate energy planning aligned with industrial policy.

Nigeria, despite its vast energy endowments—crude oil, natural gas, coal, hydro, solar, wind, and biomass—continues to suffer from energy poverty. Electricity access hovers around 55–60%, with per capita power consumption below 150 kWh/year, compared to South Africa's over 4,000 kWh/year. The consequences are dire: declining manufacturing output, high production costs, loss of competitiveness, and widespread unemployment.

The urgent question, therefore, is: How can Nigeria ensure a sustainable, resilient energy supply that drives stable industrial growth?

2. ENERGY AND INDUSTRIALIZATION: THE INSEPARABLE LINK

Industrialization depends fundamentally on reliable energy. Energy enables mechanization, manufacturing, digital infrastructure, and service delivery. Empirical evidence across economies shows a strong correlation between energy consumption per capita and GDP per capita.

Nigeria's industrial base remains narrow, dominated by low-technology manufacturing and resource extraction. The primary constraint is unreliable and expensive energy. Many firms spend 30–40% of production costs on self-generation using diesel or petrol generators. The result is reduced competitiveness, capital flight, and factory closures.



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A sustainable national energy system, therefore, is not optional—it is the foundation of a self-reliant, job-creating economy.

3. THE CURRENT ENERGY LANDSCAPE IN NIGERIA

3.1. Electric Power

Installed capacity: about 13,000 MW (mostly thermal and hydro), but actual available generation fluctuates between 3,500–5,000 MW.
Transmission capacity remains under 8,000 MW.
Distribution networks are aged, weak, and loss-prone.
Grid instability causes frequent nationwide collapses.

3.2. Oil and Gas

Nigeria has over 200 trillion cubic feet (TCF) of proven gas reserves, yet suffers gas shortages due to poor infrastructure, vandalism, and non-market pricing.
Gas flaring continues, wasting energy and harming the environment.
Petroleum product imports strain forex and worsen fiscal deficits.

3.3. Renewable Energy

Enormous potential: solar irradiation (4–7 kWh/m²/day), wind (especially in northern corridors), biomass, and small hydro.
However, renewables contribute less than 2% to the national energy mix.
Policy and investment frameworks are improving but still weak.

3.4. Industrial Energy Use

Manufacturing, cement, steel, and agro-processing sectors are heavily energy-dependent.
Energy shortages limit capacity utilization, currently below 50% in most industries.

4. CHALLENGES TO SUSTAINABLE ENERGY SUPPLY

1. Inadequate Infrastructure: Generation, transmission, and distribution bottlenecks.
2. Policy Inconsistency: Frequent shifts in energy policy discourage investors.
3. Poor Gas Utilization: Lack of gathering, processing, and transmission infrastructure.
4. Financial Constraints: Liquidity crises in the power sector value chain.
5. Technological Obsolescence: Limited local R&D capacity.
6. Weak Regulatory Enforcement: Inefficient tariff structures and poor market discipline.
7. Security and Vandalism: Pipelines and grid installations frequently sabotaged.
8. Over-centralized Grid: Lack of decentralized, regional energy solutions.
9. Climate Commitments: Transition pressures under the global energy transition agenda.

5. STRATEGIC FRAMEWORK FOR A SUSTAINABLE NATIONAL ENERGY SUPPLY

To build a resilient, future-ready energy ecosystem, Nigeria must adopt a multi-dimensional approach integrating technical, policy, financial, and institutional reforms.

5.1. Diversification of the Energy Mix

Balance between fossil fuels and renewables.
Expand gas-to-power, solar mini-grids, small hydro, and waste-to-energy projects.
Encourage hybrid energy systems for industrial clusters.



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5.2. Gas Revolution as a Transition Bridge

- Implement the Decade of Gas Policy vigorously.
- Prioritize gas infrastructure (pipelines, processing plants, metering).
- Enforce zero gas flaring and promote industrial gas utilization.
- Encourage chemical engineers to develop indigenous gas conversion technologies—LNG, GTL, methanol, and fertilizer chains.

5.3. Renewable Energy Scaling

- Mainstream solar industrial parks, especially in northern and rural Nigeria.
- Incentivize private sector participation through feed-in tariffs and green bonds.
- Localize renewable manufacturing value chains (panels, batteries, inverters).

5.4. Power Sector Reform Deepening

- Strengthen NERC's regulatory independence.
- Accelerate decentralized generation (embedded generation, microgrids).
- Improve liquidity through cost-reflective tariffs and targeted subsidies.
- Invest massively in transmission expansion and smart grid technologies.

5.5. Research, Innovation, and Human Capacity Development

- Empower universities, polytechnics, and research institutes to drive local technology development.
- Strengthen collaboration between NSChE, NASENI, and industry players.
- Promote indigenous content in energy projects—fabrication, design, instrumentation, and process optimization.

5.6. Financing Mechanisms

- Establish an Energy Infrastructure Fund leveraging sovereign wealth, pensions, and green finance.
- Encourage PPPs and concession models for generation and distribution projects.
- Promote carbon credits and climate finance access through well-structured renewable programs.

6. ROLE OF CHEMICAL ENGINEERS IN ENERGY SUSTAINABILITY

Chemical engineers are at the heart of the energy value chain. Their expertise in thermodynamics, process design, catalysis, and energy systems optimization is indispensable. Specific contributions include:

- Developing cleaner fuels and efficient conversion technologies.
- Innovating in hydrogen energy, biofuels, and carbon capture systems.
- Designing process plants for LNG, petrochemicals, and fertilizer industries.
- Leading in waste-to-energy technologies.
- Advising on energy efficiency, sustainability auditing, and industrial emissions reduction.

The NSChE must, therefore, strengthen advocacy, research collaboration, and professional development to position chemical engineers as drivers of Nigeria's sustainable energy transition.



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7. POLICY RECOMMENDATIONS

1. Declare Energy Security a National Emergency.
2. Integrate Industrial Policy with Energy Planning.
3. Accelerate Gas Commercialization and End Flaring.
4. Promote Off-Grid Renewable Solutions for Industrial Parks.
5. Strengthen Energy Data, Research, and Innovation Frameworks.
6. Enhance Regulatory Transparency and Market Confidence.
7. Incentivize Local Manufacturing of Energy Equipment.
8. Invest in Human Capital — Engineers, Technologists, and Technicians.
9. Pursue Regional Energy Cooperation within ECOWAS.
10. Maintain Policy Continuity Across Political Administrations.

8. CONCLUSION

Sustainable national energy supply is not just a technical goal — it is a strategic imperative for Nigeria's industrial survival. The industrial renaissance Nigeria seeks cannot happen without a stable, affordable, and inclusive energy system.

By embracing a diversified, innovation-driven, and environmentally responsible energy strategy, Nigeria can power its industries, generate employment, attract investment, and attain true economic sovereignty.

“Energy is development. Where energy stops, development stops.”

Let us, therefore, as engineers, policymakers, and patriots, join hands to power Nigeria's future sustainably.

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Lead Paper Three

THE ROLE AND CONTRIBUTION OF SMEs TO NATIONAL INDUSTRIAL DEVELOPMENT AND GROWTH: FOCUSING ON RAW MATERIALS DEVELOPMENT AND UTILIZATION.

A Lead Paper Presented at the Annual Conference and General Meeting of the Nigerian Society of Chemical Engineers (NSChE), Anambra/Enugu/Ebonyi State Chapter, scheduled for 13th-15th November, 2025, at the International Conference Centre, Enugu.

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Abstract

Small and Medium Enterprises (SMEs) constitute the backbone of Nigeria's economy, contributing approximately 48% to the national GDP and accounting for over 84% of employment. This paper examines the critical role of SMEs in driving industrial development through enhanced raw materials development and utilization, with particular emphasis on initiatives spearheaded by the Projects Development Institute (PRODA) Enugu. Through qualitative analysis of current technological innovations and case studies, this research highlights how PRODA's interventions in agro-processing, renewable energy integration, and mechanized production systems have significantly addressed industrial inefficiencies. The study reveals that strategic investment in local raw material development can reduce Nigeria's import dependency by 30-40% annually while creating approximately 1.5 million new jobs. The paper concludes with policy recommendations for enhancing SME competitiveness through improved access to technology, financing, and markets, positioning SMEs as catalysts for achieving Nigeria's industrialization goals under the Economic Recovery and Growth Plan (ERGP) 2025.

Keywords: *SMEs, raw materials, value addition, PRODA, agro-processing, renewable energy, mechanization.*

1.0 INTRODUCTION

Nigeria, Africa's most populous nation with a fast-growing economy, is working hard to reduce its dual challenges of diversifying its oil-dependent economy and fostering inclusive growth. Small and Medium Enterprises (SMEs) emerge as critical agents in this narrative, serving as engines of innovation, employment, and industrial advancement. Defined by the National Policy on MSMEs as businesses with fewer than 250 employees and assets below N500 million (excluding land and buildings), SMEs constitute over 96% of Nigerian businesses and are integral to sectors like manufacturing, agriculture, and services [1][2]. Despite this prominence, Nigeria's industrial development remains constrained by structural challenges, including inadequate infrastructure, limited technological capabilities, and underutilization of domestic raw materials. The sub-theme of raw materials development and utilization is particularly crucial given Nigeria's paradoxical position as a resource-rich nation that nonetheless depends heavily on imported raw materials for its manufacturing sector- a dependency that costs the economy approximately \$14.2 billion annually [3].



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The Raw Materials Research and Development Council (RMRDC) was established precisely to address this paradox through Decree 39 of 1987, with a mandate to “promote, support, and expedite industrial development and self-reliance through optimal utilization of local raw materials” [3]. This paper argues that effective linkage between SMEs and raw materials development initiatives represents Nigeria's most viable path toward sustainable industrial development. Within this ecosystem, the Projects Development Institute (PRODA) has emerged as a critical actor through its technological innovations and capacity-building programs aimed at enhancing SME productivity across key value chains.

This lead paper, presented from the perspective of the Projects Development Institute (PRODA), a federal research institute dedicated to engineering, technology development, and transfer, examines the multifaceted role and contributions of SMEs to national industrial development and growth, with a dedicated focus on the sub-theme of raw materials development and utilization. PRODA's mandate aligns seamlessly with this theme, as it has pioneered demand-driven innovations over 40 years to address industrial inefficiencies, such as post-harvest losses and energy constraints, thereby boosting economic growth through SMEs empowerment [4]. As an expert from PRODA, I emphasize how SMEs, supported by efficient raw material processing technologies like mechanized agro-systems and renewable energy tools, can drive value chains, reduce waste, and promote sustainable industrialization. The analysis is grounded in recent statistics (up to 2025), policy frameworks, PRODA's programmes, and case studies, ensuring relevance to Nigeria's context. The paper is structured to cover literature review, empirical contributions, sub-theme specifics (including PRODA's role), challenges, opportunities, and recommendations, culminating in actionable insights for experts and policymakers.

2.0 LITERATURE REVIEW

2.1 Theoretical Frameworks of SME Development

The extant literature underscores SMEs as vital to economic development in emerging markets. Globally, formal SMEs contribute up to 40% of GDP in developing economies, with informal ones amplifying this impact [5]. In Nigeria, studies highlight SMEs' role in greater utilization of raw materials, employment generation, and rural development. For instance, research by Umar et al. (2020) notes that SMEs account for 50% of GDA and 84% of employment, emphasizing their poverty alleviation potential [5].

On raw materials, literature from the RMRDC framework stresses development and utilization as foundational for entrepreneurship and industrial growth [6]. Papers like those on project sources of raw materials advocate for SMEs to establish businesses around local resources, reducing import bills and enhancing value addition [7]. Institutional contributions, such as those from PRODA, are increasingly recognized in literature for bridging R&D gaps through technology transfer to SMEs, particularly in agro-processing and renewable energy [8]. However, gaps exist in integrating sub-theme specifics with broader industrial roles and institutional interventions, which this paper addresses through Nigerian-centric lenses, incorporating PRODA's practical advancements.

2.2 Empirical Studies on Raw Materials Utilization

Empirical evidence demonstrates the economic significance of raw materials development for industrial growth. Nigeria's current effort to double soybean farmland by 2027 illustrates this strategic approach. With domestic demand standing at over 2.7 million tons against production of only 1.35 million tons, the government's intervention aims to expand cultivation from under one million hectares to two million hectares, potentially yielding an additional 460,000 metric tons annually [9]. This initiative is projected to contribute approximately ₦3.9 trillion (US\$2.55 billion) in annual revenues while creating one million jobs- demonstrating the multiplier effects of targeted raw materials development.

Studies on energy efficiency in Nigerian manufacturing reveal another critical dimension. Research indicates that energy efficiency is positively correlated with per capita income, low carbon emissions, and industrial investment [10]. However, systemic reforms have historically shown negative impacts on energy production, highlighting the policy challenge in creating enabling environments for SME growth. The literature further confirms that manufacturing SMEs demonstrate stronger preferences for reliable energy and cost-saving technologies than service-oriented enterprises [11], underscoring the importance of tailored interventions.

2.3 Gaps in the Literature

Despite extensive research on SME development, significant knowledge gaps remain regarding the specific mechanisms through which technological institutions like PRODA facilitate raw materials utilization by SMEs. Most existing studies focus either on macro-industrial policies or on micro-enterprise dynamics without examining the meso-level institutional arrangements that connect these domains. This paper addresses this gap by analysing PRODA's initiatives as bridging mechanisms that enhance SME access to technologies, skills, and markets for raw materials development.

3.0 THE ROLE OF SMES IN NATIONAL INDUSTRIAL DEVELOPMENT

SMEs are the backbone of Nigeria's industrial sector, promoting diversification beyond oil. They facilitate technology transfer, innovation, and supply chain integration, particularly in manufacturing, where they process raw materials into finished goods. In 2024-2025, SMEs have been instrumental in sectors such as agro-processing, textiles, and metal fabrication, contributing to import substitution and export promotion. Institutions like PRODA enhance this role by providing tailored technologies, such as mechanized systems for raw material processing, enabling SMEs to scale operations efficiently [12].

Table 1: Key Roles of SMEs in Nigerian Industrial Development

Role	Description	Impact
Innovation Driver	SMEs adopt flexible technologies for product development, supported by PRODA's R&D.	Enhances competitiveness; e.g., local food processing innovations via cassava systems.
Supply Chain Enabler	Link raw material suppliers to large industries, utilizing PRODA-transferred tools.	Reduces dependency on imports: local sourcing rose to 53.5% in 2023.
Regional Development	Operate in rural areas, utilizing local resources with PRODA constituency projects.	Promotes balanced growth; e.g., cassava processing in the South, creating 400,000+ jobs.
Skill Development	Train the workforce in practical skills through PRODA's SME programmes.	Builds human capital for industrial expansion.

Source: Compiled from NBS, SMEDAN, and PRODA data, 2024-2025.

3.1 Contribution of SMEs to National Growth

Economically, SMEs drive growth through GDP contributions, job creation, and fiscal revenues. As of 2025, they account for 48% of GDP and 84% of employment, with over 39.7 million MSMEs operational [13] [14]. Their multiplier effects include poverty reduction and increased per capita income, amplified by institutional supports like PRODA's technology dissemination, which has established over 1,000 agro-processing centres nationwide [4].

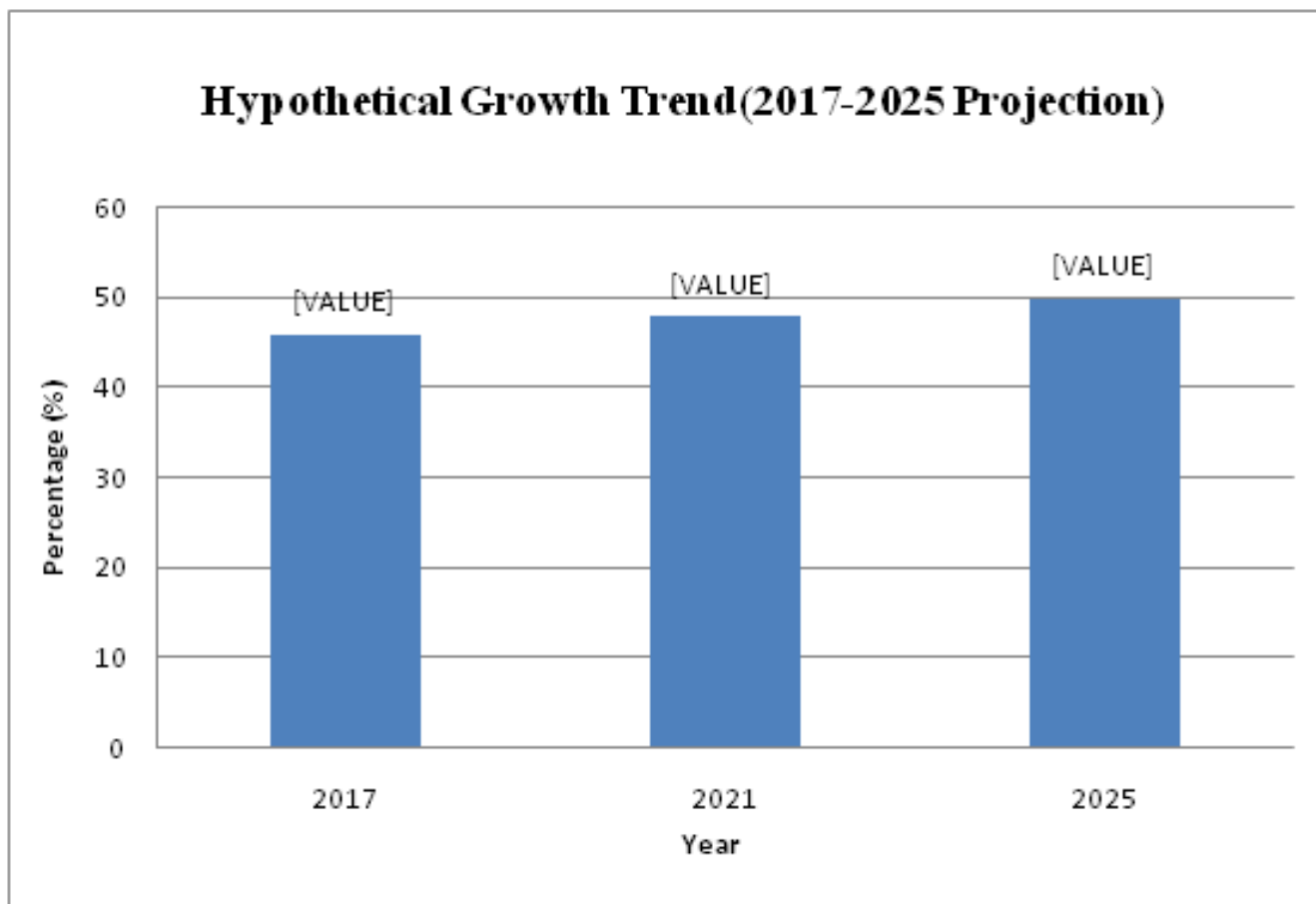


Figure 1: SME Contribution to Nigeria's GDP (2017-2025)

Sources indicate steady growth despite economic headwinds, with PRODA's interventions boosting agro-SME productivity [13] [4].

SMEs also contribute to foreign exchange earnings via exports of processed goods, aligning with Nigeria's Economic Recovery and Growth Plan, where PRODA's innovations in value-added products play a pivotal role [16].

3.2 SMEs and Raw Materials Utilization

The relationship between SMEs and raw materials utilization represents a critical nexus for industrial development. SMEs dominate many raw material-based value chains, including food processing, textiles, leather goods, and building materials. However, most SMEs face structural limitations in efficiently converting raw materials into finished products due to technological constraints, limited skills, and inadequate capabilities.

As demonstrated by the Ndiagu Cassava Cluster case study, the introduction of appropriate technology directly addresses these limitations, leading to quantum leaps in productivity and quality.

The Raw Materials Research and Development Council (RMRDC) has identified several strategic approaches to enhance SME utilization of domestic raw materials, including:

1. Formulation of policy guidelines on raw materials acquisition, exploitation, and development
2. Advising the government on raw material conservation
3. Recommending appropriate technologies for raw materials utilization



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4. Encouraging dissemination of research for local raw material sourcing [14].

These approaches align with PRODA's initiatives in developing and disseminating appropriate technologies for SMEs.

3.3 Regional Development and Poverty Reduction

Beyond aggregate economic indicators, SMEs play a crucial role in regional development and poverty reduction across Nigeria's diverse geographical zones. In the North Central region, SMEs dominate agricultural value chains, including soybean processing- a sector targeted for significant expansion under the National Soybean Production Policy and Strategy [9]. In the South East, SMEs drive manufacturing activities, particularly in machinery components, automotive parts, and household goods. The regional specialization patterns evident in Nigeria's SME sector represent competitive advantages that could be further enhanced through targeted raw materials development initiatives.

PRODA's interventions have specifically addressed regional disparities by adopting technologies to suit local raw materials endowments. For instance, in cassava-rich regions, PRODA has introduced improved graters and hydraulic presses for garri production, while in ceramic clusters, the Institute has developed mechanized potter's wheels that enhanced productivity while maintaining traditional design aesthetics.

4.0 RAW MATERIALS DEVELOPMENT: POLICIES AND STRATEGIES

4.1 Policy Framework for Raw Materials Development

Nigeria's policy approach to raw materials development has evolved through several phases, from the import substitution industrialization strategies of the 1970s-1980s to the current diversification agenda under the Economic Recovery and Growth Plan (ERGP). The establishment of the Raw Materials Research and Development Council (RMRDC) in 1987 represented a landmark institutional intervention aimed specifically at addressing Nigeria's raw materials challenges [3]. The Council's mandates include drawing up policy guidelines on raw materials acquisition, exploitation, and development; reviewing raw material resources availability and utilization; advising on the adoption of machinery and processes for raw materials utilization; and encouraging the dissemination of research findings relevant to local sourcing of materials.

The National Industrial Revolution Plan (NIRP) and the Nigeria Industrial Policy and Competitiveness strategy have further strengthened the policy framework by prioritizing backward integration programs across key sectors, including automobiles, sugar, cement, and palm oil. These policies have yielded significant results in some sectors- for instance, the cement industry now meets over 90% of domestic demand through local production- but challenges remain in translating policy objectives into widespread SME adoption.

4.2 PRODA's Strategic Initiatives in Raw Materials Development and Technological Advancement

The Projects Development Institute (PRODA) has developed a comprehensive strategy for enhancing raw materials utilization by SMEs, focusing on three strategic pillars: (1) technology adaptation and development; (2) capacity building and skills development; and (3) research-industry linkage. This approach recognizes that technological innovation alone is insufficient without corresponding improvements in technical skills and market connections.

As a leading federal institute under the Ministry of Science, Technology, and Innovation, PRODA has been instrumental in addressing industrial inefficiencies through R&D in agro-processing and renewable energy, directly supporting SMEs in raw materials utilization. Over 40 years, PRODA has created over



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400,000 jobs through constituency projects, establishing cottage industries and transferring technologies such as mechanized agro-systems to reduce post-harvest losses by up to 30% [4].

In the agro-processing sector, PRODA has developed complete processing flow lines for key commodities, including palm oil, cassava, soybean, and plantain. These systems are designed specifically for SME adoption, featuring modular scalability, energy efficiency, and ease of operation. Key advancements include:

- **Palm Oil Processing Flow Line:** PRODA's integrated system includes sterilization tanks, threshing machines, digesters, screw presses, clarification tanks, and kernel recovery systems. This flow line reduces processing time by 40% compared to traditional methods while improving oil quality through efficient separation. The system is designed for modular implementation, allowing SMEs to scale operations according to capacity.
- **Cassava Processing Technologies:** For cassava value addition, PRODA has developed complete systems for garri production, including peelers, graters, presses, fermentation vessels, rotary sieves, fryers, and packaging machines. These technologies address key constraints in traditional garri production, particularly the high labour requirements and inconsistent quality. The hydraulic press specifically reduces moisture content from 60% to 45%, shortening frying time and reducing energy consumption by 30%.
- **Soybean and Plantain Flour Processing:** PRODA has adapted technologies for soybean flour production and plantain flour processing, emphasizing nutrient retention and shelf-life extension. The soybean processing system includes destoning, toasting, dehulling, milling, and packaging. For plantain flour, PRODA's system incorporates drying technologies that maintain nutritional quality while extending the shelf life.

4.3 Renewable Energy Solutions

Energy access represents a critical constraint for SMEs in Nigeria, where unreliable power supply costs businesses an estimated \$29 billion annually in generator fuel and maintenance. PRODA has developed renewable energy solutions specifically designed for SME operations, enhancing environmental sustainability:

- **Solar-Powered Hybrid Welding Machines:** The tangible benefits of this technology are evidenced by the Adopt-A-Sun Initiative in Jos, where welders slashed energy costs and increased their operational capacity. These systems integrate solar photovoltaic technology with conventional welding equipment, reducing grid electricity dependence by 60-70%. The welding machines are particularly valuable for metalworking SMEs engaged in equipment fabrication and repair services,
- **Solar-Powered Bird Repellent Systems:** Developed for agricultural SMEs, these systems use solar-powered ultrasonic emissions to protect crops from bird damage without harmful chemicals. The technology is especially relevant for fruit growers and cereal farmers who typically experience 20-30% post-harvest losses to birds.

4.4 Food Preservation Technologies

Post-harvest losses represent a significant challenge in Nigerian agriculture, estimated at 40-50% for perishable commodities. PRODA has developed various food preservation technologies to address these losses:

- **Ovens and Dryers:** PRODA's food dehydration systems include modular dryers adaptable to various energy sources and designed for SME-scale operations. The dryers incorporate temperature control features that preserve nutritional quality while extending shelf life.

- Improved Smoking Kilns: For protein sources, PRODA has developed improved smoking kilns that reduce polycyclic aromatic hydrocarbon formation while enhancing preservation.

These preservation technologies are particularly valuable for women-owned SMEs that dominate small-scale food processing across Nigeria.

4.5 Ceramics Production Technology

The ceramics industry represents an emerging sector with significant potential for import substitution in Nigeria. PRODA's development of a mechanized potter's wheel builds on ancient pottery techniques while enhancing productivity and quality consistency. The technology features adjustable rotation speeds, ergonomic designs, and improved stability that allow artisans to produce standardized products with reduced physical strain.

The mechanized potter's wheel has been particularly impactful in the Nigerian ceramics cluster around Abuja and Kano, where traditional potters have expanded production into functional building materials and decorative items. This technology demonstrates how appropriate innovation can transform traditional crafts into viable modern industries while preserving cultural heritage.

These technological innovations are complemented by training programs that enhance SME technical capabilities in operation, maintenance, and quality control. The Institute's research and development efforts focus on addressing specific constraints in raw materials utilization.

PRODA's SME training programmes also include skill acquisition in cosmetics, soap production, and efficient stove usage, equipping entrepreneurs with hands-on expertise, ensuring technology adoption and commercialization [4].

Category	Technology	Capacity/Features	SME Impact
Agro-Processing	Palm Oil Flow	Line 1,000 L/day; Sterilization, digestion, pressing, clarification	Reduces import dependency; job creation in rural South-South.
	Cassava-to-Starch/Garri	3 tons/day plant; Washing, peeling, grating, pressing, frying	30% energy reduction, quality standardization, supports 250kg/day semi-manual for start-ups.
	Soybean/Plantain Flour	Toaster/de husker /micro-mill	Value addition from legumes/fruits; Enhances nutrition security.
	Vegetable Oil Refining	Expeller/clarifier systems	Local oil production; Export potential.
Food Preservation	Ovens/Dryers	250kg; 80 °C + thermo-control	Extends shelf life; Reduces food waste in agro-SMEs
Ceramics	Mechanized Potter's Wheel	Part of the full pottery line	Utilizes kaolin/limestone; Boosts artisan SME.
Renewable Energy	Solar Hybrid welding	Air/oil-cooled; Electrode gauges 2.5-6.3mm	Of-grid fabrication; Energy efficiency for raw material processing.
	Solar Bird Repellent	Photovoltaic integration	Crop protection; Sustainable agriculture

Source: PRODA Products and Programmes, 2025.

SMEs in agro-processing, for example, utilize cassava for starch and ethanol via PRODA systems, boosting local economies. In manufacturing, SMEs develop alternatives like bio-based materials, aligning with circular economy principles [17].

5.0 CASE STUDIES: PRODA'S TECHNOLOGIES IN ACTION

The following case studies document the deployment and outcomes of PRODA's innovations within Nigeria SME clusters.

Case Study 1: The Ndiagu Cassava Cluster in Enugu State

- **Background:** The Ndiagu Cassava Cluster small-scale processors primarily produced garri using manual methods. They faced significant challenges with low throughput (2-3 bags of garri per day per unit), inconsistent quality, and high physical drudgery.
- **Intervention:** PRODA installed a complete, small-scale Cassava-to-Garri Processing Plant in 2020. The intervention included a peeler, grater, hydraulic press, and energy-efficient communal fryer. A three-week training program was conducted for 30 cluster members on operation, maintenance, and basic business management.
- **Outcomes and Impact:**
 1. **Productivity:** Throughput increased by over 300%, with each unit now processing up to 10 bags of garri daily.
 2. **Quality:** The introduction of the hydraulic press ensured uniform dewatering, leading to a superior, crispier garri product that commanded a 15% price premium in the local market.
 3. **Economic:** The cluster reported a collective income increase of over 200% within six months. The reduced drudgery also encouraged the participation of more youth and women, thereby creating jobs and increasing local raw cassava utilization.
 4. **Quote from Beneficiary:** “Before PRODA's machine, garri production was a punishment. Now, it is a profitable business. We can meet larger orders from distributors in Enugu that we could never supply before.”

Case Study 2: Adopt-a-Sun Initiative for Welders in Jos, Plateau State

- **Background:** The “Jenta Welder's Cluster,” a group of metal fabricators, was struggling with exorbitant costs for running diesel-powered generators. Energy costs consumed over 40% of their operational expenses, making them uncompetitive against larger rivals with grid connections.
- **Intervention:** PRODA piloted its “Adopt-A-Sun” initiative, providing the cluster with two Solar-Powered Hybrid Welding Machines on a cost-sharing basis. The initiative included technical training on maintaining the solar-battery-inverter system.
- **Outcomes and Impact:**
 1. **Cost Saving:** Diesel consumption for welding operations dropped by over 70%, reducing energy costs from 40% to under 15% of total expenses.
 2. **Extended Working Hours:** The reliable solar power allowed welders to work into the evening, increasing productive hours by over 30%.
 3. **Environmental Impact:** The switch eliminated CO₂ emissions.

Table 3: Impact Assessment of PRODA's Cassava Intervention in Ndiagu Cluster

Post-Intervention (12 months)	Change
8-10	+300%
3	-62.5%
13,800	+15%
₦14.8M	+208%

6.0 CHALLENGES AND OPPORTUNITIES

6.1 Persistent Challenges in SME Development

Despite institutional interventions like PRODA's initiative, Nigerian SMEs face multifaceted challenges that constrain their growth and productivity:

- **Infrastructural Deficits:** inadequate power supply, poor transportation networks, and limited water access significantly increase production costs. Manufacturing SMEs spend 20-30% of operational costs on alternative power generation, reducing international competitiveness. [11]
- **Financial Constraints:** Limited access to affordable credit remains a critical constraint. SMEs face high interest rates and a lack of collateral; capital for mechanized equipment and PV systems is scarce.
- **Technological Limitations:** Most SMEs operate with outdated equipment and limited technical capabilities, resulting in low productivity and product quality.
- **Policy Instability:** Frequent policy changes and regulatory uncertainties discourage long-term investment by SMEs. The construction industry's experience with project delays and cost overruns [18] illustrates how institutional weakness affects productive sectors.
- **Market Access Limitations:** SMEs face challenges in accessing domestic and international markets due to limited information, standardization issues, and inadequate marketing capabilities.

6.2 Emerging Opportunities

Despite these challenges, several promising opportunities could accelerate SME development and raw materials utilization:

- **African Continental Free Trade Area (AfCFTA):** The creation of the world's largest free trade area offers Nigerian SMEs access to a market of 1.3 billion people with a combined GDP of \$3.4 trillion. Raw materials-based products, including processed foods, textiles, and leather goods, have significant export potential.
- **Digital Transformation:** Digital technologies, including e-commerce, mobile payments, and cloud-based services, are reducing traditional barriers to market entry for SMEs. Nigeria SMEs are increasingly adopting digital platforms for marketing, sales, and customer engagement.



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- Circular Economy Initiatives: Growing interest in waste-to-wealth initiatives creates opportunities for SMEs in recycling and resource recovery. PRODA's research on utilizing biomass briquettes as an alternative fuel source exemplifies this potential.
- Growing Domestic Demand: Nigeria's population growth (projected to reach 400 million by 2025) and urbanization are expanding domestic demand for processed goods, creating opportunities for SMEs in food processing, housing materials, and consumer goods.
- The 2021-2025 MSME Policy offers frameworks for capacity building and incentives [1].

7.0 CONCLUSION AND RECOMMENDATIONS

7.1 Conclusion

This paper has examined the critical role of SMEs in Nigeria's industrial development through the lens of raw materials development and utilization. The analysis demonstrates that SMEs constitute the backbone of Nigeria's non-oil economy; however, they face significant constraints in terms of productivity, competitiveness, and growth. Technological innovations developed by institutions like PRODA- spanning agro-processing, renewable energy, food preservation, and ceramics production- have shown significant potential in addressing these constraints.

The effective utilization of domestic raw materials represents Nigeria's most viable path toward sustainable industrialization. Initiatives like the National Soybean Production Policy [9] demonstrate how targeted raw materials development can reduce import dependency while creating employment and generating income. However, realizing this potential requires addressing persistent challenges in infrastructure, financing, and policy implementation.

PRODA's experience offers valuable lessons in how technology adaptation and capacity building can enhance SME productivity. The Institute's integrated approach- combining technology development with training and market linkage- provides a model for other development institutions seeking to promote SME-led industrial development.

7.2 Recommendations

Based on the analysis, this paper offers the following recommendations for enhancing SME contributions to industrial development through improved raw materials utilization:

1. Strengthen Research-Industry linkage: Enhance the connection between research institutions (including PRODA and RMRDC) and SMEs through joint research projects and industry-focused innovation challenges.
2. Strengthen Policy Coordination: Enhance coordination between raw materials development policies (led by RMRDC) and SME development initiatives (led by SMEDAN) to ensure policy coherence and implementation efficiency.
3. Address Infrastructure Constraints: Prioritize infrastructure development in industrial clusters frequented by SMEs.
4. Enhance Renewable Energy Integration: Accelerate the integration of renewable energy solutions into SME operations through targeted incentives and technical support.



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Lead Paper Four

SOLID MINERALS DEVELOPMENT AND GROWTH IN NIGERIA

Paper presented by
Distinguished Senator Osita Ngwu,
Minority Whip, 10th Senate of the Federal Republic of Nigeria,
On the occasion of
The Nigerian Society of Chemical Engineers
Annual Conference & General Meeting
On the Theme:
"The Role and Contribution of SMEs to National Industrial Development and Growth"
From 13th – 15th November 2025,
At the International Conference Centre, Enugu, Nigeria.

Abstract

Nigeria is endowed with over 44 commercially viable solid mineral resources distributed across all 36 states and the Federal Capital Territory, yet the sector's contribution to national economic output remains disproportionately low, accounting for only about 0.63% of GDP in 2021. This paper provides a comprehensive analysis of the development trajectory of the solid minerals sector in Nigeria, examining production trends, revenue performance, policy reforms, and structural challenges affecting sustainable growth. Empirical data indicate consistent increases in mineral output from 35.3 million tons in 2017 to 76.3 million tons in 2021, accompanied by progressive growth in royalties and aggregate financial flows to the Federation Account. Recent government interventions—including enhanced geological mapping, strengthened licensing frameworks, stricter compliance measures, and a strategic ₦1 trillion investment commitment—have contributed to improved sectoral performance, with GDP contribution projected to rise to 1.8% by 2025 and revenues more than doubling between 2023 and 2025. Despite these gains, persistent constraints such as inadequate infrastructure, low value addition, artisan mining dominance, weak regulatory enforcement, limited technological capacity, and financing barriers continue to impede optimal sectoral development. The paper highlights the pivotal role of Small and Medium-Scale Enterprises (SMEs) in bridging the value-chain gap through beneficiation, local processing, manufacturing, logistics, and community-based enterprises. It concludes that achieving sustainable industrial diversification and moving the sector's GDP share toward the projected 5% requires an integrated strategy anchored on SME empowerment, value-addition policies, improved transparency, environmental sustainability, and strengthened institutional capacity.

SOLID MINERALS DEVELOPMENT AND GROWTH IN NIGERIA





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SOLID MINERALS DEVELOPMENT AND GROWTH IN NIGERIA

1.0 Introduction



Nigeria is richly endowed with diverse solid minerals, including gold, limestone, coal, iron ore, lithium, lead-zinc, and industrial rocks. The country is endowed with over 44 important mineral types in commercial scales, spread across the 36 States and the Federal Capital Territory of Nigeria.

Despite this potential, the sector's contribution to Nigeria's Gross Domestic Product (GDP) remains marginal, and its full development remains a major lever for industrialization and economic diversification of the most populous black nation in the world.

This paper examines the current status, key drivers, constraints, and policy opportunities for the development of solid minerals in Nigeria, with a particular emphasis on the role of Small and Medium-Scale Enterprises (SMEs) in linking mineral exploitation to value-added industrial growth

2.0 Current Status of the Sector



2.1 Production & Output

Production Output refers to the total quantity of goods or services produced by a company, industry, or economy within a specific period. It serves as a key indicator of productivity, efficiency, and economic performance.

In the context of industrial or mining operations, production output measures the effectiveness with which resources, such as labor, machinery, and raw materials, are utilized to generate finished products.

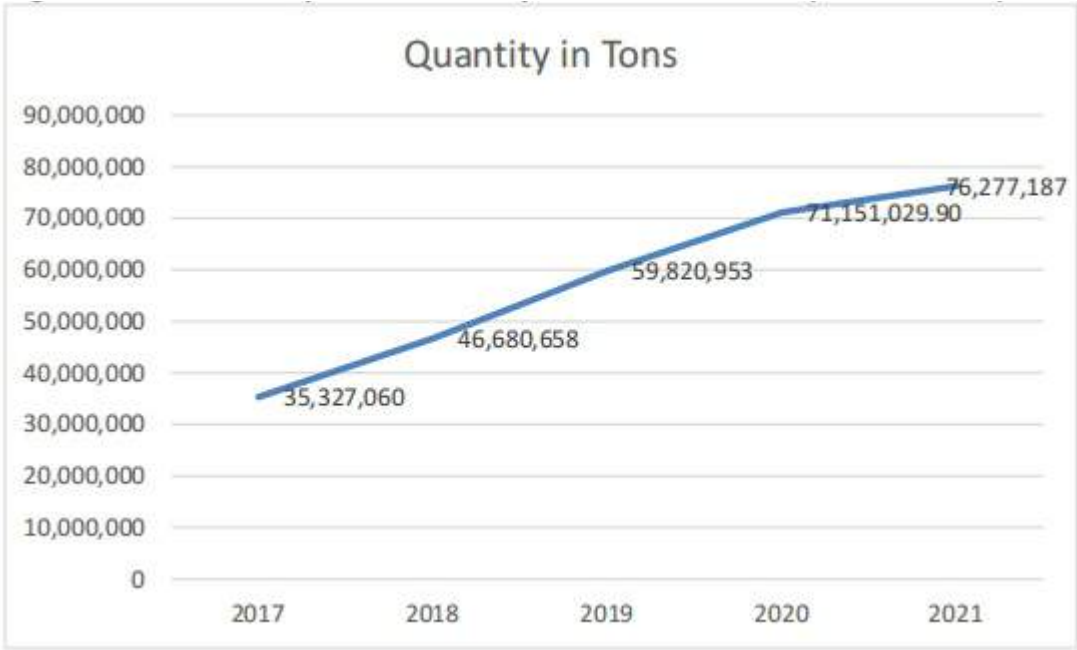
High production output often reflects improved technology, effective management, and optimal resource use, while low output may indicate inefficiencies or operational constraints.

Table 1: Production Trends (Tons) of Mineral Production in Nigeria (2017 to 2021)

Year	Quantity in Tons
2017	35,327,060
2018	46,680,658
2019	59,820,953
2020	71,151,029.90
2021	76,277,187

Source: NEITI Report 2022

Figure 1: Trend Analysis of Quantity Produced in Tons (2017 – 2021)



- The Federal Ministry of Solid Minerals Development (MSMD) Report for 2023-2024 noted that 513,600 tons of minerals were added (+343.8%) in that period, with new royalties increasing by ₦19.3 billion (+110.1%).

- The sector’s major activities are mining and quarrying, with quarrying accounting for 59% and mining operations accounting for 21%. Other activities make up the remaining 20%.

Figure 2: Distribution of Activities in the Solid Minerals Sector



Source: Derived from NEITI Report 2021

2.2 Economic Contribution

The mining and solid minerals sector plays a vital role in Nigeria’s economic diversification and industrialization drive. The Government is focused on making the sector a major non-oil driver of revenue, job creation, and foreign exchange earnings through the export of mineral commodities.

The sector supports key industries such as construction, manufacturing, and energy production by providing essential raw materials. With over 40 commercially viable minerals across more than 500 locations, mining remains a cornerstone for sustainable national growth and regional development.

Table 2: Selected Key Indicators of Nigeria’s Solid Minerals Sector

INDICATOR	VALUE (2021)	NOTES
Aggregate production (tons)	89.48 million	+39.2% from 2020
Sector share of GDP	~0.63%	NEITI report
Export value	N43.68 billion	~0.24% of national exports

SOURCES: NEITI AND NBS

- Data from the Nigeria Extractive Industries Transparency Initiative (NEITI) 2021 report shows that the solid minerals sector contributed N1.10 trillion (≈0.63%) to GDP in 2021.
- Export earnings from solid minerals in 2021 stood at N43.68 billion (≈0.24% of total exports).

2.3 5-Year Trend Analysis of Revenue



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Table 3: 5-year trend of Aggregate Financial Flows to the Federation Account

Entity	Financial flows	Years				
		2017 million N	2018 million N	2019 million N	2020 million N	2021 million N
FIRS	VAT, WHT, SD, CIT, EDT, CGT	49,162	65,689	69,918	111,475	169,517
MID	Royalty and other fees	1,586	2,211	2,553	3,037	3,619
MCO	Annual service fees, application fees, etc.	2,009	1,571	2,380	2,303	4,301
Total		52,757	69,471	74,851	116,815	177,437

Source: NEITI Solid Minerals Audit Reports 2022

2.4 General Economic Indicators

Based on reports from the Ministry of Solid Minerals Development (MSMD), the Nigeria Extractive Industries Transparency Initiative (NEITI), and the National Bureau of Statistics (NBS), here is a summary of the sector's performance:

a. Revenue generation

2023–2024: The revenue generated by the Mining Cadastre Office (MCO) more than doubled, from ₦6.1 billion in 2023 to ₦12.58 billion in 2024, a 107% increase.

2024–2025: Government revenues continued to climb in 2025. In October 2025, the Federal Government confirmed that the solid minerals sector generated over ₦38 billion in revenue in 2024.

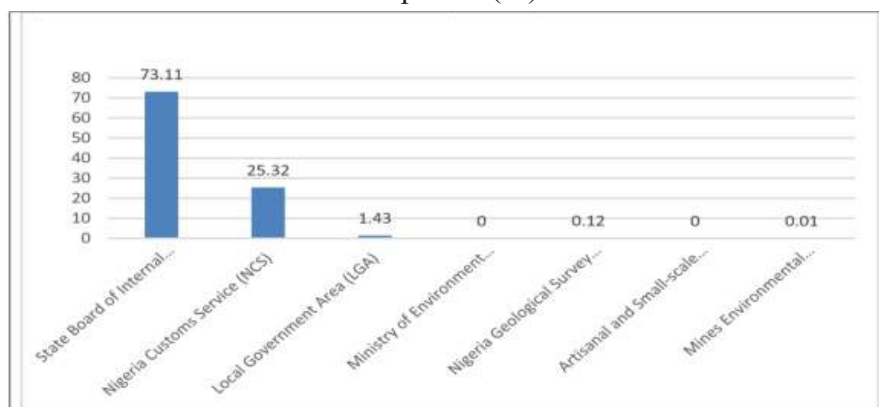
By September 2025, the sector had already surpassed its total 2024 revenue, garnering ₦44.65 billion within the first eight months of the year.

b. MDAs Revenue Collections

Payments Streams to the Government from operating Companies are basically collected at the following levels:

1. State Board of Internal Revenue (SBIR)
2. Nigeria Customs Service (NCS)
3. Local Government Area (LGA)
4. Ministry of Environment (MOE)
5. Nigeria Geological Survey Agency (NGSA)
6. Artisanal and Small-scale Mining Department (ASM)
7. Mines Environmental Compliance Department (MECD)

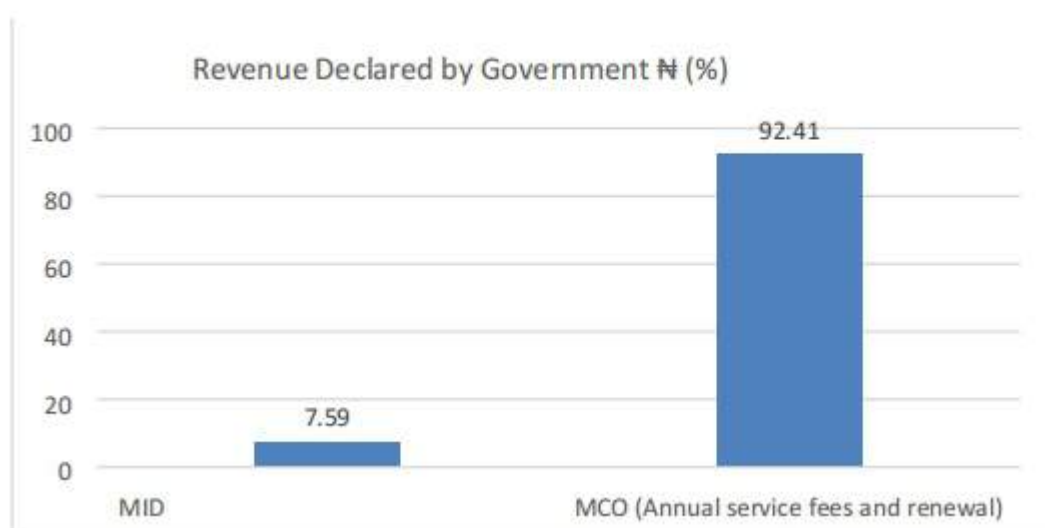
Figure 3: Revenue Collection from Companies (%)



Source: Derived from NEITI 2021 Solid Minerals Audit Template

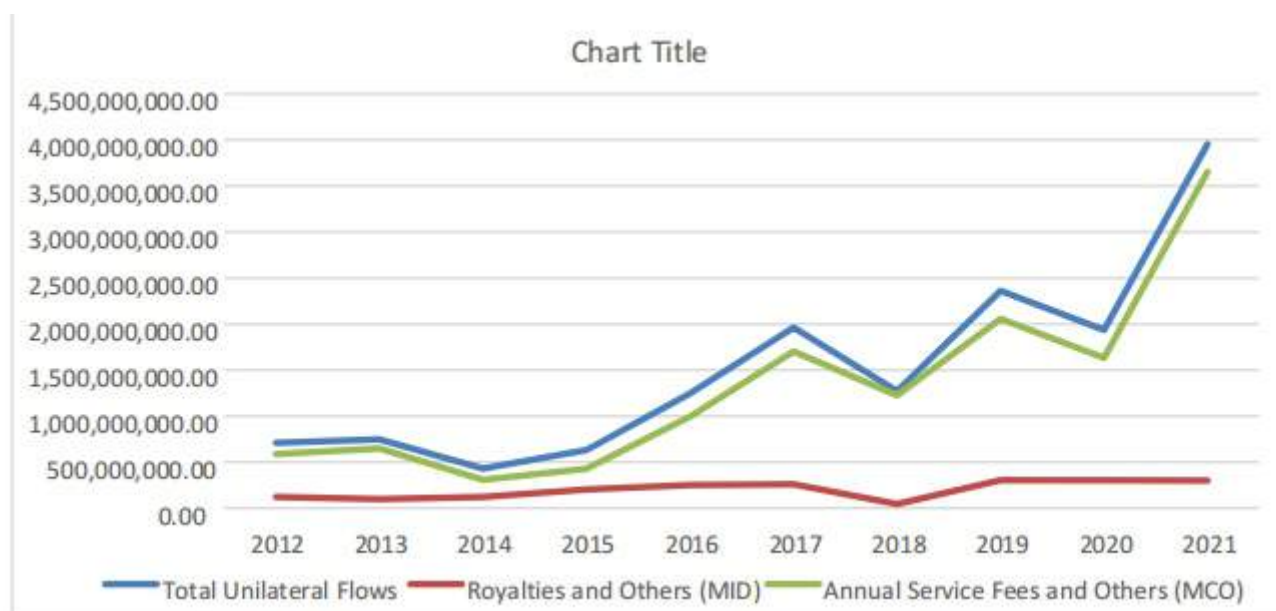
Other Revenue Heads include Revenue Declared by Government – MID (Royalty & Fees Below Threshold) and MCO (Annual service fees and renewal), as shown in naira (%) in Figure 3 below.

Figure 4: Revenue Collection from Companies



Derived from NEITI 2021 Solid Minerals Audit Template

Figure 5: Total Unilateral Disclosures 2012 – 2021 in Naira



Source: Derived from NEITI 2021 Report

The linear gradients of the graph indicate inconsistent flows of the Revenue Heads, as evidenced by fluctuations between some years. However, apart from royalty payments that showed a visible decline, there was significant growth in revenue for the years reviewed.

Table 4: Royalty Trends on Mineral Production from 2017 to 2021



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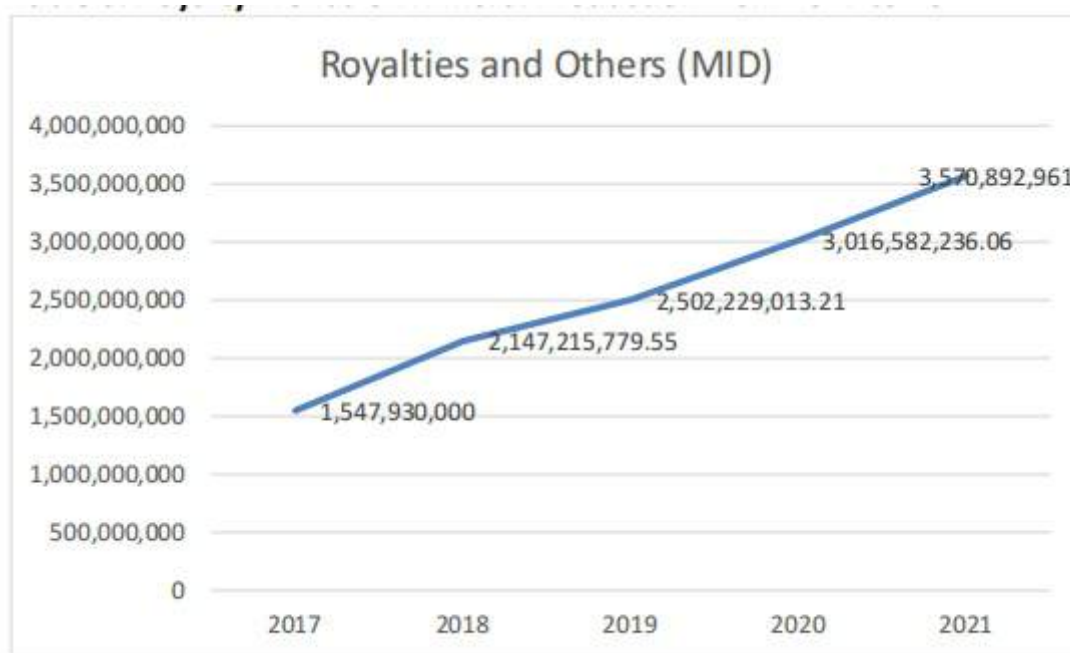


Year	Quantity in Tons	Royalties and Others (MID)
2017	35,327,060	1,547,930,000
2018	46,680,658	2,147,215,779.55
2019	59,820,953	2,502,229,013.21
2020	71,151,029.90	3,016,582,236.06
2021	76,277,187	3,570,892,961

Source: NEITI Report 2022

The table above shows steady progress in revenue from 2017 to 2021, which is an indicator that the sector is maintaining a steady growth within the period under review

Table 6: Royalty Trends on Mineral Production from 2017 to 2021



The gradient shows proportionate increments in Royalty, though the gains have not met the targets projected.

2.5 Sectoral Growth

- 2024 Growth Rate: Nigeria's mining sector achieved a significant growth rate of 4.85% in 2024, an increase from the 2.84% recorded in 2023.
- GDP Contribution: The sector's contribution to GDP grew from less than 0.5% in 2015 to about 1.8% in 2025, as confirmed by the Minister of Solid Minerals Development.

For 2024, the sector contributed ₦1.39 trillion to the GDP, with the metal ores subsector experiencing a substantial growth of 134.07%.

2.6 Sub-sector Performance in 2024:

Growth: The metal ores sub-sector was a high performer, with its contribution increasing from ₦44.22 billion in 2023 to ₦103.51 billion in 2024.

Decline: The quarrying and other minerals sub-sector saw a 24.26% decline, and the coal mining sub-sector dropped by 62.8% due to diminished investor interest.

2.7 Policy and Investment

- **Investment:** In October 2025, President Tinubu announced a ₦1 trillion investment to boost the solid minerals sector, further signaling government commitment.
- **Licensing:** Registrations of Mineral Buying and Commercialization (RMBC) companies nearly doubled, from 223 in 2023 to 431 in 2024. This was driven by stricter export regulations that required a formal RMBC status.
- **Title Revocation:** Over 800 inactive or non-compliant mineral titles were revoked in 2024, a measure aimed at improving the efficiency and transparency of the sector.
- **Exploration:** The government has conducted extensive geological and geochemical mapping in key regions to attract more investment.

3.0 Role of SMEs in the Value Chain

SMEs play a pivotal role in mineral development, especially in artisanal and smallscale mining (ASM), mineral beneficiation, local processing, logistics, and downstream services. Key observations:

- SMEs provide employment, stimulate local enterprise clusters, and foster community development around mining zones.
- A study found that while solid mineral development had an insignificant positive effect on GDP (1981-2019). Value-added processing via SMEs was a critical missing link.
- Government policy now emphasizes local processing. That is the current policy thrust of the Government, meaning that new mining licenses will be granted only to companies with domestic processing plans, incentivizing SMEs in downstream beneficiation.

SEGMENT	SME ROLE
Exploration support	Geophysical surveys, core sampling, logistics
Beneficiation & processing	Crushing, milling, refining, and packaging
Product manufacturing	Cement, ceramics, steel, lithium-battery supplies
Services & logistics	Transportation, warehousing, and environmental services
Host-community enterprises	Mining-adjacent SMEs supplying goods & labour

4.0 Key Growth Enablers & Policy Reforms

Several factors have recently emerged as enablers for sector growth:

- The MSMD’s revised licensing regime and cadastre system aim to ease access and transparency.
- Revenue Mobilization, Allocation, and Fiscal Commission’s new data rendition template (2025) for solid minerals enhances revenue monitoring and state-by-state reporting.

- Nigeria’s mining cooperation with various countries, including China, Australia, and South Africa, aims to leverage geological mapping, drone-survey tech, and value-chain development. These reforms signal institutional commitment to growing the sector. In addition, unlocking the full potential depends on aligning SMEs, infrastructure, regulation, and value addition.

5.0 Challenges & Risks

Despite the potential, the sector faces major constraints:

- Poor formalization and enrolment of operators for effective regulation of the sector and expanding the revenue net.

Figure 7: Licensed Companies showing ratio of Royalty Payments and Compliance with set materiality threshold



Royalties evasion by the licensed operators is captured in the pie charts above, showing that out of a total of 1,214 companies operating in the sector, 914 paid royalties in 2021. Out of the 914 that made royalty payments, 121 companies met the set materiality threshold and were responsible for 92% of the total royalty payments in the same year.

5.1 Other Challenges and Risks are as follows:

- Low contribution to GDP (marginally >1%) despite high mineral endowment.
- Weak infrastructure (rail, roads, power) for mining sites and transport of minerals.
- Artisanal mining dominance, informal value chains, export of raw minerals (thus low value capture).
- Environmental and social risks: inadequate remediation, community exclusion, weak regulatory enforcement.
- Financing constraints for SMEs: mining life-cycle requires long-term capital; SMEs often lack collateral.
- Security challenges
- Low technical know-how and inadequate technology

6.0 Strategic Imperatives for Nigeria’s Growth

To leverage solid minerals for national industrial growth, the following strategic imperatives are being prioritized:



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1. Value addition and downstream processing: Raw export is being minimized; SMEs need support to move up the chain.
2. SME capacity-building & financing: The Government is making efforts for dedicated funds, soft loans, or a specialized Solid Minerals Development Bank to be put in place to support SMEs.
3. Technical Know-how and Infrastructure linkage: Injection of a ₦1 trillion investment by this Government would boost the solid minerals sector in various ways, including improved technology for MDAs, linking mining sites with multimodal transportation network (road/rail/water/air), as well as power masterplans to ensure smooth logistics.
4. Environmental sustainability & community inclusion: Efforts are on to ensure that mining operations encourage host-community participation, remediation, and fair benefits.
5. Data transparency & regulatory enforcement: Improvements are being made in comprehensive cadastre, regular audits, and public disclosure protocols to align with models from advanced jurisdictions.
6. Integration with industrial policy: Minerals must feed manufacturing (e.g., cement, steel, batteries), enabling backward and forward integration and linkages for SMEs. Our laws are being directed to achieve this.
7. Security: Apart from the formal security architecture, the Government has also commissioned Mine Rangers to support the security operations in the country with a specific focus on the mining and extractive industry.

7.0 Conclusion & Call to Action

Nigeria stands at a pivotal moment: the solid minerals sector can help transition the country from oil dependence to a diversified, resilient industrial economy. But this depends on the collective action of all of us, not merely aspiration.

As chemical engineers, you too can play a vital role in the mining and solid minerals sector by designing and optimizing processes for the extraction, separation, and purification of valuable minerals from ores for value addition.

You have roles to play also, in the development of environmentally sustainable methods for mineral processing, waste management, and recovery of by-products, ensuring efficiency, safety, and minimal environmental impact throughout the mining value chain.

Finally, from this presentation, it could be deduced that SMEs are central to valuechain development. So, our policy framework is shifting from raw-material extraction to local processing, sustainability, and equitable stakeholder participation.

It is reassuring to note that Nigeria would, in the short term, realize the vision of increasing the solid minerals sector's share of GDP from the marginal 1% to 5% as projected, through ongoing bold reforms, concerted SME mobilization, infrastructure investment, and community-centric environmental governance.

Thank you for your attention

Lead Paper Five

Driving Industrial Growth through Sustainable Waste Management: The Pivotal Role of SMEs

Presenter: The Managing Director, Scientific Equipment Development Institute (SEDI), Enugu.

Engr Dr Lois Nwobodo.

Event: 55th International Conference, Exhibition & Annual General Meeting of the Nigerian Society of Chemical Engineers.

Theme: The Role and Contribution of SMEs to National Industrial Development and Growth.

Sub-Theme: Waste and Environmental Management and Sustainability.

Date: November 13th - 15th, 2025.

Location: Enugu, Nigeria

Abstract

Small and Medium Enterprises (SMEs) are the undisputed engines of Nigeria's industrialization, accounting for nearly 90% of the workforce and approximately 50% of the GDP. However, this growth has historically cast a long shadow: the environmental burden of unmanaged waste. This paper, presented from the frontline perspective of SEDI Enugu, argues that the future of Nigerian industrial development is inextricably linked to the adoption of sustainable waste management practices. We conduct a comparative analysis of industrial and municipal waste streams, highlighting their distinct challenges and convergences. Using Enugu State as a microcosm of the national experience, the paper moves beyond problem identification to present a practical, actionable framework for SMEs. This framework is grounded in the circular economy and leverages policy enablement, technological innovation (a core mandate of SEDI-ENUGU), and strategic collaboration. We posit that for SMEs, environmental sustainability is not a regulatory burden but a fundamental pillar of long-term competitiveness, resilience, and profitable growth in the 21st-century economy.

Keywords: SMEs, Industrial Development, Circular Economy, Waste Valorization, Environmental Compliance, Policy, Technology, Enugu State, SEDI.

Introduction:

Distinguished guests, fellow engineers, policymakers, and leaders of industry. It is a great privilege to stand before you in the Coal City, a symbol of Nigeria's rich industrial heritage, to discuss our sustainable future. The theme of this conference rightly places SMEs at the heart of national development. But we must ask: what is the quality of this growth? Is it growth that depletes our natural capital and pollutes our cities, or is it growth that regenerates, innovates, and endures?

As the Managing Director of SEDI Enugu, an institution established to catalyze technological self-reliance, I see this not as an abstract question but a daily operational challenge. Our work with countless SMEs across the South-East reveals a dual reality: immense entrepreneurial energy alongside a growing environmental footprint. The sub-theme of waste management is, therefore, not a sidebar conversation; it is the main event. It is the critical path to reconciling our industrial ambitions with the health of our planet and our people.

Today, I will outline the strategic importance of SMEs, dissect the complex nature of our waste streams, and propose a concrete, multi-stakeholder action plan to position Nigerian SMEs as global leaders in sustainable industrial production.



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Looking at the strategic imperative of SMEs, which are more than just numbers. The statistics indicates over 40 million SMEs form the bedrock of our economy. But their true value lies beyond these numbers. Imperatively, there impact can be felt as I will be mentioning them below:

1. Job Creation & Skill Development:

SMEs are Nigeria's largest employer and most prolific vocational academy, providing hands-on skills in machining, fabrication, agro-processing, and manufacturing. This singular and vital area has been a pivot in showcasing Nigerian contents in industrialization and national dependency and as such preserving the glory of our fathers land.

2. Innovation and Adaptability:

Their small size allows for agility and frugal innovation, creating solutions tailored to local needs and constraints. Generating new ideas and venturing into new opportunities with absolute evaluations for sustainability and equity.

3. Economic Resilience:

Distributed across urban and rural landscapes, they diversify our economic base and buffer against macro-economic shocks. Massive creativity of value chains in our home grown products that has created much attractions and competitiveness with foreign and acceptable standards.

4. Deepening Local Value Chains:

By supplying raw materials, components, and services to larger industries, SMEs are the connective tissue that strengthens our industrial autonomy. Adding technical values to our industries and salvaging the nation from over depending on importation that has decline our forex exchange to a non-enviable state.

However, this vital sector operates under immense pressure, often viewing environmental management as a costly distraction. Our mission is to reframe this perception and create sustainable waste management as a powerful tool for reducing cost, mitigating risk, and unlocking new revenue. Looking at the waste landscape, and drawing a comparative analysis of industrial and Municipal Streams, it is noted that effective management requires precise understanding. To move towards effective management, we must first move beyond viewing "waste" as a single, monolithic problem. A precise understanding of its two primary streams, industrial and municipal, is essential, as their origins, characteristics, and management requirements are fundamentally different.

Industrial waste, particularly from SMEs, typically originates from specific, identifiable point sources like factories, workshops, and processing plants. Its composition is a key differentiator: it is generally homogeneous and predictable, directly tied to the industry's activity. For example, a metalworking shop generates shavings and spent lubricants, a textile factory produces off-cuts and dye effluents, and a food processing plant creates organic pulp and packaging rejects. This specificity is a double-edged sword; while it makes the waste stream easier to identify, it often comes with a moderate to high hazard potential. These streams can contain oils, chemical solvents, heavy metals, and other toxic substances that demand specialized handling and treatment to prevent severe environmental contamination and public health risks. Consequently, the primary management focus for industrial waste must be pollution prevention at the source through in-plant recycling, process efficiency upgrades, and pre-treatment before any potential discharge or disposal. However, this homogeneity also presents a significant circular economy opportunity through industrial symbiosis, where one SME's waste output can become another's valuable raw material, creating a closed-loop system within an industrial cluster.



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In stark contrast, Municipal Solid Waste (MSW) emanates from diffuse sources, millions of households, markets, streets, and commercial offices. This decentralized origin is the root of its greatest challenge: its heterogeneous and highly variable composition. MSW is a complex, mixed slurry of primarily organic matter (accounting for 50-65% of the total volume), entangled with plastics, paper, textiles, glass, and a growing fraction of hazardous household items like used batteries and expired medicines. While its overall hazard potential is generally lower than concentrated industrial waste, the constant mixing and contamination render it incredibly difficult and costly to manage effectively. The management focus for MSW, therefore, necessarily prioritizes public health and material recovery. This entails building efficient collection systems to prevent dumping and the spread of disease, and implementing widespread segregation at source to unlock the immense "waste-to-wealth" potential within this stream. The high organic content is ideal for large-scale composting or anaerobic digestion to produce energy, while the segregated recyclables can provide a critical feedstock for local manufacturing industries.

The critical, and often disastrous, intersection of these two streams occurs when untreated industrial waste is improperly disposed of into the municipal waste flow. This act poisons the entire MSW stream, making safe recycling impossible and transforming a municipal dump into a hazardous waste site. Conversely, the failure of municipal systems to effectively segregate and recover materials deprives local industries of a reliable source of secondary raw materials, perpetuating a linear economy of extraction and disposal. Understanding this dichotomy is the first step toward designing intelligent, separate, and effective management systems for each stream.

The critical intersection occurs when untreated industrial waste enters the municipal stream, poisoning recycling efforts, or when inadequate municipal management deprives industry of reliable secondary raw materials.

Looking at the Enugu Case Study: From Coal City to Green City, Enugu State provides a potent microcosm to study these challenges and innovate solutions via the following salient areas:

1. The Legacy and The Opportunity:

Our history as a coal mining hub gives us a deep industrial identity. Now, we have the opportunity to lead a new, green industrial revolution.

2. Clusters of Challenge and Innovation:

The Emene and Emulu industrial clusters host numerous SMEs in plastics, pharmaceuticals, and manufacturing. Their concentrated waste streams are a visible challenge but represent a concentrated opportunity for circular economy interventions.

3. Policy Environment: The Enugu State Waste Management Authority (ESWAMA) is making strides, and the Enugu SME Centre is a critical ally for capacity building. However, a policy gap remains in incentivizing industrial symbiosis and supporting SME compliance.

4. Emerging Green Shoots:

We are witnessing the rise of innovative startups: plastic recycling initiatives turning waste into pavement tiles, agro-processors composting organic waste, and fabricators looking to build local waste-handling equipment. This is where SEDI's mandate becomes crucial

The SEDI ENUGU Mandate, in providing the Technological Backbone for SME Sustainability

At SEDI Enugu, our role transcends research. We are builders and enablers. Our contribution to this national agenda is practical and focused on equipment, expertise, and ecosystem development.

1. **Fabrication of Appropriate Technology:**

We are designing and prototyping cost-effective, robust, and easy-to-maintain machinery for SMEs. This includes:

- Shredders and Granulators: for size reduction of plastics and organic waste.
- Briquetting Presses: to convert organic and paper waste into solid fuel for both domestic and industrial source of sustainable energy that is proven and widely use
- Compact Balers: to densify recyclables like plastics and cardboard for efficient transportation.
- Small-Scale Composting Units: for agro-processing SMEs to manage organic waste.

2. **Capacity Building and Training:**

We host technical workshops for SME owners and technicians on operating this equipment, integrating waste reduction into production processes, and understanding environmental compliance.

3. **Collaborative Partnerships:**

We are forging partnerships with ESWAMA to develop tailored solutions for industrial estate waste and with the Enugu SME Centre to make our technologies accessible through financing schemes.

4. **Policy Advocacy:**

We provide evidence-based advice to state and national governments, advocating for policies that support green manufacturing and circular economy investments, one of which is the NASENI green house plant that is widely growing direct use vegetables for our green consumption.

In translating vision into reality, this will always require a concerted effort from all stakeholders. However, I stand firm to propose the following action agenda for both: Government & Regulatory Bodies (NESREA, ESWAMA etc.)

1. **Develop & Enforce Differentiated Regulations:**

Create tiered compliance frameworks for SMEs based on size and sector, focusing on support before punishment.

2. **Establish Shared Infrastructure:**

Fund and develop Material Recovery Facilities (MRFs) and Common Effluent Treatment Plants (CETPs) within industrial clusters. This will be a replica like what we have in electroplating workshop in SEDI-ENUGU funded by UNIDO.

3. **Create Green Procurement Policies:**

Prioritize government contracts for SMEs with verifiable environmental management credentials.

4. **Implement Fiscal Incentives:**

Offer tax breaks, reduced import duties on green tech, and grants for SMEs adopting circular practices.



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For Financial Institutions:

5. **Design Green Finance Instruments:**

Develop accessible loan products and venture funding specifically for waste-to-wealth startups and SMEs investing in cleaner production tech.

6. **De-risk Sustainability Investments:**

Provide credit guarantees for banks' lending to SMEs for environmental upgrades.

For SMEs Themselves:

7. **Conduct Waste Audits:**

Understand your waste stream; you cannot manage what you do not measure.

8. **Adopt a "Reduce, Reuse, and Recycle" Mindset:**

Start with simple, low-cost actions like reducing packaging, reusing containers, and segregating waste for sale to recyclers.

9. **Explore Industrial Symbiosis:**

Network with neighboring businesses to see if your waste can be their resource.

10. **Invest in Skills:**

Train your staff on efficient material use and waste management protocols.

For Research & Technology Institutions (Like SEDI, PRODA etc.)

11. **Focus on Frugal Innovation:**

Develop affordable, context-appropriate technologies for waste processing and valorization.

12. **Act as Knowledge Hubs:**

Bridge the gap between academic research and on-the-ground SME needs, providing continuous technical support.

Conclusively, Our Collective Responsibility,

Ladies and gentlemen, the path forward is clear. The choice between industrial development and environmental sustainability is a false one. The only development that will stand the test of time is sustainable development.

SMEs, with their ingenuity and dynamism, are best placed to lead this charge. But they cannot do it alone. They need enabling policies, access to finance, and appropriate technology. From the Coal City, we can send a powerful message to the nation: that Nigeria's industrial might will be built not on extraction and pollution, but on innovation, efficiency, and circularity.

At SEDI Enugu, we are ready to play our part. We invite you our policymakers, industrialists, financiers, and engineers, to join us in this critical endeavor. Let us work together to ensure that our national industrial growth is both prosperous and sustainable, creating a legacy we can all be proud of.

Thank you.

We remain and are still, Scientific Equipment Development Institute (SEDI), Enugu "Driving Technological Innovation for Sustainable Industrial Growth.



55TH INTERNATIONAL CONFERENCE “COAL CITY 2025”



A. Raw Materials and Solid Minerals Development, Utilization and Growth

Extraction Of Neem Oil – A Means Of Economic Emancipation In Nigeria

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Abstract

A 50 kg/day capacity scale-up plant was used for extracting neem oil from neem seed using ethanol as a solvent. The global monetary projection of neem oil necessitates its extraction for economic emancipation. The qualities of the extracted neem oil were 4.20 mg KOH/g, acid value; 60.10 gI/100 g, iodine value and 210.0 mg KOH/g, saponification value. The projected cost price of #1,000 per kg was used against the current price of #3,471 per kg for the cost estimation. The scale-up plant needs a total capital investment of #6 627 889 with a payback period of 2.77 years and a 36.13% rate of return. These investment figures are highly attractive to business entrepreneurs, and the neem oil will be more available and accessible to households and industries at a cheaper rate; thereby serving as a source of economic emancipation. The quality of the extracted neem oil agreed with current literature values; therefore, it favoured its industrial application after pre-treatment for a particular application.

Keywords: Quality of neem oil, factor estimate method, Total capital investment, pay-back period and rate of return.

1.0 Introduction

The neem tree was introduced in Nigeria by the colonial masters in 1928. The neem tree is found almost everywhere in Nigeria, and it occupies 3, 400 hectares of land in Katsina, Kebbi, Sokoto, Borno and Zamfara states (Abidina *et al.*, 2020). Neem oil is a vegetable oil that is obtained from the neem seed, and it contains a high percentage of fatty acids (Kishore *et al.*, 2023; Kamble *et al.*, 2022). Fatty acids are not freely found, but naturally found in combination with glycerol (an alcohol) in the form of triglyceride (Sadiq *et al.*, 2022). It appears in many colours such as golden yellow, dark brown, yellowish brown, greenish brown or bright red (Semere, 2023). The oil has a bitter taste and its odour is like the mixture of garlic and peanut (Usman *et al.*, 2013). The bioactive components in the neem oil include nimbin, nimbidin and nimbolides (Ayinde *et al.*, 2020). The extraction yield of the oil from neem seed is the percentage of the extractable oil from the total weight of the neem seed under specified conditions (Mich *et al.*, 2023; Omotehinse & Ovuworie, 2021).

The popular methods for extracting oil from neem seed include: Mechanical pressing, Solvent extraction, Supercritical fluid extraction and Enzymatic extraction (Kamble *et al.*, 2022; Hussein *et al.*, 2021). The mechanical pressing is the most popular method, and it involves crushing the seed and squeezing the oil by applying pressure in the form of a hydraulic or screw press to force oil out of the oil-bearing seed (Kabutey *et al.*, 2021). It produces oil of low yield and poor market value due to its turbidity (Usman *et al.*, 2013). The solvent extraction method proved to be a better method due to low residue of oil in the cake of about 0.5% (Workneh, 2011) compared to the mechanical method that leaves a residue of 18% (Kamble *et al.*, 2022).

The quality of neem oil is of industrial importance, and it depends on its iodine, acid and saponification value (Workneh, 2011). Acid value indicates the level of free fatty acid in the oil, Iodine value is a measure of the level of unsaturation of the oil, and it indicates the long-term stability properties of the oil, a factor to consider in the storage of the oil. The saponification value is an indicative of the presence of lower molecular components / short-chain fatty acids in the oil (Hussein *et al.*, 2021).

The global neem oil market is valued at USD 3.8 Bn by 2030 (Neem Oil Concentrates Market Size, Share & Industry Outlook and Neem Oil Concentrates Market Size, Share & Industry (n.d)) and is highly demanded by emerging economies such as India and China (Vasavada, 2023).

Economic emancipation is the ability and power to determine one's own financial position and future. Being economically emancipated is the main goal of every person; it allows one to be independent and not rely on parents or the government for survival. However, in contrast to rich nations, the vast majority of Nigerians live in extreme poverty (Kayode, 2022); hence the need to explore ways of income generation.

The need for large-scale production of neem oil to meet increasing demand has been emphasized by (Nde & Foncha, 2020). To increase the production capacity, a 9.65 kg/day capacity solvent extraction pilot plant was used by Usman *et al.* (2013); the pilot plant was scaled up to 50 kg/day and used by Usman *et al.* (2024) to extract neem oil.

This study aims to determine the cost estimation of establishing the scaled-up (50 kg/day) solvent extraction plant for a successful large-scale production of neem oil. The cost estimation is very crucial in attracting entrepreneurs to the neem oil extraction business and is currently scarce in the literature. The extraction of oil from neem seed shows great potential to lift many above the poverty line by keying into the global stage through the export of neem oil or using the neem oil domestically, since neem seed is massively underutilized in Nigeria (Sadiq *et al.*, 2022). The multiplying factors for evaluating the total fixed capital investment are shown in Table 1.

Table 1: Typical percentges of fixed capital investment values for direct and indirect cost.

S/NO	Components	Range, %
Direct cost		
<i>f</i> ₁	Purchased of equipment	15 – 40
<i>f</i> ₂	Purchased equipment installation	6 – 14
<i>f</i> ₃	Instrumentation and control	2 – 8
<i>f</i> ₄	Piping installation	3 – 20
<i>f</i> ₅	Electrical installation	2 – 10
<i>f</i> ₆	Building	3 – 18
<i>f</i> ₇	Service facilities installation	8 – 20
<i>f</i> ₈	Land	1 – 2
Indirect cost		
<i>f</i> ₁	Engineering	4 – 21
<i>f</i> ₂	Construction expenses	4 – 16
<i>f</i> ₃	Contractor's fee	2 – 6
<i>f</i> ₄	Contingency	5 – 15

Source: (Peters & Timmerhaus, 1991)

2.0 Material and Method

2.1 Extraction of Oil

The neem oil was extracted using the scale-up plant used by Usman *et al.* (2024) and shown in Plate 1. The best extraction parameters of 0.42 mm particle size, 40 minutes extraction time and 60 °C extraction temperature used by Usman *et al.* (2024) will be adopted, with the exception of the mass of neem seed kernel for the extraction. The mass of neem seed kernel for the extraction will be based on the plant design for processing 50 kg/day at 4 hours per run; this translates to 6 runs per day, which is equal to 8.33 kg per run.

10 litres of ethanol and 8.33 kg of neem seed kernel of size 0.42 mm were charged into the extractor **B** via valve V1. The extraction temperature of 60°C was set using the temperature controller, the contact time of 40 minutes was set using the timer and the flat blade turbine impeller was operated at 77 rpm using the speed regulator. The temperature controller, timer and the speed regulator are incorporated in the control panel **A**. The leaching of the neem oil took place in **B**, and the separation of the miscella from the cake took place in the filtration unit **E** under atmospheric conditions. The mixture of oil and solvent was separated in the evaporator **F** at the boiling point of ethanol, 78°C. Finally, 2.17 kg of neem oil was collected from the evaporator via valve V6.

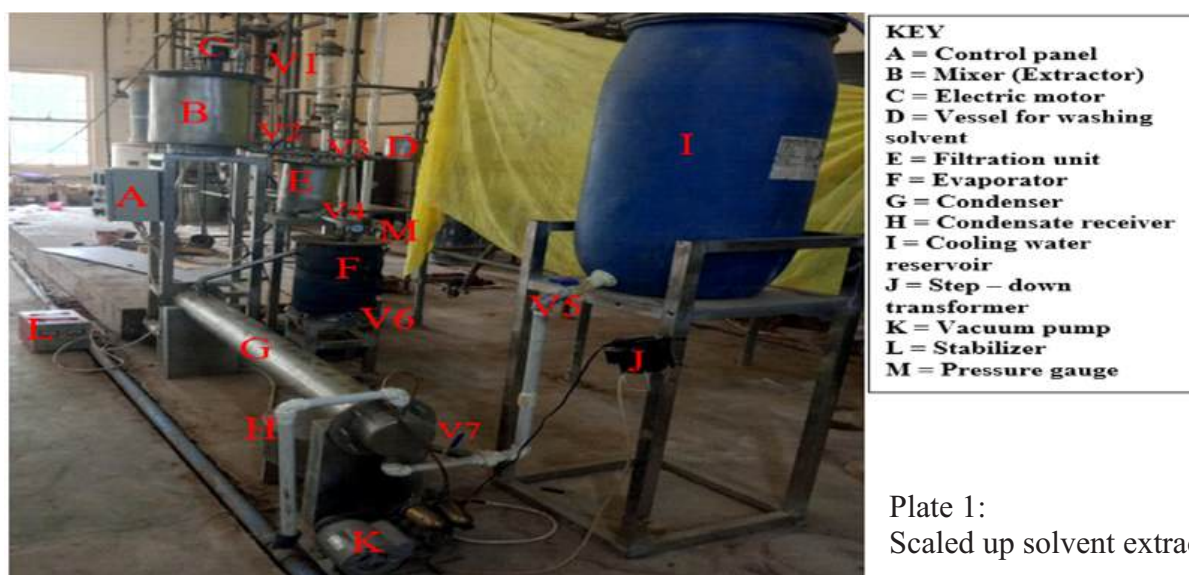


Plate 1:
Scaled up solvent extraction plant

2.2 Calculation of Extraction Yield

The extraction yield is calculated using Equation 1 (Guirrou *et al.*, 2024).

$$\text{Yield} = \frac{W_1 - W_2}{W_1} = \frac{\text{Mass of extracted oil (g)}}{\text{Mass of neem particle (g)}} \times 100 \quad 1$$

2.3 Quality Determination of Neem Oil

The acid, iodine and saponification values of the extracted neem oil were determined using the AOAC (1990) method adopted by Utono *et al.* (2024), Sulaiman *et al.* (2024) and Utono *et al.* (2024), respectively.



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2.4.4 Operating cost and raw materials

Total sell

Quantity of neem seed to be processed per day = 50 kg

Total quantity of neem oil produced from the 50 kg = $\frac{50 \times 2.17}{8.33} = 13.02$ kg

2.4 Cost Estimate and Analysis

2.4.1 Cost of major equipment

The direct cost of the fabrication of major equipment is shown in Table 2

Table 2: Cost of major equipment/component

S/NO	Equipment	Amount (Naira)
1	Extractor	400 000
2	Shell and Tube heat exchanger	800 000
3	Evaporator	350 000
4	Filtration unit	150 000
5	Condensate receiver	100 000
6	Water reservoir	100 000
Total (I_E)		1 900 0000

2.4.2 Cost of auxiliary equipment

The cost of auxiliary equipment was calculated using the factor estimate method

$$I = (1 + \sum f_i) I_E \quad 2$$

I = total fixed capital investment

I_E = cost of major equipment (fixed capital investment)

f_1 = multiplying factor for the estimation of cost of piping, structure and so on.

f_2 = multiplying factor for the estimation of indirect expenses such as engineering fee, contractors' cost and contingency (Backhurst and Harker, 1983).

From Table 1, the $\sum f_i$ for direct cost is computed as follows:

$f_1 = 0.4$, $f_2 = 0.14$, $f_3 = 0.08$, $f_4 = 0.2$, $f_5 = 0.1$, $f_6 = 0.18$, $f_7 = 0.2$ and $f_8 = 0.02$.

$\sum f_i = 1.35$

$$\text{Total direct cost} = (1 + \sum f_i) I_E \quad 3$$

(Backhurst and Harker, 1983)

Total direct cost = $(1 + 1.35) \times 1\,900\,000 = \text{\#}4\,465\,000$

Indirect cost

$f_1 = 0.21$, $f_2 = 0.16$, $f_3 = 0.06$ and $f_4 = 0.15$

$\sum f_i = 1 + 0.58 = 1.58$

Total fixed capital investment, $I = (1 + 1.35) \times 1.58 \times 1\,900\,000 = \text{\#}7\,505\,550$.

2.4.3 Working capital

This includes money used on raw materials and cash kept at hand for engineering, salaries and miscellaneous activities. The estimation was based on one year of inventory holding one year of wages.



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Total working days = 317 days per year

Quantity of neem oil produced per annum = $13.02 \times 317 = 4\,127.34$ kg

Assumed 1 kg of neem oil cost #1 000

Total sell = $4\,127.34 \times 1000 = \text{#}4\,127\,340$

Let cost of raw material be 30% of the total sell = $0.3 \times 4\,127\,340 = \text{#}1\,238\,202$

Assumed one-month wages = #300 000

Total wages for the year = $12 \times 300\,000 = \text{#}3\,600\,000$

Working capital = wages + cost of raw materials = $3\,600\,000 + 1\,238\,202 = \text{#}4\,838\,202$

Total capital investment = total working capital + fixed capital investment
 $= 4\,838\,202 + 1\,900\,000 = \text{#}6\,738\,202$

2.4.5 Depreciation

Assuming plant operates for 317 days

Plant useful life = 8 years

Salvage value = 10% of total capital investment

The straight - line method of depreciation is used:

$$\text{Depreciation} = \frac{(\text{Adjustment cost})}{(\text{Plant useful life})} = \frac{(\text{Total capital investment} - \text{salvage value})}{(\text{Plant useful life})}$$

(Wallstreetmojo Team, 2024)

$$\text{Depreciation} = \frac{(6\,738\,202 - (0.1 \times 6\,738\,202))}{8} = \text{#}758\,047.73 / \text{year}$$

For a successful investment decision, the following profitability measures are considered to make the project attractive.

2.4.6 Profitability

Total generated revenue = #4 127 340

Profit before tax = total revenue – cost of raw materials = $\text{#}4\,127\,340 - \text{#}1\,238\,202 = \text{#}2\,889\,138$ Let

Corporate rate tax (R) = 50%

Profit after tax = Profit before tax $\times (1 - R) = 2\,889\,138 \times (1 - 0.5) = \text{#}1\,444\,568$

Cash flow = Profit after tax – Depreciation = $\text{#}1\,444\,568 - \text{#}758\,047.73 = \text{#}686\,521.27$

Payback period

The payback period is the time it takes to reach the breakeven point. The payback period is calculated using Equation 5 (Kagan, 2024).

$$\text{Payback period (PBP)} = \frac{(\text{Fixed capital investment})}{(\text{Cash flow})} \quad 5$$

$$\text{Payback period (PBP)} = \frac{(1\,900\,000)}{(686\,521.27)} = 2.77 \text{ years}$$



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Rate of return

The rate of return on investment is ordinarily expressed on a yearly percentage basis (Peters & Timmerhaus, 1991).

$$\text{Rate of return (ROR)} = \frac{(\text{Cash flow})}{(\text{Fixed capital investment})} \times 100 \quad 6$$

(Murphy, 2021)

Rate of return is calculated using Equation 6

$$\text{Rate of return (ROR)} = \frac{(686\,521.27)}{(1\,900\,000)} \times 100 = 36.13\%$$

3.0 Result And Discussions

The quality of the extracted neem oil is shown in Table 3, and the summary of the cost estimate and analysis is shown in Table 4.

Table 3: Quality of extracted neem oil

S/NO	Quality	Standard value	Value
1	Acid value (mg KOH/g)	0.4 – 4 (ASTM D6751)	4.20
2	Iodine value (gI ₂ /100 g)	65 – 80	60.10
3	Saponification value (mg KOH/g)	200 – 220 (ASTM 763)	210.0

The 4.20 mg KOH/g acid value obtained is lower than 8.3 mg KOH/g reported by Kishore *et al.* (2023) and higher than 1.70 and 2.36 mg KOH/g reported by Sulaiman *et al.* (2024) and Sadiq *et al.* (2023), respectively. The extracted neem oil has a higher value than the maximum limit of 4.0 mgKOH/g; the neem oil can easily be subjected to pre-treatment before application in the industry. The reported iodine value of 60.10 gI₂/100g is close to 58 gI₂/100g reported by Yami *et al.* (2020) but lower than 75, 122.5 and 119.8 gI₂/100g reported by de Paulo Barbosa *et al.* (2023); Hundai *et al.* (2022); and Sulaiman *et al.* (2024) respectively. The reported saponification value of 210.0 mgKOH/g is within the standard range value of 200 – 220 mgKOH/g. The value is higher than 185.05 mgKOH/g, 184.78 mg KOH/g and 189.4 mgKOH/g reported by Yami *et al.* (2020); de Paulo Barbosa *et al.* (2023) and Kishore *et al.* (2023), respectively, but lower than 268 mgKOH/g reported by Sulaiman *et al.* (2024). The quality variation of the extracted neem oil from the report qualities by previous researchers can be attributed to differences in locations where the neem seed was obtained, the time of harvesting the neem seed and soil composition (Jessinta *et al.*, 2014). Based on the quality of the neem oil, it is highly recommended for industrial applications after pretreatment.



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Table 4: Cost estimation

Parameter	Value
Total working days	317 days / year
Quantity of neem oil produced	13.02 kg
Cost of 1 kg of neem oil	# 1 000
Plant useful life	8 years
Fixed capital investment	# 1 900 000
Working capital	# 4 838 202
Total capital investment	# 6 738 202
Payback period	2.77 years
Rate of return	36.13%

The current price of the major equipment and the factor method were used in carrying out the cost estimation of the scaled-up plant. At a unit price of #1,000 per kilogram of the produced neem oil, the plant needs #6, 627, 889 as total capital investment, which comprises #1, 900, 000 as fixed capital investment and #4, 727, 889 as working capital. The plant has a payback period of 2.77 years with a rate of return of 30.01%. Based on the profitability study, it shows that the extraction of neem oil using the scaled-up plant is profitable and feasible since the unit price (#1000/kg) is less than the current price of #3 471/kg (Neem Oil Premium, Packaging Size: 1 kg).

4.0 Conclusion,

The acid, iodine and saponification values of the extracted neem oil were 4.20 mg KOH/g, 60.10 gI₂/100 g and 210.0 mg KOH/g, respectively; while the unit price of the neem oil is #1 000 per kg as against #3 471 per kg. The scale-up plant needs a total capital investment of #6 627 889 with a payback period of 2.77 years and a 36.13% rate of return. The acid, iodine and saponification values of the extracted neem oil are close to values obtained by previous researchers and show great potential for industrial usage after pre-treatment for specific usage. The neem oil will be more available and accessible to households and industries at a cheaper rate; thereby serving as a source of economic emancipation and highly attractive to business entrepreneurs due to its low payback period and high rate of return.



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Surface Modification And Characterization Of Ikpobia Clay

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Abstract

This study evaluated the surface modification and characterization of Ikpobia clay. The refined clay (RC), calcined clay (CC) and acid modified clay (AC) were characterized by pH, Fourier transform infrared (FTIR), x-ray diffraction (XRD), scanning electron microscope/electron dispersive x-ray (SEM/EDX), Brunauer-Emmett-Teller (BET) surface area, thermal gravimetric/differential thermal analysis (TGA/DTA) and methylene blue adsorption. The pH was more acidic in AC (5.15) and slightly acidic in RC and CC (6.84 and 6.56). The FTIR and XRD peaks suggested the presence of O–H, Si–O or Al–O, Al–OH and Si–O–Al or Si–O–Si, which were characteristics of kaolinite, illite, siderite, and quartz minerals. The BET surface area increased from 235.50 m²/g for RC to 313.70 m²/g for AC, but reduced to 213.80 m²/g for CC. The maximum adsorption capacity, Q_{max}^2 of methylene blue was 40.30 mg/g for RC. The adsorption was a monolayer removal of methylene blue onto a heterogeneous surface of the RC adsorbent, as well as ionic interaction between methylene blue and RC due to the predominance of negatively charged oxygen functional groups of carbonyl (C=O) and hydroxyl (O–H), ion exchange and electrostatic attraction. The RC had proven to be a credible candidate for cationic pollutants in wastewater.

Key words: Clay samples, calcination, acid impregnation, adsorption, methylene blue.

1. Introduction

Clay is a colloidal hydrous aluminosilicate mineral, which occurs naturally and is found in soil, water and sediments. It has a particle size of less than 2 μm and belongs to the family of phyllosilicates, which consist of tetrahedral silicate and octahedral oxide sheets (García *et al.*, 2020; Damilola *et al.*, 2019). Based on these sheets, clay minerals are further classified as kaolin-serpentine, pyrophyllite-talc, smectite, vermiculite, mica, chlorite and interstratified clay minerals (García *et al.*, 2020). Clay minerals also possess some unique characteristics such as high ion-exchange ability, good thermal stability, high specific surface area, high adsorption power and porosity (Jawad *et al.*, 2023).

These characteristics of clay minerals have made it a veritable source of economy in various areas (Muwawa *et al.*, 2024). Notable among these applications is in the construction industries for bricks, cement and tiles production (Muwawa *et al.*, 2024), in the pharmaceutical industries as excipients and adsorbents (Da Rocha *et al.*, 2022), in the electrical industries as insulators (Kalendova *et al.*, 2024), in the petroleum industries as drilling mud (Ogolo and Onyekonwu 2023), in the textile industries as adsorbents (Bujdák 2023), in the agricultural industries for fertilizer production (Alghamdi *et al.*, 2023) and in nuclear field as storage for radioactive waste to ensure stability of the waste (Singh and Um 2023). Meanwhile, the presence of non-homogeneous impurities in natural clay has made its technological application difficult, hence the need for its modification before it can be put to useful applications (García *et al.*, 2020).



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Thermal and acid modifications of clay are often employed to eliminate impurities and increase the number of active sites, specific surface area, surface acidity and porosity (España *et al.*, 2019; Lamrani *et al.*, 2025). Acid modification results in the reduction or elimination of cations such as calcium, magnesium, potassium and metal oxide, hence creating vacant adsorption sites (Lamrani *et al.*, 2025). Commonly used acids are phosphoric, nitric, acetic, oxalic and carboxylic acid (Thiebault *et al.*, 2020). Their impacts depend on the quantity used (Thiebault *et al.*, 2020). Thermal modification, also known as calcination, results in weight loss, increased porosity and increased surface exposure for ion exchange (Georgopoulos *et al.*, 2023).

Ikpobia clay has found application as an additive in the production of ordinary portland cement. It is available in very large quantities. Beyond its usage as an additive for cement production, no work has been found on the physicochemical characterization and surface modification of this clay. Therefore, this study evaluated the physicochemical properties and surface modification of Ikpobia clay as a potential adsorbent. Thermal and acid modification were carried out on the raw pretreated clay sample, and all three samples were characterized for thermal stability, mineral and chemical composition, microstructure and morphology, and methylene blue removal from wastewater to estimate the essence of the surface modification.

2. Materials and Methods

2.1 Chemical Reagents

All the chemical reagents used in this study were of analytical grade; Oxalic acid (99%, Merck, Germany), hydrochloric acid (37% Fisher scientific Waltham, USA), sodium hydroxide pellets (97% LOBA CHEMIE PVT LTD, Mumbai, India), calcium chloride (94% UniClean, America) and methylene blue (98%, Merck, Germany). All solutions were prepared using distilled water from the Chemical Engineering Department, Edo State University, Iyamho, Nigeria. A clay sample was collected from Ikpobia quarry, Okpella, Edo State, Nigeria.

2.2 Preparation and Surface Modification of the Clay Sample

A raw clay sample was collected from the Ikpobia deposit site (quarry) in Okpella, Etsako West Local Government Area of Edo State, Nigeria. Five (5) kilograms of the clay sample were comminuted. Five hundred (500) grams of the comminuted sample were soaked in 250 mL of distilled water for 24 h. The mixture after 24 h was stirred at ambient temperature for 3 h on a magnetic stirrer at 600 rpm, and left to age for four (4) days to allow for the sedimentation of quartz impurities. Meanwhile, for each day, the clay-water mixture was decanted and replaced with fresh distilled water until the mixture became less milky. The colloid clay was separated from the quartz impurities, filtered using Whatman filter paper, dried in an oven at 105 °C for 180 min and stored in a desiccator. The dried clay sample was milled to 125 µm and designated as refined clay (RC) (Patanjali *et al.*, 2020) Twenty (20) grams of (RC) was collected



and calcined at 300 °C (being the optimum adsorption response temperature from the design of experiment) for 3 h, left to cool at ambient temperature and designated as calcined day (CC) Another 20 g of RC was collected and impregnated with oxalic acid in the ratio of 1.1 (being the optimum adsorption response blend ratio from the design of experiment) for 24 h and clacined at 300°C for 3 h. The sample was left to cool, washed with distilled water until a pH of 7, dried in an oven at 105 °C for 180 min and designated as activated clay (AC) (Oliveria *et al*, 2020. Georgopoloset *al*, 2023. Abd-EIF attah *et al*, 2025 Lamraniet al, 2025). The RC, CC and AC were all stored in a desicator before characterization.

2.3 Characterization of RC, CC and AC

The density of the clay samples, which was associated with their porosity was determined using Archimedes' principle. One gram of each sample was wrapped in a polyethene bag and immersed in water. The water initial and final volumes were recorded, and the density was calculated as:

$$\text{Density (p)} = \frac{m_s}{v_2 - v_1} \quad (1)$$

where, m_s was the mass of each sample, v_2 was final volume of water, and v_1 was the initial volume of water.

The water binding capacity (WBC) of the samples, which reflected their textural properties, was determined according to Asokogene *et al.* (2019). Ten (10) milliliters of distilled water was added to 0.5 g of the clay sample in a 5 mL centrifuge tube. The mixture was shaken for 10 min at intervals of 5 s and left undisturbed for 30 min at ambient temperature. It was later centrifuged at 150 rpm for 60 min. The solid clay sample was weighed after the supernatant was decanted and the water binding capacity was calculated as:

$$\text{WBC (\%)} = \frac{(\text{Water bound (g)})}{(\text{Initial sample weight (g)})} \times 100 \quad (2)$$

The pH of the samples, which reflected the surface characteristics as either acidic or alkaline, was determined according to the AOAC 2007 method. One gram of the sample was soaked in 20 ml of distilled water, stirred with a glass rod and left undisturbed for 60 min. The pH of the supernatant was measured with a pH meter.

The point of zero charge (PZC), which suggested the surface charge of the clay samples and gave insight into how to optimize adsorption pH, was determined by adding 11 mL of 0.01 M calcium chloride solution into 1 g of each sample. The pH of each mixture was adjusted to 2, 4, 7, 9, and 11 using 0.1 M HCl and NaOH solution. The mixture was left for 24 h, and the final pH was measured. The change in pH was plotted against the final pH (Gatabi *et al.*, 2016).

FTIR spectrometer (Thermo Scientific Nicolet ISI 10, USA) was used to determine the surface functional groups of the clay samples at a wavenumber range of 4,000–600 cm^{-1} . A 50 mg of each sample and 120 mg of KBr were mixed, triturated, compacted into a disk form with a hydraulic press, dried at 80 °C for 16 h and analyzed



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An X-ray diffractometer (XRD) with monochromatic Cu-K α radiation (BRUKER Corporation, Germany) was adopted to determine the crystallinity of the clay samples. The samples were mounted as an evaporated hexane film in a vertical arrangement, 45 kV and 40 mA voltage and current, respectively, were applied. A continuous mode spectrum was obtained over a 2 θ range of 0 to 70° and a scan rate of 2°/min.

Scanning electron microscope/Energy dispersive X-ray spectroscopy (SEM/EDX) techniques were adopted to determine the micrograph (surface shape and texture) and elemental composition of the clay samples. The Karl Zeiss Company, Germany-type instrument was adopted for the SEM/EDX analysis and was carried out in a vacuum environment. The clay samples were coated with Au, dispersed onto sticky C or Al tapes, which were supported on metallic disks, and images of the sample surfaces were captured at specific magnifications. Meanwhile, for the EDX, the X-ray beam influenced the electrons in the inner shell of the atom of the samples. The quantity of energy lost in the process was unique to each element; hence, this different energy was used to denote the element from which it emanated. Each fluorescence energies that was unique to the elements in the samples were found.

The Thermo Scientific (USA) surface area analyzer was adopted to determine the textural properties of the clay samples according to the Brunauer-Emmett-Teller (BET) method. The clay samples were outgassed overnight at varying increased pressure, 250 $\pm$ 1 °C and exposed at 77 K to nitrogen gas.

Orton TGA/DTA analyzer (USA) was adopted to determine the thermal decomposition of the clay samples. The analysis was carried out at 1000 °C test temperature from room temperature, under nitrogen gas flow at 20 °C/min, and the resulting DTA and TGA signals were recorded continuously.

The adsorption capacity of methylene blue of the clay samples was determined in a batch experiment. A stock solution of methylene blue was prepared by dissolving 1000 mg of standard analytical grade methylene blue powder (98%, Merck, Germany) in 1000 mL of distilled water. Working concentrations of methylene blue solutions (1, 2, 5, 8, 10, 20, 30, 50, 100, 200 and 400 mg/L) were prepared by serial dilution.

Fifty milliliters (50 mL) of each working concentration was added to 50 mg of the clay samples in Beatson bottles, sealed, shaken and left undisturbed at 24 °C for 72 h. This period was long enough for equilibrium adsorption to be obtained (Asokogene and Zaini, 2025). The solution was withdrawn and the residual concentrations were determined by measuring their absorbance at 700 nm with an E. Track Instruments England Standard (model N6000) double beam ultraviolet-visible (UV-Vis) spectrophotometer. The methylene blue solution was kept at its natural pH of 6.48. The absorbance values were converted to concentration using a calibration curve, and the adsorption capacity, q_e (mg/g), was calculated using the mass balance equation as:

$$q_e = \left(\frac{C_o - C_e}{m} \right) \times V \quad (3)$$

where C_0 and C_e (mg/L) are the initial and equilibrium concentrations, respectively, V (L) is the volume of solution, and m (g) is the mass of the adsorbents.

The interaction between the adsorbate molecules and the adsorbent was investigated using the nonlinear Langmuir, Freundlich and Sips isotherm models presented in Equations (4), (5) and (6), respectively (Abadian *et al.*, 2023; Ahsani-Namin *et al.*, 2022)

$$q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \quad (4)$$

$$q_e = K_F C_e^{\frac{1}{n}} \quad (5)$$

$$q_e = \frac{Q_m (K_S C_e)^{n_S}}{1 + (K_S C_e)^{n_S}} \quad (6)$$

where, q_e (mg/g) is the dye removal capacity, Q_m (mg/g) is the maximum monolayer removal capacity, K_L (L/mg) is the Langmuir equilibrium constants, C_e (mg/L) is the solution dye concentration, K_F (mg/g) (L/mg)^{1/n} and n are Freundlich equilibrium constant, K_S (L/mg) and n_S are Sips affinity constants which gives insight to the surface heterogeneity. The Langmuir model describes a monolayer removal onto an adsorbent homogeneous surface, the Freundlich model talks about a non-ideal multilayer irreversible adsorption on a heterogeneous adsorbent surface, and Sips describes heterogeneous surface adsorption by combining the features of Langmuir and Freundlich (Francis and Zaini, 2023; Abadian *et al.*, 2023; Ahsani-Namin *et al.*, 2022). Non-linear regression of Microsoft Excel *Solver* was deployed to determine the isotherm model constants, which validate the methylene blue adsorption onto RC, CC and AC, Figure 1 presents the framework of this study

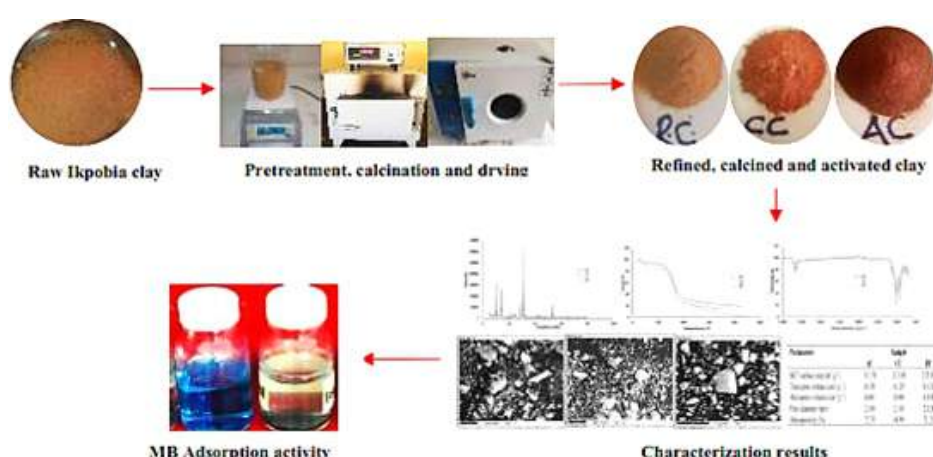


Fig. 1. Framework of surface modification and characterization

2. Results and Discussion

2.1 Physicochemical Characteristic of RC, CC and AC

The preliminary analysis results are presented in Table 1.

Table 1: Preliminary analysis results of RC, CC and AC

Clay	PZC	WBC (%)	Density (g/cm ³)	pH
RC	5.8	46.35	0.68	6.84
CC	5.6	44.20	1.02	6.56
AC	7.0	58.20	1.02	5.15

The values of RC, CC and AC presented in Table 1 showed that all the clay samples had a density less than 1.5 g/cm³ and WBC in the range of 40-60%. This suggested that the adsorbent samples have high permeability and porosity (Munvuyi *et al.*, 2022; Moussa *et al.*, 2022; Damilola *et al.*, 2019). The adsorbent samples revealed acidic pH in the range of 5-7. This suggested either the minimal presence or absence of soluble salts with basic attributes as silicates, bicarbonates and carbonates (Munvuyi *et al.*, 2022; Sorgo *et al.*, 2011). However, the higher acid pH of AC (5.15) could slow adsorption of cation materials in aqueous solution due to its competition for the H₃O⁺ and other ions in the solution (Munvuyi *et al.*, 2022; Sorgo *et al.*, 2011). The results obtained for the PZC of each adsorbent sample suggested the optimum pH for adsorption (Amar *et al.*, 2021). The PZC of RC, CC and AC were 5.8, 5.6 and 7.0, respectively.

The FTIR spectrum of the clay samples (RC, CC and AC) in the wave number range of 4000- 500 cm⁻¹, which reflected their functional groups, mineral identification fingerprint, and molecular water distinction from hydroxyl constituent, are presented in Figure 2.

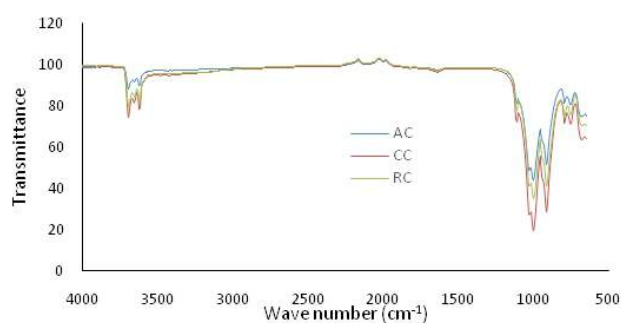


Fig. 2. FTIR spectra of RC, CC and CC

All three adsorbent samples exhibited bands located at 3690, 1640, 998, 909 and 790 cm⁻¹. However, the bands exhibited by AC and CC in the region of 685 and 678 cm⁻¹ were not present in RC. Meanwhile, the band exhibited at 3690 cm⁻¹ corresponded to the characteristics of the O–H stretching vibration, which is typical of hydroxyl groups in kaolinite (Munvuyi *et al.*, 2022; Bentahar, 2017). The band at 1640 cm⁻¹ corresponded to the H–O–H bending vibration of water molecules. The Si–O stretching vibration, which is characteristic of silicate mineral, is found in the band at 998 cm⁻¹. The band at 909 cm⁻¹ corresponded to the Al–OH bending vibration, which is typical of clay minerals. The band at 790 cm⁻¹ is characteristic of the Si–O–Al or Si–O–Si bending vibrations in clay. The band at 685 and 678 cm⁻¹ could be attributed to the Si–O or Al–O vibrations (El Kerdoudi *et al.*, 2023; Munvuyi *et al.*, 2022; Alexander *et al.*, 2018)

The XRD spectra of the RC, CC and AC samples, which define their mineral compositions, are presented in Figure 3.

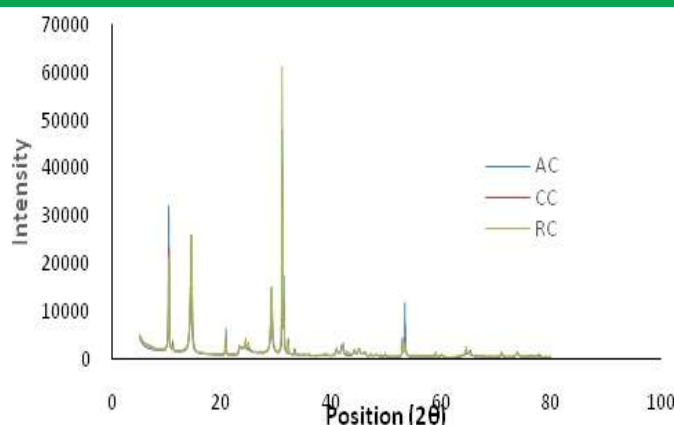


Fig. 3. XRD spectra of RC, CC and CC

The 2θ values are highest in AC than in RC and CC, suggesting greater lattice parameter phase values in AC than in RC and CC. The XRD patterns of RC, CC and AC showed peaks at $2\theta = 10^\circ, 14^\circ, 29^\circ$ and 31° which corresponded to the presence of illite, kaolinite, siderite and quartz minerals (Muwawaet *et al.*, 2024; El Kerdoudiet *et al.*, 2023; Munvuyi *et al.*, 2022; Atia *et al.*, 2020). Meanwhile, AC revealed an additional peak at $2\theta = 53.5^\circ$ which reflected the presence of a new phase after oxalic modification. The XRD results showed that calcination at 300°C did not degrade the mineralogical phases of the RC, thereby suggesting high chemical stability of the RC mineral mixtures (García *et al.*, 2020).

The SEM micrographs of RC, AC and CC, which describe their surface texture and morphology, are shown in Figure 4. The images all presented a similar morphological multiphase structure of flake-aggregate and flake-like sharps. A similar result was reported by Garcia *et al.* (2020). This multiphase structure has made the clay samples good candidates for adsorption (El Kerdoudi *et al.*, 2023).

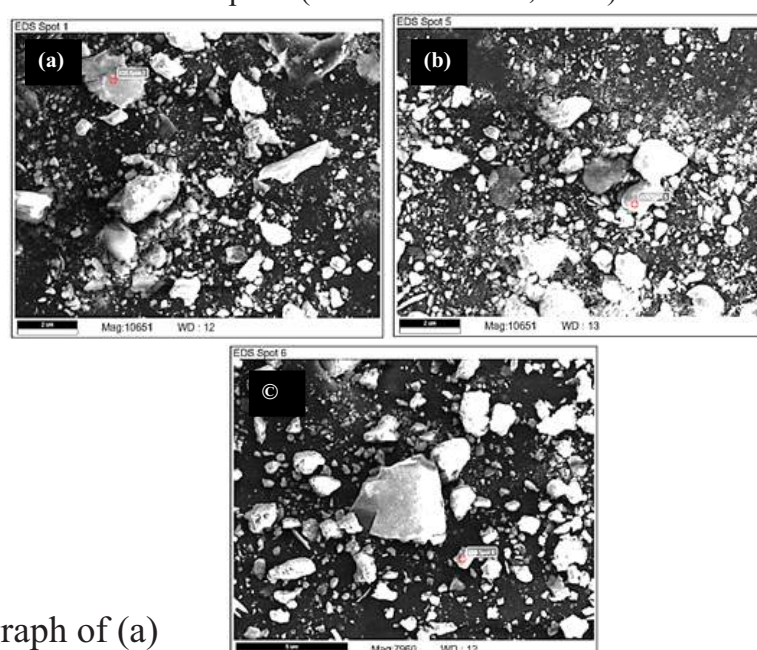


Fig. 4. SEM micrograph of (a) RC, (b) CC and (c) AC



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The EDX result of RC, CC and AC in terms of their weight percentage of the elemental composition is presented in Table 2. The analysis revealed that O had the highest composition in all three samples, which can be attributed to the presence of oxygen-rich structure in mist clay minerals and the introduction of oxygen-rich functional groups resulting from oxalic acid modification (García *et al.*, 2020). Next was C, which could be attributed to the presence of organic matter and/or oxalic acid modification. This can lead to a more porous structure, increased surface area and enhanced adsorption capacity. Next to carbon was silica, followed by aluminium in RC and CC, suggesting that the clay samples are aluminosilicate.

Meanwhile, low K composition in RC and CC suggested that they are poor in illite. The Si to Al ratio of 1.09, 1.13 and 0.91 of RC, CC and AC, respectively, were indications of the absence of free quartz, low permeability and low percentage humidity of the clay samples, which are consistent with the density values in Table 1 (Munvuyi *et al.*, 2022; Gourouza *et al.*, 2013; Emeruwa *et al.*, 2008).

Table 2. Elemental composition of RC, CC and AC

Element	RC	Clay samples (wt%) CC	AC
C	29.17	11.68	20.19
O	52.29	51.15	54.94
Al	5.81	10.16	10.02
Si	6.31	11.52	9.16
Fe	4.08	9.75	4.77
Mg	0.98	1.03	ND
K	1.37	3.05	ND
Ti	ND	0.91	0.19
Ba	ND	0.75	ND
Na	ND	ND	0.72

The textural properties of RC, CC and AC are shown in Table 3. AC presented the largest BET surface area, total pore volume, micropore volume and mesoporosity of 313.70 m²/g, 0.158 cm³/g, 0.043 cm³/g and 72.78%, respectively, suggesting the effect of acid modification. These increased textural properties could increase the monolayer adsorption capacity of AC over RC and CC. Meanwhile, the decreased BET surface area of RC and CC could be a result of particle aggregation and less developed pore structure. Based on the definition of IUPAC, all the clay adsorbent samples are mesoporous with pore diameters in the range of 2-50 nm, suggesting the possibilities of ions and macromolecules penetration (Atiaet *et al.*, 2020; Mistar *et al.*, 2020; Asokogene *et al.*, 2019; Alexander *et al.*, 2018)

Table 3. Surface Textural Properties of AC, CC and RC Materials

Parameters	Sample		
	AC	CC	RC
BET surface area ($\text{m}^2 \text{g}^{-1}$)	313.70	213.80	235.50
Total pore volume ($\text{cm}^3 \text{g}^{-1}$)	0.158	0.129	0.132
Micropore volume ($\text{cm}^3 \text{g}^{-1}$)	0.043	0.040	0.038
Pore diameter (nm)	2.100	2.138	2.128
Mesoporosity (%)	72.78	68.99	71.21

The thermal transition profile at varying temperatures of RC, CC and AC, which the TGA/DTA results represented, is presented in Figure 5. The thermogram of the clay adsorbent samples exhibited a similar pattern with two thermal degradation transitions or endothermic peaks. Comparing the curves, there was a first endothermic peak between 28 °C and 149 °C for RC, 28 °C and 183 °C for CC and 28 °C and 177 °C for AC, suggesting weight loss as a result of desorbed water molecules evolution which was loosely attached to the crystal and evaporated at low temperature (Munvuyi *et al.*, 2022; García *et al.*, 2020; Alexander *et al.*, 2018). The second endothermic peak was between 244 °C and 712 °C, 295 °C and 611 °C and 225 °C and 632 °C for RC, CC and AC, respectively, suggesting weight loss due to dihydroxylation as a result of the removal of chemisorbed water in the crystal lattice of the clay samples which required higher temperature (Alexander *et al.*, 2018; Motawie *et al.*, 2014; Abdou *et al.*, 2013). Between 800 °C and 1000 °C, the clay minerals in RC and AC went through crystallization or reorganization, which was associated with considerable stability in their thermal transition, otherwise known as exothermic peak. (Munvuyi *et al.*, 2022; Amon *et al.*, 2017).

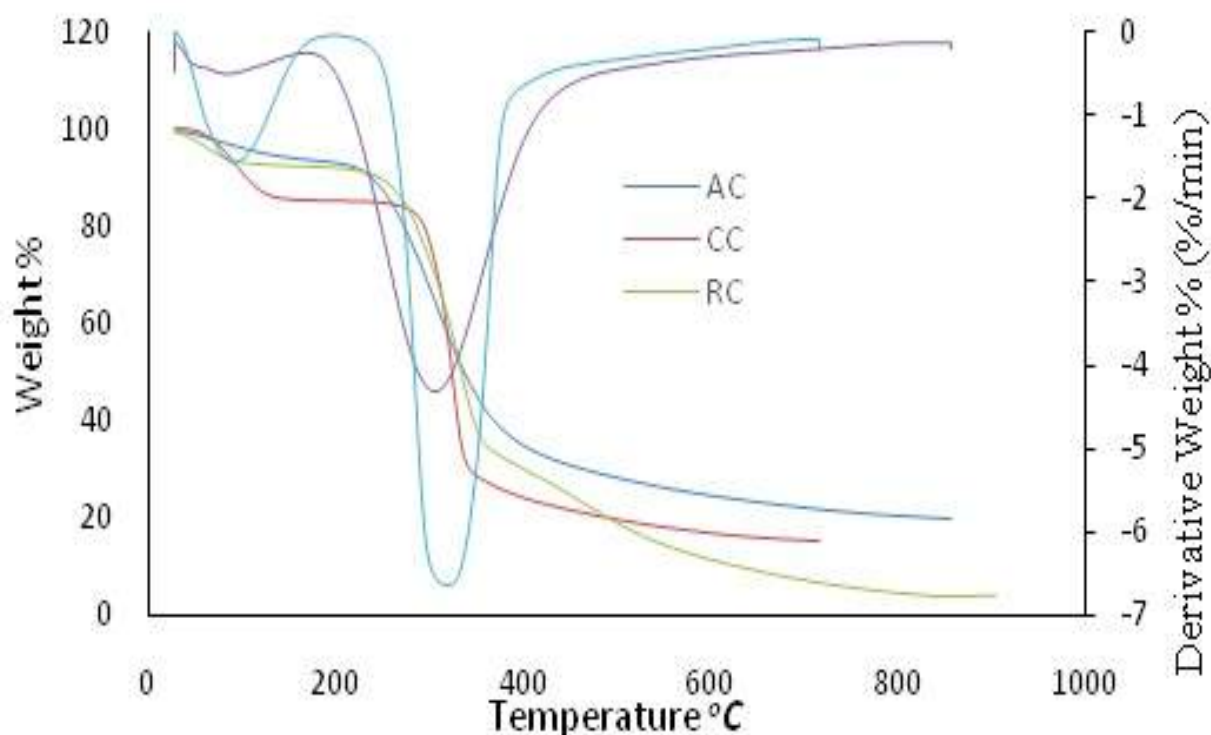


Fig 5. TGA/DTA curves of RC, CC and AC

2.2 Methylene Blue Adsorption

Methylene blue adsorption with initial concentration onto RC, CC and AC is presented in Figure 6.

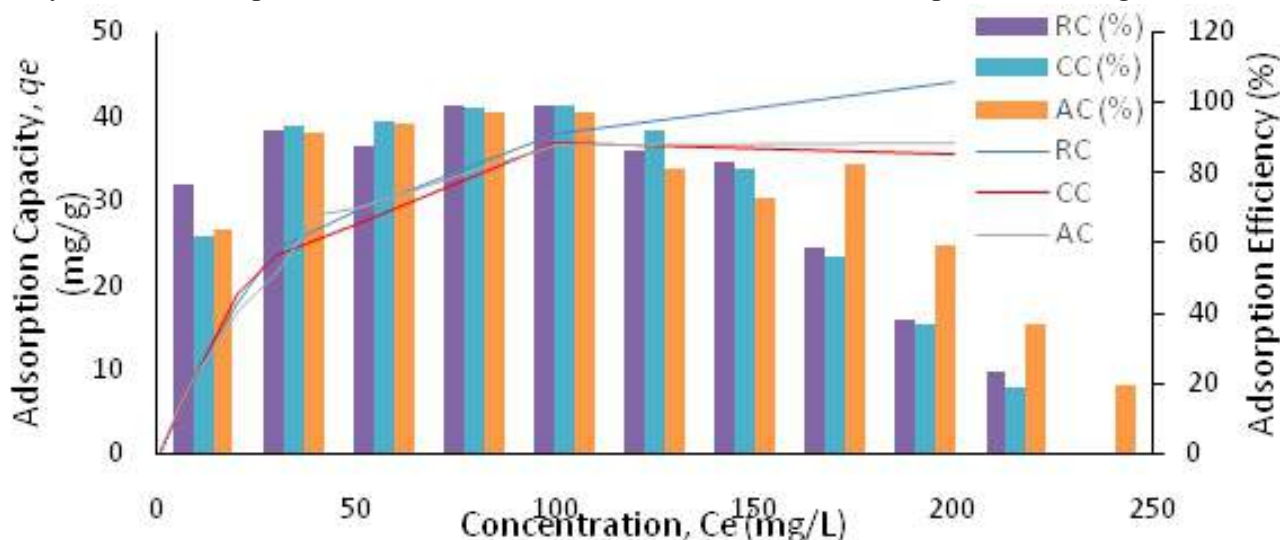


Fig. 6. Effects of initial concentration on methylene blue adsorption by RC, CC and AC

Methylene blue adsorption generally increased with increasing concentrations from 1 to 200 mg/L up until the maximum adsorption or equilibrium point. The adsorption efficiency was higher at lower concentrations for all adsorbents because the adsorption sites of the adsorbents were easily filled by the methylene blue molecules. Meanwhile, higher adsorption capacity was observed with increasing methylene blue concentrations, which could be attributed to the increased driving force that the adsorbate concentration gradient created to overcome the mass transfer resistance of the adsorbent (Francis and Zaini, 2023; Zhao *et al.*, 2022). Nevertheless, RC exhibited the best adsorption capacity among CC and AC due to its higher surface area (Table 3) when compared to CC (Francis *et al.*, 2023). The higher acid value of AC (Table 1) when compared to RC could have been responsible for the lower adsorption capacity of methylene blue because at that acid pH, cation materials in aqueous solution are less adsorbed due to its competition for the H_3O^+ and other ions in the solution (Munvuyi *et al.*, 2022; Alexander *et al.*, 2018; Sorgo *et al.*, 2011).

The results and fittings of the isotherm models are presented in Table 4 and Figure 7, respectively. The isotherm models of Langmuir, Freundlich and Sips were good in describing the methylene adsorption of methylene blue onto RC, CC and AC. However, RC adsorption data fitted better to the Langmuir and best to the Sips models than the Freundlich model. This revealed that the adsorption was a monolayer adsorption on a heterogeneous surface of the adsorbent (Francis and Zaini, 2023; Mistar *et al.*, 2020). The SSE and R^2 values from the Sips model were 124.80 and 0.9416, respectively, which suggested better adsorption fittings with the least SSE and higher R^2 . The maximum methylene blue adsorption,

Table 4. Isotherm models constants of methylene blue onto RC, CC and AC adsorbents.



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Isotherm model	Parameters	Adsorbents		
		RC	CC	AC
Langmuir	$Q_m(\text{mg/g})$	40.301	33.988	37.486
	$K_L(\text{L/mg})$	0.2989	0.6437	0.2115
	R^2	0.9310	0.9204	0.9582
	R_L	0.0767	0.0437	0.1120
	SSE	184.20	145.46	106.90
Freundlich	$K_F(\text{mg/g})(\text{L/mg})^{1/n}$	12.185	12.209	10.641
	n	3.7310	4.1986	3.6760
	R^2	0.9176	0.8672	0.9165
	SSE	179.71	230.14	153.25
Sips	$Q_m(\text{mg/g})$	53.549	38.450	44.196
	$K_S(\text{L/mg})$	0.0931	0.3585	0.1277
	n_S	0.5320	0.6622	0.6193
	R^2	0.9416	0.9307	0.9671
	SSE	124.80	116.78	57.258

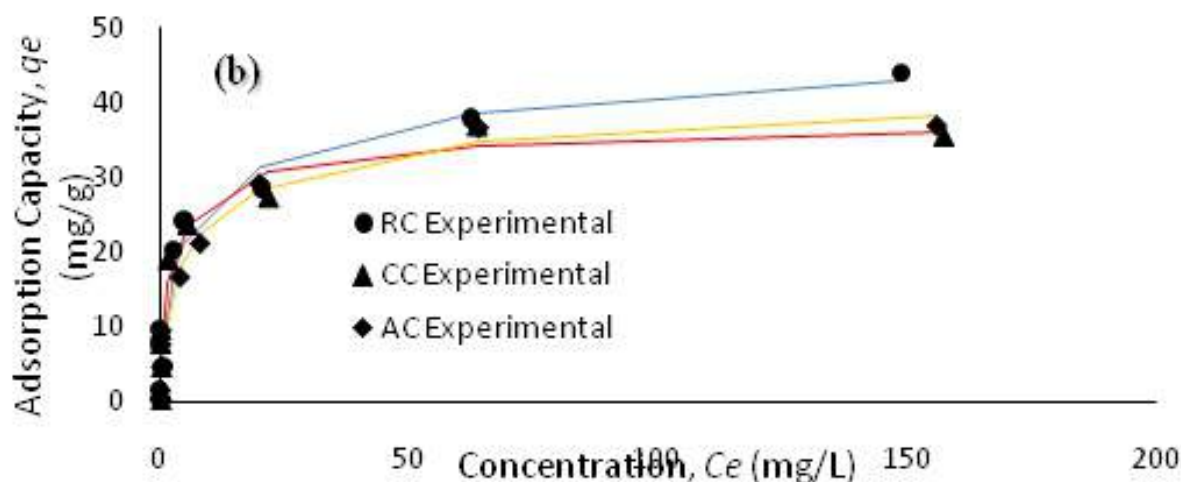
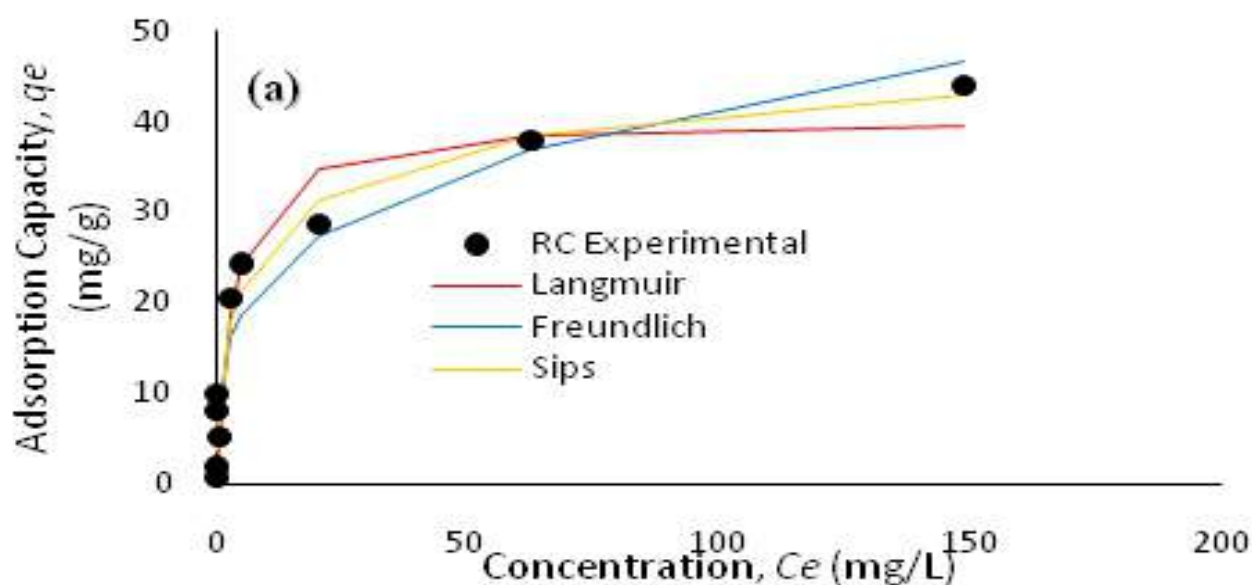


Fig. 7. Methylene blue adsorption equilibrium (a) fittings of isotherm models for RC adsorbent, and (b) fittings of Sips model

Table 5 presents a comparison of the current study on the effectiveness of methylene blue adsorption from wastewater using RC, CC and AC with previous studies and clay-based mineral adsorbents. The surface areas of the adsorbents in this study were undoubtedly lower than those of SG, SG-ES and SE-Si (Juzsakova *et al.*, 2023), but higher than that of Kaolinite (H₂SO₄) (Sagita *et al.*, 2021). However, the adsorbents in this study demonstrated a higher maximum adsorption capacity, Q_{max} , than most of the adsorbents in previous studies, including the adsorbents with higher surface area. This suggested that the adsorption process in this study was based on pore fillings and ionic interactions.

Table 5: Methylene blue adsorption by different clay-based mineral adsorbents.

Adsorbent	Surface area (m ² /g)	Adsorbent dosage (mg)	C_o (mg/L)	pH	Temp. (°C)	Q_m (mg/g)	References
RC	235.50	50	1–200	6.48	24	40.301	This study
CC	213.80	50	1–200	6.48	24	33.988	This study
AC	313.70	50	1–200	6.48	24	37.486	This study
Bentonite clay (NaOH)	74.15	900	200	7	25	22.131	Hamad <i>et al.</i> , 2024
Kaolinite (H ₂ SO ₄)	76.86	200	20	-	-	3.40	Sagita <i>et al.</i> , 2021
Malaysian kaolinite (HCl)	-	-	20-70	6	25	1.35-1.37	Sandollah <i>et al.</i> , 2020
SG	633	250	10	7	25	34.30	Juzsakova <i>et al.</i> , 2023
SG-ES	360	250	10	7	25	32.00	Juzsakova <i>et al.</i> , 2023
SG-SI	330	250	10	7	25	22.80	Juzsakova <i>et al.</i> , 2023
Clay composite/TiO ₂	-	1500	200	8	30	6.3	Aljar <i>et al.</i> , 2021
Pakistani clay	-	40	100	-	25	107.18	Rehman <i>et al.</i> , 2021

2.3 Mechanisms of Methylene Blue Adsorption on RC

The mechanism of adsorption in this study was a monolayer removal of the methylene blue onto a heterogeneous surface of the RC adsorbent, as delineated by the isotherm model fittings of Sips (Table 4). There was also an ionic interaction between the methylene blue and the RC, which could be attributed to the predominance of negatively charged oxygen functional groups of carbonyl (C=O) and hydroxyl (O–H), ion exchange, electrostatic attraction, Si–O stretching vibration and Al–OH bending vibration Figure 4) (Hamad *et al.*, 2024). Additionally, the formation of mesopores and the high surface area of RC (Table 3) also enhanced the adsorption efficiency of methylene blue molecules on it. Figure 8 delineates a schematic mechanism of the adsorption of methylene blue onto RC adsorbent.

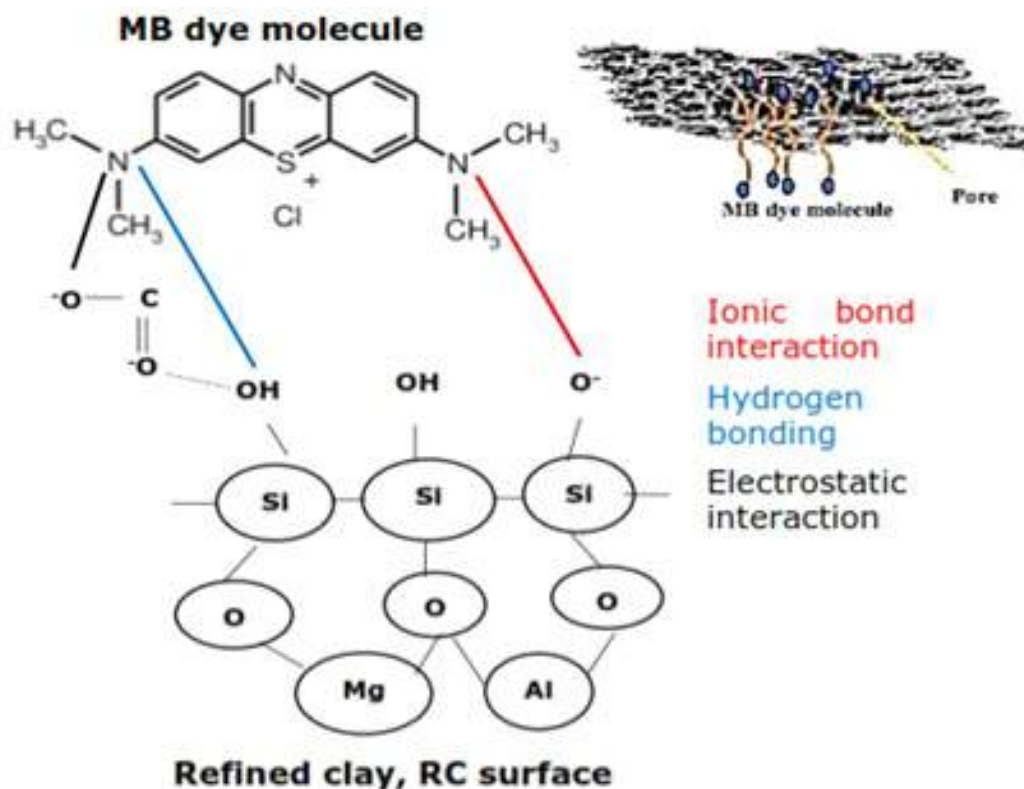


Fig. 8. Mechanism of methylene blue adsorption onto RC adsorbent

3. Conclusion

Ikpobia clay and its derivative surface-modified adsorbents were characterized for their physicochemical properties, and the adsorption mechanism of the refined clay, RC, was proposed. The adsorbent samples showed the presence of kaolinite, illite, siderite and quartz minerals. Multiphase structure of the adsorbent samples was identified. The pH of the oxalic acid-modified adsorbent, AC, was more acidic than the refined clay, RC and the calcined clay, CC, though it possessed the highest surface area. Consequently, this acidity reduced its adsorption capacity for methylene blue compared to RC. The maximum adsorption capacity of RC was 40.301 mg/g compared to the 33.988 mg/g and 37.486 mg/g of CC and AC, respectively. The adsorption mechanism suggested a monolayer removal of methylene blue onto a heterogeneous surface of the RC adsorbent, as well as ionic interaction between methylene blue and RC due to the predominance of negatively charged oxygen functional groups of carbonyl (C=O) and hydroxyl (O–H), ion exchange, electrostatic attraction, Si–O stretching vibration and Al–OH bending vibration.

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Hair Attachment Production from Plantain Stem (Sucker)

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Abstract

*This study evaluated the feasibility of producing sustainable hair attachments from plantain (*Musa paradisiaca*) pseudo-stem fibres, an underutilized agro-waste in tropical regions. Fibres were extracted by mechanical decortication and subjected to three retting methods: water retting, mild alkali (2% NaOH), and benchmark alkali (5% NaOH). Retting conditions significantly influenced fibre performance. Water retting yielded the weakest fibres (72 MPa tensile strength, 1.3% elongation, 14.2 tex linear density), while mild alkali treatment improved strength (115 MPa), elongation (1.9%), and reduced density (11.6 tex). Benchmark alkali retting produced superior properties with 165 MPa tensile strength, 2.3% elongation, and 9.8 tex linear density, confirming its efficiency in delignification. Comparative analysis showed plantain fibres possess tensile strength (70–165 MPa) lower than synthetics (200–300 MPa) but comparable to human hair (150–220 MPa). Their biodegradability (65% in 60 days), low cost (₦1,635 per bundle), favourable moisture regain (7–9%), and thermal stability (200 °C) position them as cost-effective, eco-friendly alternatives, requiring optimization for softness and flexibility.*

Keywords: Plantain fibres, Hair attachment, Sustainable materials, Fibre retting, Biodegradability.

1.0 Introduction

The growing demand for sustainable materials has intensified interest in natural fibres as alternatives to synthetic polymers, which are widely criticized for their environmental persistence and lack of biodegradability. Agro-industrial residues, particularly those from banana and plantain crops, are increasingly recognized as valuable yet underutilized sources of structural fibres (Kodu Technology, 2023; Santhanam et al., 2024). Plantain (*Musa paradisiaca*), extensively cultivated in tropical regions such as West Africa, produces pseudo-stems that are generally discarded after harvesting. These stems are rich in lignocellulosic fibres that can be transformed into sustainable materials, simultaneously promoting waste valorization and environmental responsibility (Pelissari et al., 2022).

Plantain pseudo-stems are primarily composed of cellulose, hemicellulose, and lignin, with cellulose content often exceeding 60%. This composition provides mechanical strength and stiffness comparable to bast and leaf fibres used in textiles (Wikipedia, 2025). Characterizations of banana and plantain stalk fibres report tensile strengths up to 82 MPa and Young's modulus values above 2.6 GPa, making them suitable for fabrics, ropes, and geotextiles (Heliyon, 2024). Their thermal stability, with decomposition beginning at 200–300 °C, supports processing in textile applications (Discover Applied Sciences, 2025). Moreover, chemical treatments such as alkali conditioning have been shown to boost tensile strength by more than 150% and nearly double stiffness (ResearchGate, 2020). These properties underscore their potential as substitutes for synthetic fibres where durability, flexibility, and biodegradability are required.



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One promising application is in the global hair attachment industry, which includes wigs, weaves, and extensions. Current products rely on either human hair—expensive, scarce, and ethically contentious—or synthetic fibres like polyester and PVC, which are affordable but non-biodegradable and linked to microplastic pollution (Wikipedia, 2025; Marsh, 2021). Synthetic fibres may also cause scalp irritation due to chemical residues (Times of India, 2024). As sustainability shapes consumer preferences, eco-friendly alternatives are needed. Plantain fibres, with their strength, biodegradability, and availability as agricultural waste, offer a compelling solution (Okeke, 2020; Rubiano-Navarrete et al., 2024). Valorizing these residues could also deliver socioeconomic benefits, particularly in Nigeria, by creating local industries that generate jobs and support sustainable development (Ekunwe & Ajayi, 2010; Okeke & Chukueggu, 2021).

However, their use in hair attachments is almost unstudied. Research to date has concentrated on plantain fibres in composites, bioplastics, and geotextiles (Oladele et al., 2022; Begum et al., 2024). While such studies highlight mechanical improvements, they focus on short fibres rather than the long, soft strands required for cosmetic applications (Rubiano-Navarrete et al., 2024). Fibre extraction techniques like retting and decortication are well documented but have not been optimized for achieving softness, sheen, and scalp compatibility (Adeniyi et al., 2020; Gomes et al., 2024).

This gap is critical. No life cycle assessment, economic feasibility analysis, or consumer perception study has been conducted for plantain fibre-based hair products (Rodríguez et al., 2018; Nakkazi, 2025). To address this, the present study investigates the feasibility of producing hair attachments from plantain pseudo-stems. It focuses on extraction and processing methods, evaluation of mechanical and functional properties, and the challenges of industrial scale-up. By combining materials science, sustainability, and consumer perspectives, this work positions plantain fibres as a promising eco-friendly alternative in the global hair attachment market.

2.0 Materials and Methods

2.1 Materials

The primary materials used were fresh plantain (*Musa paradisiaca*) pseudo-stems, sodium hydroxide (NaOH), glacial acetic acid (CH_3COOH), non-ionic detergent, food-grade glycerol, cationic textile softener, and commercial reactive dyes for cellulosic fibres. Pseudo-stems were harvested from farms in Port Harcourt, Nigeria. NaOH and acetic acid (BDH Chemicals), glycerol and softener (local suppliers, Lagos), and reactive dyes (Dystar Nigeria Ltd.) were used. Distilled water was prepared in-house for washing and rinsing.

Key equipment included a mechanical decorticator, stainless-steel retting vats (20 L), thermostatic water bath, analytical balance (± 0.01 g), drying oven (10–250 °C), pH meter, carding brushes, spinning tools, lab-scale ring frame, sewing machine, tensile testing machine (Instron 3369), moisture analyzer, and grey-scale kit for colour fastness. A sensory evaluation booth and basic glassware (beakers, cylinders, funnels, filtration setups) supported laboratory work.

2.2 Methods



Fig. 1: Hair Attachment Production Flow Diagram

2.2.1. Collection and preparation of plantain pseudo-stems

Fresh pseudo-stems of plantain (*Musa paradisiaca*) were collected immediately after fruit harvest from farms in southern Nigeria. The outer decayed sheaths were removed, and stems were cut into lengths of 0.5–1.0 m for ease of handling. The samples were rinsed with tap water to remove soil and surface contaminants, drained for 30 minutes, and stored under ambient laboratory conditions before fibre extraction (Okeke & Chukueggu, 2021).

2.2.2. Mechanical decortication

Fibre bundles were extracted from the pseudo-stems using a hand-operated mechanical decorticator. The process involved longitudinally splitting the sheaths and scraping off the parenchymatous tissues, leaving behind long lignocellulosic bundles. This step served to liberate continuous fibres for subsequent retting and cleaning, in line with methods reported for *Musa* fibres (Rubiano-Navarrete et al., 2024).

2.2.3. Retting and delignification

Three different retting methods were employed to facilitate the separation of cellulose fibres from lignin and hemicellulose:

Water retting: Bundles were submerged in fresh water at room temperature for 72 h, with water replaced every 24 h.

Mild alkali retting: Bundles were immersed in 2% NaOH solution (solid-to-liquor ratio 1:20) at 50 °C for 45 min with intermittent agitation.

Benchmark alkali retting: Bundles were treated in 5% NaOH solution (1:20 w/v) at 70 °C for 60 min, following reported optimal parameters for plantain pseudo-stem fibre purification (Adeniyi et al., 2020; Rubiano-Navarrete et al., 2024).

All alkali-treated fibres were subsequently rinsed with tap water until near-neutral pH, followed by immersion in 0.5% acetic acid solution for 5 min to neutralize residual alkali. Final rinsing was performed with deionized water.

2.2.4. Drying of fibres

The washed fibres were spread on perforated trays and oven-dried at 70 °C for 6–8 h until constant mass was obtained. Dried fibres were conditioned at 21 ± 2 °C and $65 \pm 5\%$ relative humidity for 24 h before further processing. This drying regime is consistent with standard fibre treatment protocols (Oladele et al., 2022).

The **moisture content (MC%)** was calculated as:

$$MC(\%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \quad (1)$$

where w_{wet} is the initial wet mass (g) and w_{dry} is the oven-dry mass (g).

2.2.5. Combing and grading

Dried fibres were gently beaten to remove pith residues and combed progressively using fine-toothed combs to obtain aligned slivers. Fibres were then graded into length categories (25 cm, 35 cm, and 45 cm) suitable for hair extension applications. Unlike short fibre milling used in composite production, long continuous fibres were deliberately preserved to mimic human hair strands (Begum et al., 2024).

The **production yield (%)** of usable fibres was determined by:

$$Yield(\%) = \frac{W_{fiber}}{W_{stem}} \times 100 \quad (2)$$

where W_{fibre} is the mass of dried extracted fibres (g) and W_{stem} is the wet mass of pseudo-stem input (g).

2.2.6. Softening and conditioning

To improve softness and tactile properties, two post-treatment options were investigated:

Immersion in 0.5% cationic softener at 40 °C for 10 min, followed by drying at 50 °C.

Immersion in 2% glycerol solution for 15 min, followed by air-drying.

These treatments aimed to enhance pliability and scalp comfort, addressing a key gap in adapting plantain fibres for cosmetic use (Matchum et al., 2024)

2.2.7. Strand formation and weft construction

Aligned slivers were hand-drafted and spun into low-twist strands to maintain softness. Bundles of 0.8–1.0 g were tied at the root end and sewn onto cotton bias tape using a zig-zag stitch to produce machine-sewn wefts. For comparison, some strands were hand-tied into lace mesh to simulate premium wig construction.

2.2.8. Dyeing and finishing

Reactive dyes suitable for cellulose were applied following manufacturer protocols (40–60 °C, salt/alkali fixation). Dyed fibres were rinsed, neutralized, and conditioned with 0.5% softener. Curl and wave styles were imparted through steam setting at 100 °C for 3 min, followed by cooling. This ensured style retention and improved resemblance to conventional human hair extensions (Marsh, 2021).

2.2.9. Quality control tests

Mechanical and functional evaluations were carried out:

Linear density (Tex):

$$Tex = \frac{W}{L} \times 1000 \quad (3)$$

where, W is mass (g) and L is length (m)

$$\sigma = \frac{F}{A} \quad (4)$$

where F is the breaking load (N) and A is cross-sectional area (mm²).

Percentage elongation at break (ε%):

$$\varepsilon(\%) = \frac{L_f - L_0}{L_0} \times 100 \quad (5)$$

where L₀ is the initial length and L_f is the final length at break

Color difference (ΔE) after wash fastness test:

$$\Delta E = \sqrt{(L_2 - L_1)^2 + (a_2 - a_1)^2 + (b_2 - b_1)^2} \quad (6)$$

using, CIELAB values before (L₁, a₁, b₁) and after (L₂, a₂, b₂) washing

Residual pH of aqueous extracts was measured to ensure scalp safety (target pH 6–7.5)

3.0 Results and Discussion

Table 1 presents the tensile strength, elongation at break, and linear density of fibres subjected to water retting, mild alkali (2% NaOH), and benchmark alkali (5% NaOH) treatments.

Table 1: Mechanical Properties of Plantain Stem Fibers under Different Retting Treatments

Treatment	Tensile Strength (MPa)	Elongation at Break (%)	Linear Density (Tex)
Water Retting	72	1.3	14.2
Mild Alkali (2% NaOH)	115	1.9	11.6
Benchmark Alkali (5% NaOH)	165	2.3	9.8

Table 2: Comparative Properties of Plantain Stem Fiber, Human Hair, and Synthetic Fibers

Property	Plantain Stem Fiber	Human Hair Extensions (Virgin/Remy)	Synthetic Fiber (Kanekalon/Toyokalon)
Fiber Length (cm)	15–40	20–60	25–55
Diameter (μm)	70–110	60–100	80–120
Linear Density (tex)	10–15	4–7	8–12
Moisture Regain (%)	7–9	10–15	0.5–1
Tensile Strength (MPa)	70–165	150–220	200–300
Elongation at Break (%)	1.3–2.5	20–50	10–30
Young's Modulus (GPa)	2.2–3.0	2.5–4.0	3.5–5.0
Thermal Stability (°C)	200	230–250	170–200
Cost (USD/100 g bundle)	1–6	40–100+	5–20

Results indicate that retting strongly influences fibre quality. Water-retted fibres exhibited the lowest tensile strength (72 MPa) and highest linear density (14.2 tex), suggesting incomplete removal of lignin and hemicellulose. Mild alkali treatment improved strength (115 MPa) and reduced density (11.6 tex), confirming better fibre purification. Benchmark alkali treatment yielded the best performance, with tensile strength reaching 165 MPa, elongation 2.3%, and linear density 9.8 tex. These results highlight the significance of optimized alkali retting in enhancing the structural properties of plantain fibres for hair attachment applications. Improved tensile strength ensures durability under styling forces, while reduced linear density promotes softness and flexibility. Thus, benchmark alkali retting provides the most suitable fibre characteristics for cosmetic use.

Table 2 compares key physical, mechanical, and functional attributes of plantain stem fibres with human hair and synthetic fibres (Kanekalon/Toyokalon). Plantain fibres exhibit intermediate tensile strength (70–165 MPa) relative to human hair (150–220 MPa) and synthetics (200–300 MPa). Their elongation is low (1.3–2.5%), indicating brittleness compared to the flexibility of human hair (20–50%). However, plantain fibres outperform synthetics in moisture regain (7–9% vs 0.5–1%) and demonstrate superior biodegradability (65% weight loss in 60 days), making them environmentally sustainable. Thermal stability (200 °C) is sufficient for hair styling, though slightly lower than human hair. Cost is a key advantage: plantain bundles (USD 1–6) are significantly cheaper than human hair (USD 40–100+). While softness and scalp comfort require enhancement, plantain fibres combine affordability, biodegradability, and acceptable strength, positioning them as a sustainable alternative for eco-friendly hair attachments.

Table 3: Cost Analysis

Item	Description / Quantity	Cost
Raw Material	Plantain/banana pseudostem sourcing &	15,000
Fibre Extraction	Labour + tools	25,000
Degumming & Softening	NaOH, water, energy	35,500
Finishing	Oils, dyeing, drying	23,000
Labour	Weaving (4 workers)	30,000
Packaging	Wraps, labels, cartons	20,000
Overhead	Miscellaneous	15,000
Total	Grand Total (100 bundles)	163,50

Table 3 shows that producing hair attachments from plantain/banana pseudostem fibres is feasible at ₦1,635 per bundle. This cost is affordable compared to synthetic hair (₦3,500–₦5,500). Major expenses are labour, degumming, and finishing, while raw material is nearly free. The process offers sustainability, employment, and eco-friendly market positioning.

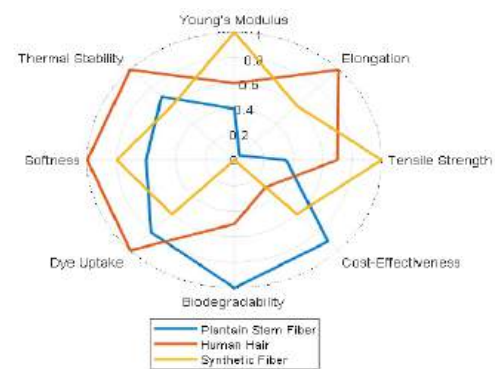


Fig. 2: Radar Chart of Comparative Fiber Properties

The radar chart Figure 2 visualizes the relative performance of plantain stem fibre, human hair, and synthetic fibres across multiple metrics, strength, elongation, modulus, thermal stability, softness, dye uptake, biodegradability, and cost-effectiveness. The polygonal spread reveals that synthetic fibres dominate in tensile strength and modulus but lack biodegradability. Human hair excels in elongation, softness, and dye uptake, maintaining its status as the premium material for hair attachments. Plantain fibres, while lower in elongation and softness, perform strongly in cost-effectiveness and biodegradability, forming a balanced profile that bridges sustainability and affordability. This graphical representation makes trade-offs between materials explicit, showing how plantain fibre can complement rather than fully replace existing options. It also emphasizes research priorities: improving softness and elongation while maintaining eco-friendly attributes. The radar chart thus highlights plantain stem fibres as a promising eco-conscious alternative in the hair industry, especially for cost-sensitive, sustainability-driven markets.

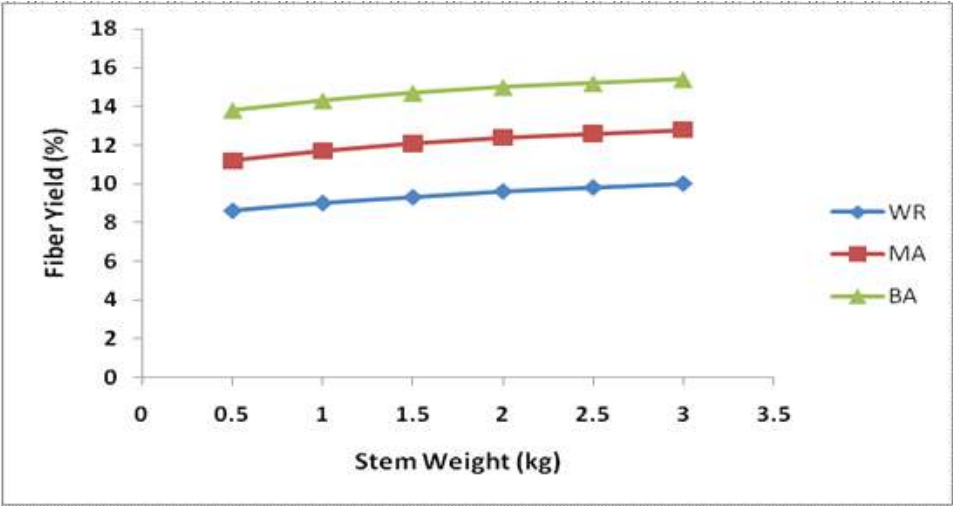


Fig. 3: Effect of Retting Method on Fiber Yield Relative to Plantain Stem Weight

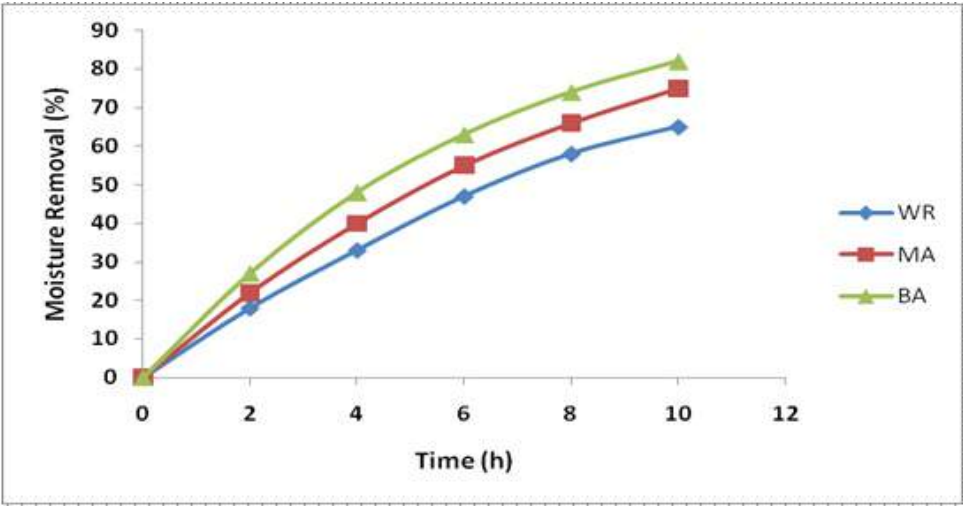


Fig. 4: Moisture Removal Profiles of Plantain Fibers over Drying Time under Different Retting Methods

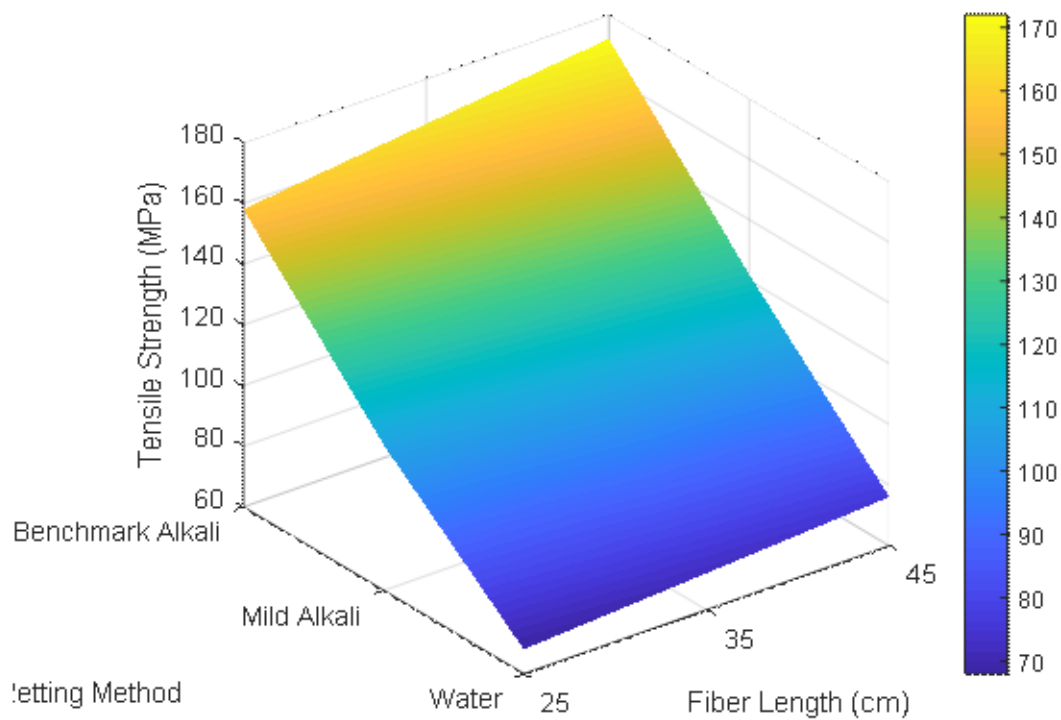


Fig. 5: Influence of Fiber Length and Retting Method on the Tensile Strength of Plantain Fibers

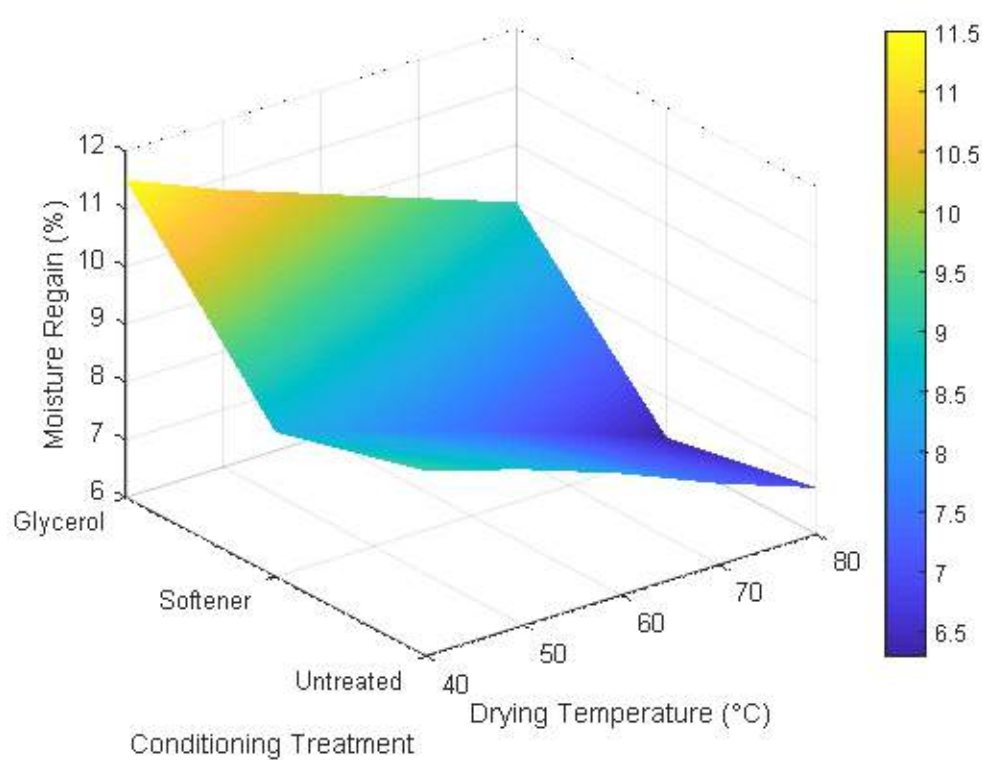


Fig. 6: Variation of Moisture Regain with Drying Temperature for Plantain Fibers Subjected to Different Retting Treatments

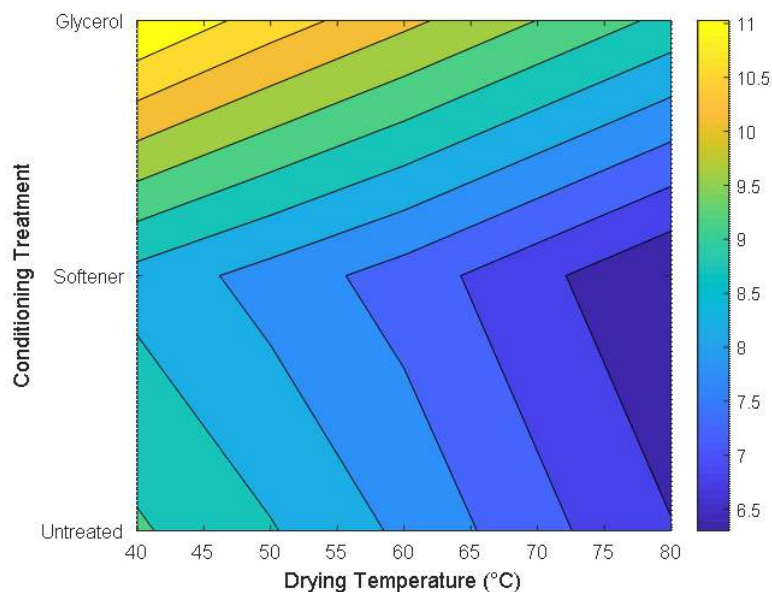


Fig 7: Contour Plot of Moisture Regain as a Function of Drying Temperature and Retting Conditions

Figures 3–7 collectively demonstrate how retting methods and processing conditions influence the performance of plantain pseudo-stem fibres for hair attachment applications. In Figure 3, Fibre yield increased significantly with alkali treatments, with benchmark alkali retting producing the highest recovery due to effective removal of lignin and hemicellulose (Adeniyi et al., 2020; Rubiano-Navarrete et al., 2024). Moisture removal profiles in Figure 4 further showed that benchmark alkali-treated fibres dried faster, reducing processing time and energy requirements, which is critical for industrial scalability (Gomes et al., 2024). The 3D tensile strength plots in Figure 5 highlighted the dual importance of retting and fibre length, with benchmark alkali retting and longer strands producing the strongest fibres, suitable for withstanding styling stresses (Heliyon, 2024). Moisture regain analyses of Figures 6 and 7, revealed that benchmark alkali retting produced fibres with controlled regain (7–9%), balancing comfort and durability while avoiding brittleness or excessive swelling (Okeke & Chukueggu, 2021; Nakkazi, 2025). The contour plot emphasized the role of drying temperature in fine-tuning fibre hydrophilicity for scalp safety and user satisfaction (Oladele et al., 2022). Together, these figures confirm benchmark alkali retting as the most effective treatment, optimizing yield, strength, and moisture behaviour, while offering practical guidelines for developing sustainable, eco-friendly hair attachments.

4.0 Conclusion

This study demonstrated the potential of plantain pseudo-stem fibres as a sustainable raw material for hair attachment production. Fibre quality was found to depend strongly on retting conditions, with benchmark alkali treatment (5% NaOH, 70 °C) producing the highest tensile strength (165 MPa), improved elongation (2.3%), and reduced linear density (9.8 tex), making it most suitable for cosmetic applications. Comparative evaluation revealed that plantain fibers exhibit intermediate strength relative to human hair and synthetic fibers, while excelling in moisture regain (7–9%), dye uptake, biodegradability (65% weight loss in 60 days), and affordability (₦1,635 per bundle). Despite lower elongation and moderate softness compared to human hair, plantain fibers provide a balance of durability, cost-effectiveness, and environmental sustainability. With further processing improvements to enhance softness and scalp comfort, plantain stem fibres can serve as an eco-friendly alternative, reducing reliance on synthetic plastics and expensive human hair in the global hair industry.



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55TH INTERNATIONAL CONFERENCE “COAL CITY 2025”



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Influence of oxide distribution and quartz substitution on the physical properties of reactor wall linings formulated using ashes from organic wastes

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Abstract

The formulation of a ceramic composite suitable for the production of porcelain for wall linings of reactors was investigated. The binder used was kaolin, which was mixed with quartz at designated ratios of 100/0, 90/10 to 30/70, since 20/80 to 0/100 are not moldable. The 50/50 kaolin/quartz mix was the best pick since other ratios either behaved as chalks (40/60 and 30/70) or suffered high shrinkage (100/0 to 60/40). With the 50/50 mix as the new sample, ashes from organic sources (RHA and TA) obtained from rice husk and timber wastes after calcining at 700°C for 20 min were added, keeping the kaolin at 50% and varying the quartz/ash ratio to reduce the porosity and vitrify the mix to obtain a porcelain. The effect of temperature (900°C – 1200°C) and the effect of soaking time (0 – 30 min) were carried out on the formulations. The chemical profile of the materials (ashes, kaolin and quartz) was determined using the X-Ray fluorescence machine (XRF). Refractoriness was higher with RHA samples than with the TA samples, although all were $\geq 1500^\circ\text{C}$. The most important properties of porcelain, among others, include the flexural strength (FS) and porosity, which were chosen as the responses in this study. The 50/20/30 formulation is the strongest, while 50/0/50, where the quartz was completely replaced with ash, being the weakest. The ratio of basic (fluxes) to acid oxides (glass formers) in RHA was 1:11 and 8:1 in TA. The more the fluxing oxides, the easier the melting of oxides and silica to form mullite glass. This explains why TA reinforced porcelain formulations showed lower porosity than with RHA due to vitrification and mullitization. FS obtained was also higher with TA than RHA, but was slightly below the ISO 13006 B1a standard of 35 MPa. The higher concentration of alkaline oxides in TA implied better fluxing of meta kaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) at mid-temperature of 1200°C and decomposition to pseudo-tetragonal mullite and subsequent orthorhombic mullite [$(3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2)$]. Both ashes (RHA and TA) were good additives for porcelain production, and the best ratio was 50/20/30.

Keywords: Timber Ash (TA), Rice Husk Ash (RHA), Kaolin/Quartz/Ash ratio, Refractory, Flexural Strength (FS), Porosity

1.0 Introduction

The materials used for the inner lining of reactor walls during construction, depending on conditions of operation, are carefully selected to prevent heat losses, resist corrosion initiated by the product being handled, such as corrosive gases, and provide very high resistance to mechanical and thermal stresses, strains, adhesion and abrasion. The effectiveness of these materials and consequently the reactors depend on their chemical composition, method of production and method of usage/implementation (Sadik et al, 2014). These materials are used to make refractories and porcelains and are used in steel industries, petroleum and petrochemical industries (Chidambaram, 2018). These high-temperature-resistant inner

linings are normally called refractories, but they have certain porosity to avoid thermal shock. However, for liquid and gaseous products, porosity is not desired and so the refractories are modified to function as porcelains with impervious characteristics (Ochen et al, 2021).

The quality and productivity of the final product, for example, liquid steel, is always influenced by the performance of the inner walls lining, which in this case are porcelain, and other parameters (Lou and Heuer, 1990). Similarly, petrochemical industries use linings of various basic refractories and porcelain for walls and pressure vessels on their hot face sides (Chidambaram, 2018). However, the performance of the reactor walls lining is reduced if it is operated outside the temperature it was designed to withstand. Understanding the mechanical and chemical composition of materials helps in the careful selection of additives to modify the properties during production. Failure of wall linings in reactors results in corrosion of metallic casings and materials contamination (Potgieter 2004). It is therefore important to carefully study the materials used in their formulation and production to avoid failure, as well as to control the conditions of operation. The underlying interest here is to produce linings with mullite as part of their final phase composition since mullite microstructure shows that it contains low-melting-temperature glass and some clay and silicon as primary starting materials. (Lima et al, 2022; Serra et al, 2015).

Timber wastes are basically sawdust and other wood wastes and are classified as organics. When wood is used as an energy source, ashes are generated as waste. These ashes have been used as compost manure, soap making, control of soil pH, fertilizer source, insect control and maintenance of soil texture, and odour control. RHA has been used as a filler in water purification (Shukla, 2020), steel making and coating, semiconductors and paper (Olusesi and Udoeye, 2021), fire retardant, and adsorption of dyes and colouring pigments from water (Liou and Wang, 2020). Utilizing ashes faces several challenges, which include purity level, temperature gradient utilized during calcination, particle shape and size, processing method and variation in associated inorganic impurities. (Vignesh Nayak et al, 2022).

The use of these ashes to modify the engineering properties of bricks suitable for lining reactor walls to avoid leakages, and corrosion of the metal casings, while remaining chemically neutral to the reactions taking place in the reactors, has not been reported. Porous linings tend to encourage absorption and adsorption while also encouraging accumulation. When accumulation occurs, an unsteady state system is created, resulting in poor utilization of resources and factors of production. This study seeks to report the effect of these ashes in improving the flexural strength of the wall linings for improved operation processes and hence convert these wastes into wealth.

2.0 Materials and Methods

2.1 Equipment and Tools

Equipment used in this research is: Meter balance (Mettler Toledo with sensitivity of 0.001), refractory crucible tong, drying oven (DHG-9101-1SA, 75L, Gallenkomp, England), Hood type electric furnace (Cone art kiln Inc, model BX 119D, Canada), Steel molds, Pan mill (Quanzhou Xinhaineng machinery co



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ltd, model PSJ-SS5040 China), rotary ball mill (William Boulton Ltd, model F.S 8470, England), 300 μ m sieve (BS), digital display double-Arm tensile testing machine (LT-10kn, model no; 202200534, accuracy level 1, Luotai precision instruments, Dongguan co. ltd, china), pestle and mortar, hand gloves, safety helmets and eye goggles, veneer caliper and XRF (NITON LLC model XLt 898).

2.2 Materials Preparation.

The Kaolin clay obtained from Ukpok in Nnewi South local government area of Anambra state was crushed using the pan mill into smaller particles, sieved (180 μ m mesh) and stored in moisture-free containers for this study. Wood ashes were collected from food vendors, Maryland timber market, Uwani Enugu, and homes where wood is used as an energy source. The effect of wood type was insignificant according to the design of this work. This is because the ashes were certainly not of the same source and all were wood-based. Whether soft or hard wood, whether gmelina or cedar source, the wood type was ignored. Emphasis was on utilizing wood ashes successfully since they are wastes often discarded into the environment. Rice husks, which are organic wastes, were obtained from Amagu Rice Mill, Abakaliki, Ebonyi state, and all the wastes were calcined to 700 °C in the muffle furnace and allowed to stand for 20 minutes to obtain the Timber ash (T.A) and Rice husk ash (RHA). The time it takes the furnace to reach the desired temperature is always ignored since it is dependent on voltage, size of furnace, nature of samples, among other factors. The ash samples obtained were then stored in water-free airtight containers for the study.

2.3 Formulation of Test Samples

The dried powdered samples were measured to obtain 2kg each of the various formulations, and distilled water at ambient conditions in a 2L measuring cylinder was carefully added at intervals while mixing in a pan until a homogenous moldable dough was obtained. The plastic dough obtained was kneaded to remove trapped air pockets, and thereafter, test samples were made according to the sizes of moulds available. Formulation of rectangular, cylindrical and square test pieces according to the method described by Abuh et al. (2019) and Pena et al. (2016) was made. The cylindrical steel mould of dimension 100 x 20 x 20 (mm) was made for flexural strength (FS), while the rectangular steel mould of dimension 80 x 41 x 21 (mm) was used for porosity. The mixing was manually done with hands after wearing safety gloves. The quantity of water used was 22% wt of the sample, and the water was at ambient conditions. The mixture was consistently homogenized with hands, and the time used was between 5 and 8 minutes, depending on the strength of the dough. The plastic dough was pressed into the moulds to obtain test bricks, which were dried at room temperature for 3 days before drying at 120 °C for 2 days to constant weight using the dryer. After sintering to experimental temperature (900 °C–1200 °C).

2.4 Test Method

Chemical Analysis. The handheld energy dispersive X-ray fluorescence (EDXRF) machine (Niton LLC model XLt 898) was used. The sample was irradiated with light from the equipment, and the measurement

was displayed on the instrument screen, which was saved to the memory card. The elemental compositions were read, which were later converted to the oxides.

2.4.1 Flexural strength

A 3-point bend tester in line with ASTM C-648 / ISO 14704 standard for testing modulus of rupture was carried out using the digital display double-arm tensile testing machine (LT-10kn, model number 202200534, accuracy level 1, Luotai precision instruments, Dongguan Co., Ltd. China). The machine was switched on and electrically operated as force was applied on the test brick until it shattered. The force applied was recorded in kg as displayed in the digital display screen. The FS was then calculated using equation 1.

$$FS \text{ (mpa)} = \frac{3pl}{2WH^2} \quad (1)$$

Where: p = Breaking load (kg), L = Distance between supports (7cm), W = Width of sample (cm) along shattered area, H = Height (cm)

2.4.2 Porosity

ASTM C373 and the ISO 10545-3 were used. Test bricks were weighted before boiling (W_f) and after boiling (W_s) in distilled water for 2 hours. Suspended weight (W_p) was obtained by tying a rope to the sample and displacing it in water while the other end of the rope was tied to a spring balance to measure the weight of water displaced according to Archimedes' principle. Porosity was calculated using equation 2.

$$Porosity(\%) = \frac{W_s - W_f}{W_s - W_p} \times 100 \quad (2)$$

2.4.3 Refractoriness

The refractoriness of the composites was estimated using the Shuen formula as stated in equation 3.

$$K = \frac{360 + Al_2O_3 - RO}{0.228} \quad (3)$$

Where K = Refractoriness ($^{\circ}C$), Al_2O_3 = Alumina content in the formulation and RO = sum of all the oxides without SiO_2 in the formulation (Odewale et al, 2023; Odewole et al, 2019).

3.0 Results and Discussions

3.1 Chemical Composition of Samples

Chemical compositions of samples were obtained using XRF (NITON LLC model XLt 898) and presented in Table 1.



55TH INTERNATIONAL CONFERENCE “COAL CITY 2025”



Table 1: Summary of chemical profile of the samples

Oxide	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	TiO ₂
RHA	82.29	2.82	1.15	1.73	2.32	2.38	0.42	
T.A (SDA)	7.81	3.64	1.33	51.41	4.96	19.83	3.8	0.32
Ukpor Kaolinite	49.25	33.3	1.16	0.58	0.15	2.52	1.3	0.52

Table 2: Oxides distribution in RHA

Oxide	RHA	Distribution1	Amount	Ratio1	Distribution2	Ratio 2
SiO ₂	82.29	Acid Oxide	82.29	29.4	Acid Oxide	21
TiO ₂	0					
Al ₂ O ₃	2.82	Amphoteric	3.97	1.4	Amphoteric	1
Fe ₂ O ₃	1.15					
CaO	1.73	alkaline earth	4.05	1.4	Basic	2
MgO	2.32					
K ₂ O	2.38	Alkaline	2.8	1		
Na ₂ O	0.42					

Table 3: Oxides distribution in TA

Oxide	T.A(SDA)	Distribution1	Amount	Ratio	Distribution2	Ratio 2
SiO ₂	7.81	Acid	8.13	1.6	Acid	2
TiO ₂	0.32					
Al ₂ O ₃	3.64	Amphoteric	4.97	1	Amphoteric	1
Fe ₂ O ₃	1.33					
CaO	51.41	Alkaline earth	56.37	11.3	Basic	16
MgO	4.96					
K ₂ O	19.83	Alkaline	23.63	4.8		
Na ₂ O	3.8					

Table 1 shows that the SiO₂ of RHA was clearly higher than that of the TA and the binder (Ukpor kaolin). Karthik et al. (2017) reported a value of 88.32% for SiO₂, and another author reports 94.50 (Ahmaruzzaman and Gupta, 2011). The alumina content for the ashes is very low, while the kaolin has up to 33.3% making the clay very refractory (Bareiro et al, 2018). Table 1 shows a summary of the oxides in the raw materials before the various blends, while Table 2 and 3 show the distribution of oxides in the ashes. The oxide amounts are quantified by adding the composition of all the oxides belonging to the various distributions. The alkaline oxides are formed by adding the K₂O and Na₂O, and any other available group 1 element oxide present in the samples, as shown in the Tables 2 and 3 above. The group 2 elements form the alkaline earth oxides, and all the oxides in group 2 available in the chemical profile are added, and both group 1 and 2 form the basic oxides. The ratio of Basic to Acid oxides for RHA is 1: 11 while in T.A the Basic/acid oxide ratio is 8:1. The basic oxides are fluxes and the more they are in a batch recipe, the more the ease of mullitization and



55TH INTERNATIONAL CONFERENCE “COAL CITY 2025”



vitrification (Dimitrov and Komatsu, 2005; Zhou et al, 2013) The basic oxides (Fluxes) are responsible for melting silica to impervious glasslike coating of surfaces and are further classified into the primary alkaline oxides (Group 1A elements such as Lithium, sodium, Potassium, rubidium, cesium and francium) and the secondary alkaline earth oxides (Group 2A elements of the periodic table, elements such as Beryllium, Magnesium, Calcium, strontium barium and radium). The ratios of the alkaline oxides (Na_2O and K_2O) to the acid oxides (SiO_2 and TiO_2) in the ashes are 1:1 for RHA and 1:2 for T.A. It is important to understand the distribution of these minerals to predict the behaviour of materials, which the introduction of these ashes in any recipe implies.

Alkaline – alkaline earth oxides distribution: These oxides determine what temperature the composite/formulation would melt to achieve a glasslike coating. The alkaline oxides are more likely to melt at a lower temperature than alkaline earth oxides, and so the recipe would have a lower melting point if the alkaline oxides are higher than the alkaline earth oxides in the basic oxides' distribution (Dasilva et al, 2012; Eke, 2010).

Basic – Acid oxides distribution. This ratio primarily determines the temperature of the melt to glass. Fluxes (basic oxides) are inorganic materials, mostly in oxide form, utilized as an additive in ceramic bodies, glass, and glazes to reduce their high vitrification point. They function by promoting partial or complete liquefaction of the main glass-forming constituents, usually silica and alumina (Richard & Eppler, 2005; Abdulmughniy and Olurotimi, 2024). The acid oxides are the glass formers. For glass formers to melt, there must be fluxing oxides, which are the basic oxides. The closer the ratio is, the easier the ease of glass formation (Abdulmughniy and Olurotimi, 2024). RHA had a 1: 11 ratio compared with TA, which had 8:1 ratio. For the RHA, it means that for every 1 g of basic oxide available, 11 g of glass former (acid oxides) are present to be melted. Also, for TA, it means that for every 8g of basic oxides available, only 1g of acid oxide is available to be melted. Although both are ashes, formulations with TA clearly melted to achieve impervious glasslike coatings at lower temperatures than with RHA, which needed higher temperatures.

Amphoteric – acid oxide ratio: The amphoteric oxides are also called binders or stabilizers. The closer this ratio is, the more firmly bonded the particles of the formulation will be. This ratio also controls the strength of the material. RHA had a ratio of 1:21 when compared with TA, which had 1:2. This means that for every 1g of amphoteric oxide available, 21g of acid oxides are available to bond for RHA, while for TA, every 1g of amphoteric oxide has 2 g of acid oxides present to bond. Clearly, this explains why formulations with TA were firmer, smoother and stronger than formulations with RHA at every reference temperature.

Basic – amphoteric oxide ratio: this ratio controls the refractoriness and bonding of the composite. The closer this ratio is, the less the refractoriness. RHA had a ratio of 2:1 while for TA, it was 16:1. This means that clearly the RHA samples are more refractory than the TA, which was the observation.

3.2 Physical Analyses:

3.2.1 Effect of the addition of quartz in the kaolinite matrix:

Porosity: The effect of silica/quartz on the kaolin was initially determined to remove all forms of product failure due to excessive contraction, cracks and shrinkage. Increasing the quartz addition while reducing the kaolin is the same as reducing the plasticity and alumina content of the composite. The clay always has associated mineral impurities, which help to vitrify the composite at high temperatures and reduce porosity.

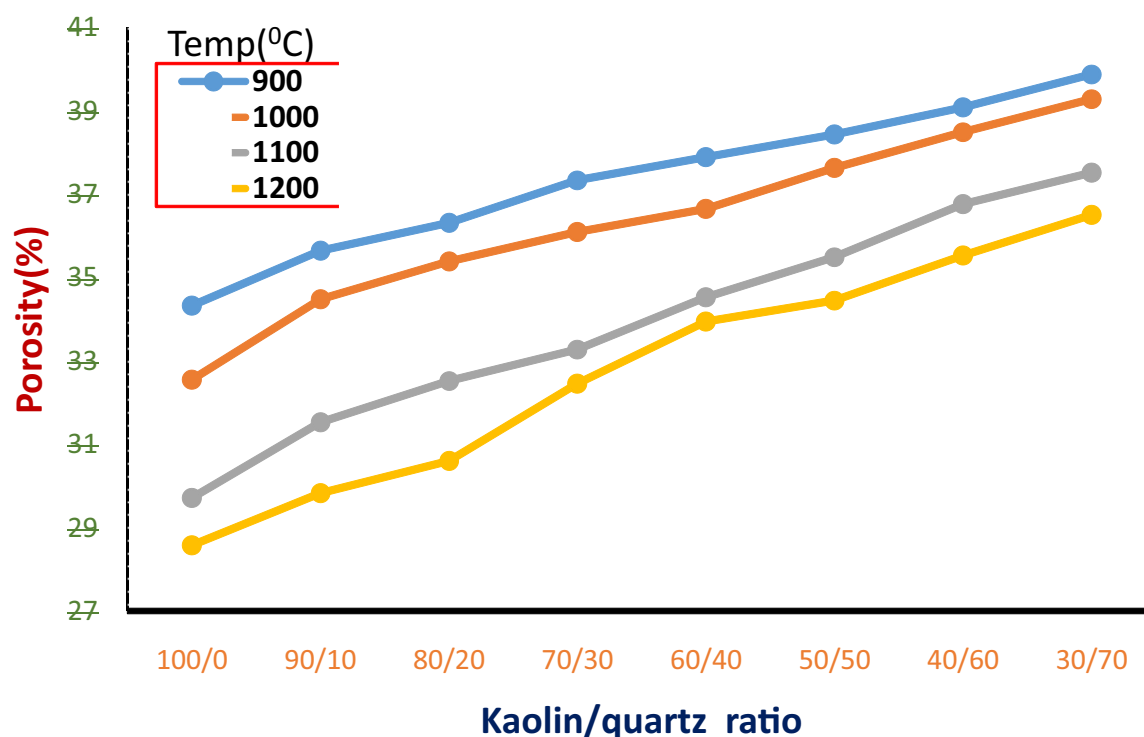


Fig. 1. Response of porosity to quartz addition.at various temperatures

Figure 1 shows a decrease in porosity with an increase in temperature for every formulation. Also, the porosity increased with an increase in silica addition. This is due to an increase in the addition of non-elastic/non-plastic materials (SiO_2) and the replacement of plastic kaolin, which increased the sizes of pores and reduced bonding. (Sawadogo et al, 2024; Ituma et al, 2018).

Flexural strength: For every composite formed, FS increased with an increase in temperature and at every temperature, FS reduced with an increase in quartz addition, as shown in Figure 2. The basic oxides inherent in kaolin, as shown in Table 1 are reduced as more quartz (acid oxide) is added, decreasing the minimum basic to acid oxide ratio required to vitrify the composite. Quartz is expected to increase the strength of the composite, but only when it is vitrified. Higher temperatures and fluxes are required for FS to increase as quartz substitution increases (Odewole et al., 2019; Duraid, 2017).

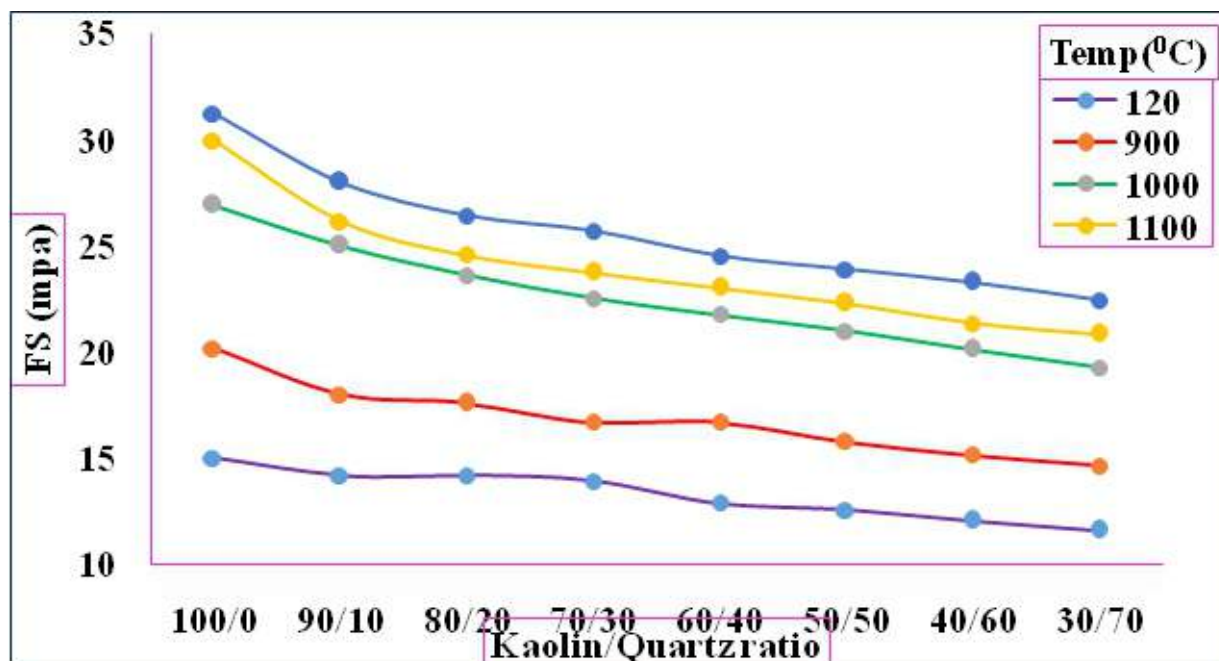
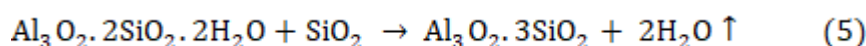
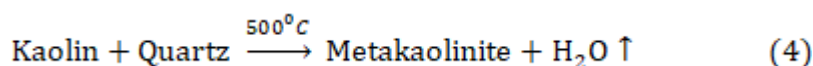
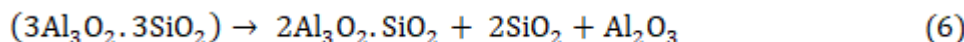


Fig. 2 Response of FS to effect of quartz addition

Addition of quartz also reduced the shrinkage and problems such as cracks associated with drying (Odewole et al., 2019; Zauro, 2010). The 50/50 combination was chosen since the 40/60 and 30/70 kaolin/quartz behaved like chalks and could write very well. 20/80, 90/10 and 0/100 were not moldable and could not bind and hence were not studied. Oxides interaction with the Kaolin and quartz as shown in equations (4) to (5).



At high temperatures of above 900°C the $\text{Al}_3\text{O}_2 \cdot 3\text{SiO}_2$ formed is very unstable and quickly disintegrates to form the more stable mullite and cristobalite in the reaction shown in equation (6).



The interaction of kaolin and quartz, as seen in Equation 5, leads to the melting of a mixture of oxides with a dehydroxylation reaction occurring (Zhou et al., 2013). However, the water could also play a fluxing role and induce a reduction of the melting temperature and formation of mullite as shown in Equations 4 & 5, which greatly increases the strength. Mullite formed has high thermal stability, excellent thermal shock resistance, low thermal expansion and conductivity, adequate mechanical strength, and creep resistance (Lima et al., 2022).

3.2.2 Effect of ash addition as a substitute for quartz in 50/50 (Kaolin/Quartz)

Apparent porosity: The 50/50 kaolin/quartz formulation had high porosity, which prompted the use of oxide-rich ashes to induce vitrification at moderate temperatures. Figure 3 below shows a decrease in the Porosity of the composite with an increase in the addition of ashes.

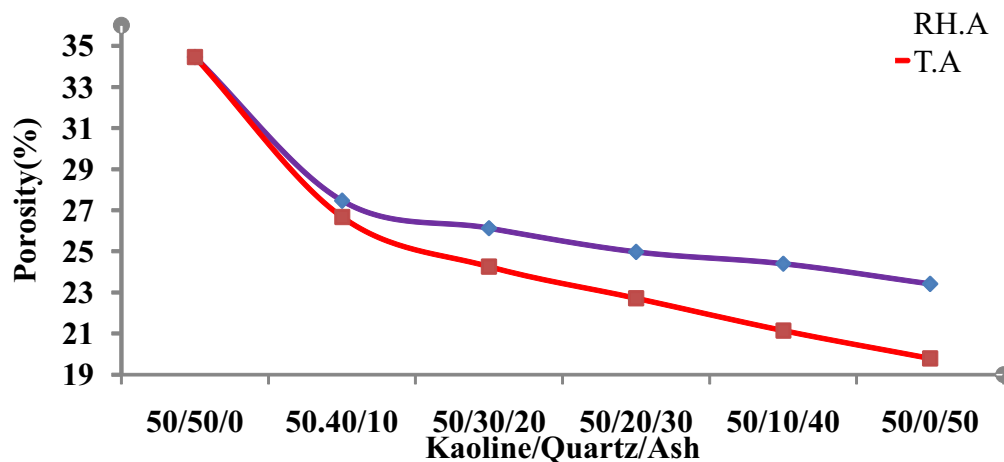


Fig. 3: Response of porosity to ash type as replacement for quartz at various temperatures.

The porosity was however, lower with Timber ash (T.A) than with Rice Husk ash (RHA). The ratio of the distribution of basic/acid oxide is responsible for easy mullitization and glassification. For RHA, basic/acid oxide is 1/11, which means that 1g of fluxes has 8g of acid oxide to melt to induce mullitization and vitrification, which brings about a reduction in porosity under the experimental conditions when compared with TA, which had a basic/acid oxide ratio of 8/1 and implies that 8g of fluxes had only 1g of acid oxide to melt. These oxides clearly account for the differences in response of the composites to porosity, as shown in Figure 3. Values of porosity obtained at 1200°C for TA samples range from 26.7% for 50/40/10 to 19.8% for 50/0/50, which were higher than the ISO 13006 B1a standards, which stipulate a porosity of below 0% for refractory porcelain and insulating porcelain (Dondi et al, 1999). Values obtained for RHA were in the range of 27.8 % for 50/40/10 – 23.4% 50/0/50, which were even higher than that obtained for TA, while the porosity obtained for the samples without ash (50/50/0) was 34.3% all at 1200 °C. These values were however, higher at lower temperatures.

Flexural Strength: Flexural strength increased with an increase in ash content as partial replacement for quartz, with peak strength obtained at 50/20/30, before a considerable decrease was observed from 50/40/10 and 50/0/50, representing Kaolin/quartz /ash ratio, respectively. Both T.A. and RHA gave similar trends, but T.A. had slightly higher strength than RHA, as shown in Figure 4.

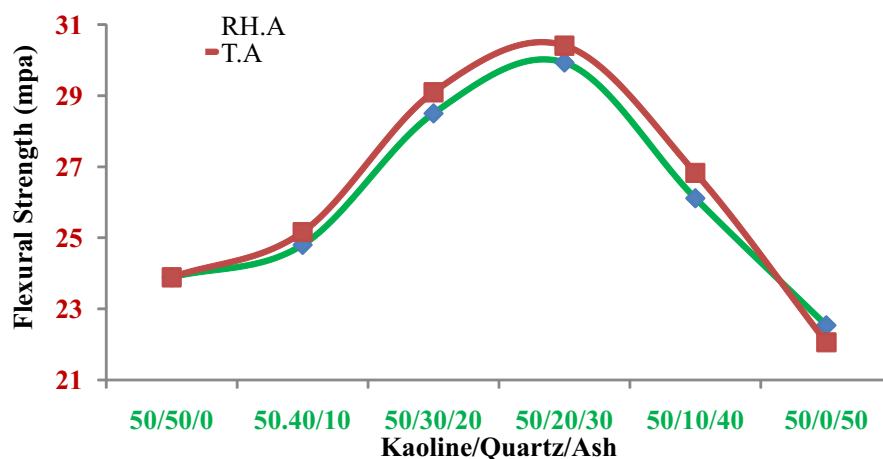


Fig. 4: Response of Flexural strength to ash as replacement for quartz at various temperatures.

The 50/0/50, which represents 100% quartz replacement with ash, was weakest for all the ash types as shown in Figure 4. As previously explained, this could be due to the complete replacement of quartz as in 50/0/50 and excess introduction of fluxing oxides (bases) without adequate acid oxides (Glass formers or silica) to interact with to form the stronger Si – O bonds Al – Si bonds and Al – O bonds associated with mullite, spinel, cristobalite, and corundum (Zhou et al, 2013). The weak bonds of Na – O, K – O, Ca – O, and Mg – O and their interactions in the absence of Si and Al do not offer enough strength to samples Timber ash samples (TA) were stronger than Rice husks ash (RHA) samples as shown in figure 4 (Dimitrova and Komatsu, 2005; Ekeh, 2010; Serra et al, 2015).

The flexural strength of 50/20/30, representing 60% replacement of quartz with ash, had higher strength as shown in Figure 4. This is due to adequate silica and fluxing oxides interaction leading to mullitization and complete vitrification (Serra et al, 2023; Zhou, 2013). The low flexural strength of 50/0/50 is probably due to the complete replacement of quartz and the increased presence of fluxing oxides without adequate silica to be vitrified. The only available silica is that present in the kaolin, which wasn't enough to consume the available fluxing oxides. The weakness of 50/50/0 is probably due to the absence of fluxing oxides to cause vitrification of the quartz content. For strength to increase, the silica has to melt which involves disintegration of the Si – RO (RO basic oxides such as Na₂O, K₂O, MgO, ZnO, CaO, FeO, and BaO) bonds to form stronger bond such as Si – Al, Si – O and Al – O bond and the interaction of these new bonds greatly increases the strength of the composite material (Zhang et al, 2023, Hongxu et al, 2023, Duraid et al, 2017, Sawadogo et al, 2024). Values obtained for FS at 1200°C for 50/20/30 TA, which was the highest, was 30.7MPa, while that obtained for 50/20/30 RHA was 29.8MPa, and both were below the ≥35MPa recommended by ISO 13006B1a for FS. The 50/50/0 (sample without ash had FS of 23.7MPa and sample without quartz, 50/0/50 for TA had FS of 22.1MPa and that for RHA had FS of 22%.

3.3 Effect of Temperature on 50/20/30 (Kaolin/Quartz/Ash) Recipe

Porosity: The strong fluxing action of Na₂O and K₂O induces formation of cristobalite at lower temperature (Zhou et al, 2013). The formation of orthorhombic mullite 3Al₂O₃ · 2SiO₂ from kaolinite/quartz mix is greatly influenced by the fluxing (Basic) oxides in the recipe and the temperature.

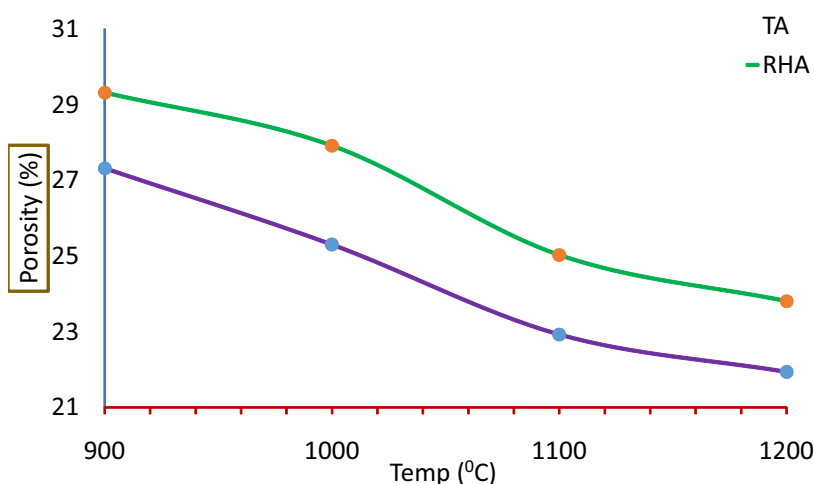
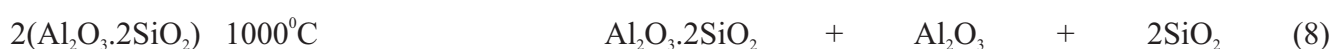
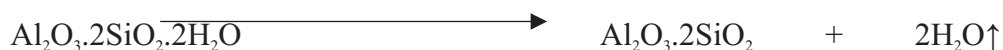


Fig. 5: Response of Porosity to temperature for the 50/20/30 (Kaolin/Quartz/Ash) formulation

The control sample, as shown in Figure 5, was more porous for all the experimental temperatures. The introduction of ash, irrespective of type, greatly reduced the porosity for all the temperatures, with the lowest porosity observed at complete replacement of quartz (50/0/50). This is due to the withdrawal of crystalline silica and the introduction of fluxing oxides enough to liquidize the kaolin, forming glassy solid (mullite and cristoballite) without pores.



The pathway involved in how kaolinite undergoes phase transformation to mullite is not clearly understood, but it is generally accepted that at 450 – 600°C, the hydroxyl in kaolinite is lost, resulting in the formation of the distorted phase meta-kaolinite (Zhou et al., 2013; Dimitrov et al., 2005; Perelomov et al., 2021). At 980 °C and above, the meta-kaolinite is transformed to pseudo-tetragonal mullite with formation of spinel and amorphous cristoballite (SiO₂) (Perelomov et al., 2021; Zhou et al., 2013). These interactions are greatly influenced by the alkaline oxides to occur at reduced temperatures of below 1300°C as shown in Figure 5 above. The alumina-rich mullite initially formed incorporates silica to approach 3Al₂O₃ · 2SiO₂ composition at higher temperatures (Zhou et al., 2013). T.A. showed lower porosity than RHA, as shown in Figure 5, which is due largely to the Basic: acid oxides distribution.

Flexural strength: the FS increased with an increase in temperature, as shown in Figure 6, with the TA samples having higher strength.

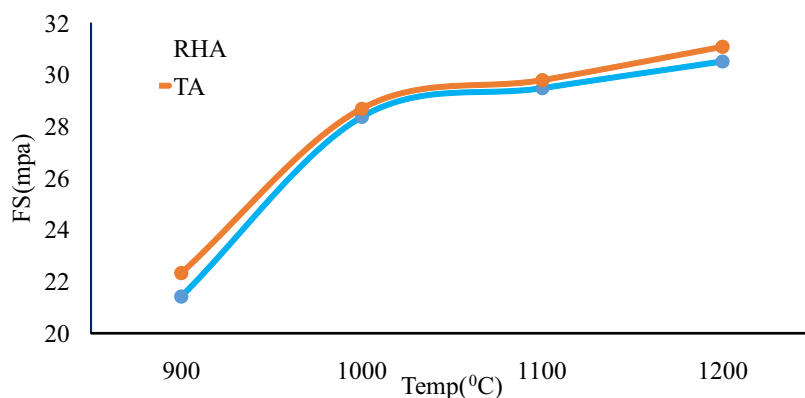


Fig. 6 Response of FS to effect of time for 50/20/30 (ash) formulations

As previously stated, a higher concentration of basic oxides in TA completely causes mullitization and vitrification, which increases the FS when compared with RHA, which needs more. At higher temperatures. As temperatures rise, more bonds are broken and new bonds are formed, which alter the mechanical properties of the composite. The presence of a high quantity of oxides leads to faster disintegration of bonds and reformation to form new products with higher strength and lower porosity.

3.4 Effect of Resident (Soaking) Time

Porosity: the porosity of the composite with the ashes at 50/20/30 tended to decrease expectedly at every temperature with an increase in resident time, as shown in Figure 7 for TA and RHA.

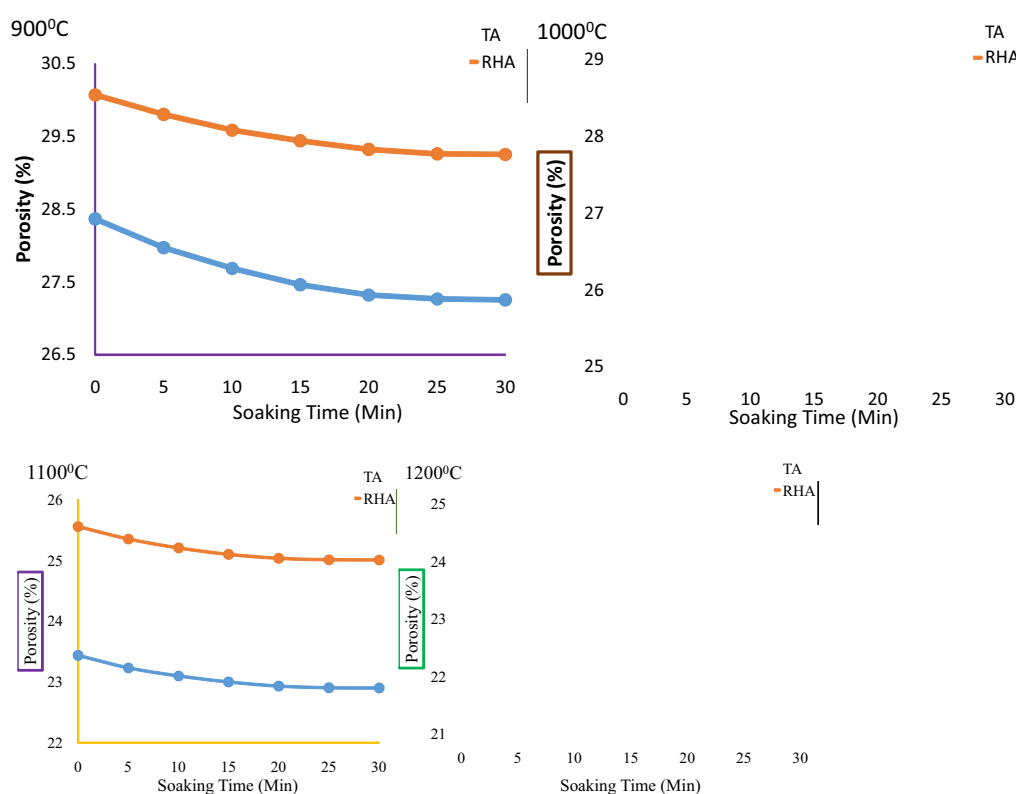


Fig. 7. Response of porosity to the effect of resident time for 50/20/30 (ash).

The longer the composite stayed in the furnace, the lower the porosity, especially at lower temperatures of 900 – 1000°C. At higher temperatures of 1100 – 1200°C, resident time after 20 minutes was not significantly altering the porosity of the composite. This means it is safe to assume 20 minutes at the equilibrium temperature, beyond which no significant impact is observed on the changes in porosity, as shown in Figure 7. The figure also shows lower porosity for the TA than the RHA, which is consistent with the differences in their oxide distribution as reported earlier.

Flexural strength: FS also increased with an increase in resident time at all the temperatures, irrespective of ash type, as shown in Figure 8.

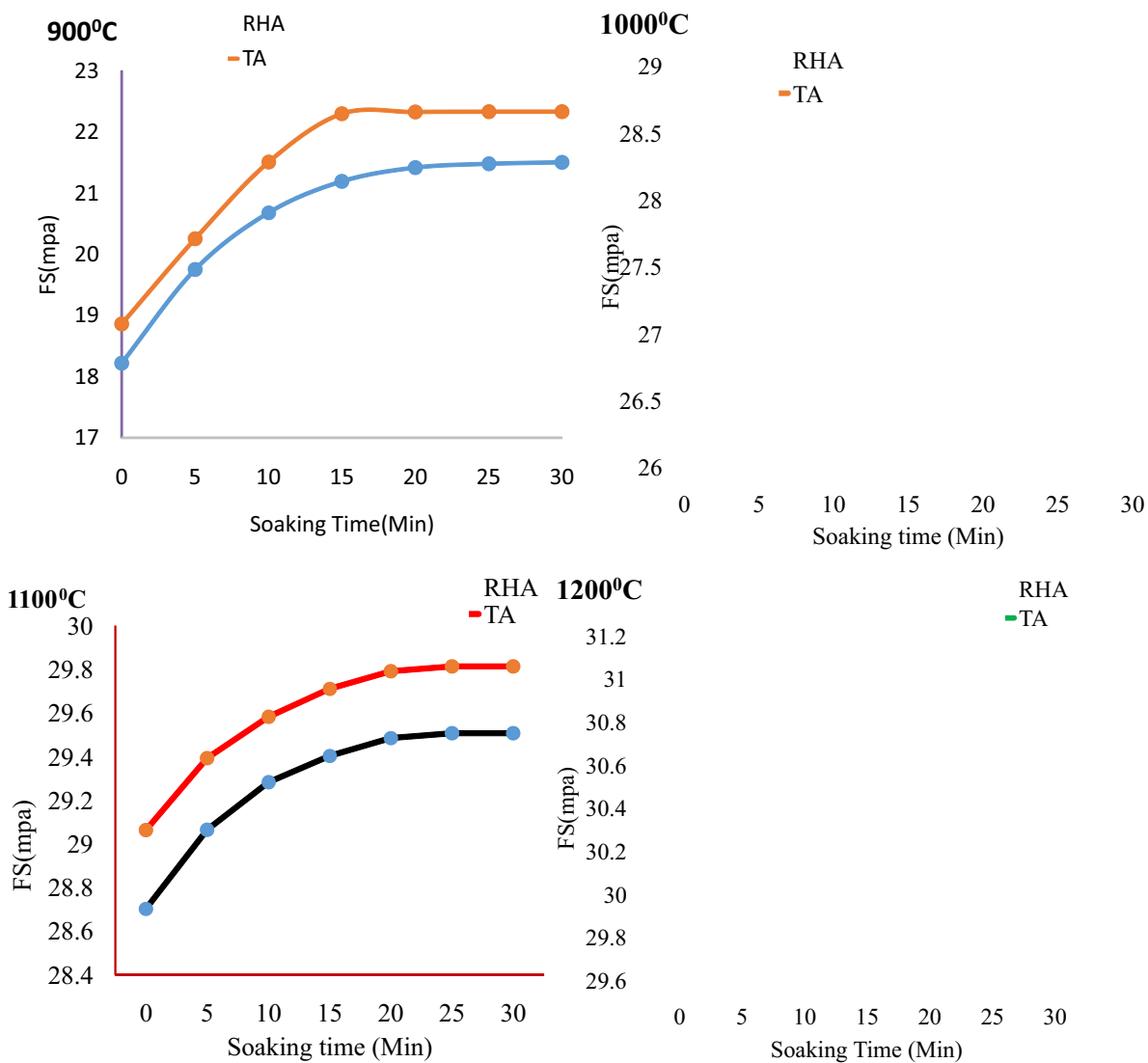


Fig 8 Response of FS to the effect of resident time for 50/20/30(ash).

The difference in FS became significant at higher temperatures, as seen in 1100 – 1200°C. As the soaking time increased, the FS increased until after 20 minutes, as well, when no noticeable change was observed, as seen in Figure 8 above. It can be assumed that beyond 20 minutes of soaking, resident time has no influence, and for optimization purposes, the maximum recommended time for soaking should be 20 minutes.

3.5 Refractoriness

The refractoriness decreased with an increase in ash addition, as shown in Table 4. Below is Figure 9. The Pyrometric Cone Equivalent (PCE) test shows that 50/50/0, 50/40/10 and 50/30/20 with refractoriness as shown in Table 4 for RHA had refractoriness range of greater than cone 30 (>1636°C) but less than cone 31 (≤1661°C) while the other samples had PCE of cone 30 (Odewale et al., 2021; Hsieh, 2019).

Table 4: Summary of Refractoriness of 50/50/ash samples.

Summary of Refractoriness						
	50/50/0	50/40/10	50/30/20	50/20/30	50/10/40	50/0/50
RHA	1641.84	1641.029	1640.184	1639.336	1638.473	1637.596
TA	1641.84	1632.855	1623.791	1614.648	1605.424	1596.355

The TA sample of 50/40/10 corresponded to cone 29 (≥ 1624 but < 1636). The refractoriness of 1623.79, which is approximately 1624 °C for the TA sample of 50/30/20, also belongs to the Ortone standard cone 29. For the TA sample of 50/20/30, the refractoriness of approximately 1615 °C belongs to ortone PCE of 27 (≥ 1614 but < 1619 °C) (Ortone cone chart, 2000). Again, 50/10/40 and 50/0/50 for TA corresponds to cone 26 ($1589^{\circ} - 1614^{\circ}\text{C}$) (Nyikos and King, 1996).

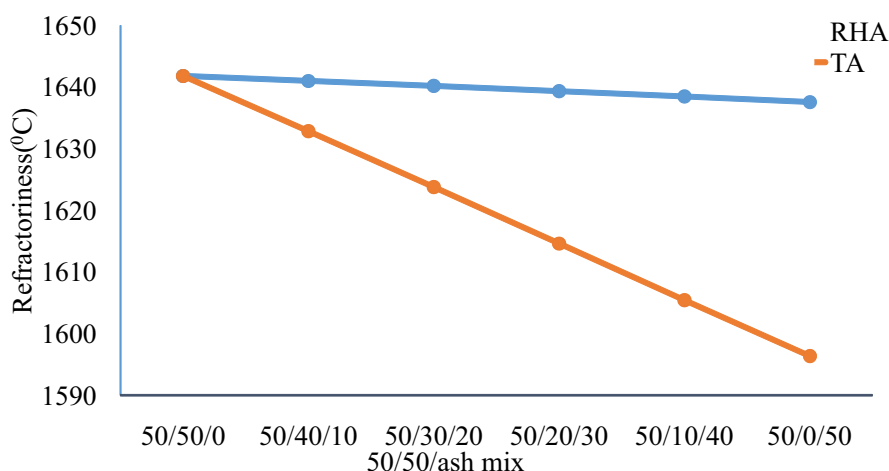


Fig. 9. Comparison of refractoriness between the RHA and TA 50/50/ash samples.

Figure 9 shows a decrease in refractoriness for the TA samples when compared with the RHA samples. The fluxing ability of the high percentage of basic oxides in TA (24.24%), as shown in Table 4, when compared with 3.21% present in RHA, is probably responsible for this observation. The higher the fluxing oxides, the lower the refractoriness (Sawadogo et al, 2024).

4.0 Conclusion

The use of quartz as a partial replacement for kaolin actually reduced the shrinkage, and the 50/50 ratio was preferred due to flexural strength considerations. The use of ash as a partial or total replacement for quartz was best achieved at 60% quartz replacement, which led to the 50/20/30 kaolin/quartz/ash ratio formulation, especially when the flexural strength was considered. The TA samples displayed higher flexural strength but lower refractoriness than the RHA samples, and this was due to higher fluxing oxides (bases), also called basic oxides, in the TA. Both TA and RHA samples are suitable for wall linings formulation at higher temperatures of 1100 °C and above. Porosity decreases and flexural strength increases with an increase in temperature, irrespective of ash type, and both ashes (TA and RHA) were suitable in adding fluxing oxides and modifying the composite for suitable industrial application. The resident (soaking) time suggested is 20 min, especially at high temperatures of 1100 – 1200 °C. Another additive needs to be incorporated to make the porosity and FS meet the ISO 13006 B1a standard.



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Optimization of Inhibition Efficiency of Polymeric Composite Inhibitor for Aluminum Corrosion Prevention in Acidic Medium

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Abstract

This study focuses on optimizing the inhibition efficiency of a novel polymeric composite inhibitor for aluminium corrosion prevention in acidic media. Utilizing Ukpok clay integrated with polyaniline (PANi), the composite was synthesized via in-situ polymerization and characterized through FTIR, SEM, and GC-MS analyses. The corrosion inhibition performance was evaluated using gravimetric methods across varying concentrations, temperatures, and exposure times, with response surface methodology (RSM) employed to identify optimal conditions. Results demonstrated a maximum inhibition efficiency of approximately 89.97% at an inhibitor concentration of 0.72 g/L, temperature of 312.55 K, and 3.6 hours of exposure. The quadratic relationship among factors highlights the interplay between inhibitor concentration, temperature, and time in influencing corrosion protection. Surface analyses confirmed the formation of a protective film on aluminium, corroborating the efficacy of the Ukpok/PANi composite. These findings suggest that the developed polymeric nanocomposite offers a sustainable and effective solution for aluminium corrosion mitigation in acidic environments.

Keywords: Inhibition Efficiency, Polymeric composite, Corrosion, Acidic Medium, Ukpok Clay, Polyaniline.

1. Introduction

Metallic materials are integral to various industries, including engineering, construction, and automotive sectors, owing to their mechanical strength and durability. However, their widespread application is often compromised by corrosion, an electrochemical process whereby metals deteriorate upon interaction with their environment, particularly in aggressive, acidic media encountered in refining, oil recovery, and industrial cleaning processes. Corrosion not only undermines the structural integrity of metals but also leads to significant economic losses, safety hazards, and environmental pollution. Consequently, effective corrosion prevention strategies are essential to prolong the service life of metallic components (Wang et al., 2023).

Among these strategies, the use of corrosion inhibitors has gained prominence due to their practicality and efficiency. These inhibitors function primarily by adsorbing on a metallic surface, developing an inhibitive passive film that impedes the electrochemical reactions responsible for corrosion (Fateh et al., 2020; El Ibrahim et al., 2020). Recent advancements have highlighted the potential of polymeric materials, especially conductive polymers such as polyaniline (PANi), in corrosion inhibition applications. Additionally, incorporating inorganic materials like clays into polymer matrices to form polymeric composites offers a promising approach to enhance barrier properties, thermal stability, and environmental friendliness of corrosion inhibitors (Wang et al., 2023).



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The incorporation of inorganic materials such as montmorillonite, zeolite, and silica into polyaniline can significantly improve the gas barrier properties of the resulting composite (Wang et al., 2023). This enhancement effectively increases the tortuosity of the pathways through which corrosive agents like oxygen and moisture diffuse, thereby reducing the rate of corrosion and imparting better anti-corrosion performance. Zhang et al. (2017) examined the impact of alkaline and acidic doping types of polyaniline on cold-rolled steel via electrochemical corrosion assessments, finding that coatings treated with zinc nitrate exhibited superior protective qualities compared to other systems. This observation aligns with findings by Yeh et al. (2002), who developed polyaniline-clay nanocomposite (PCN) through doped montmorillonite (MMT) into polyaniline. The PCN demonstrated a 400% reduction in permeability and enhanced corrosion resistance relative to conventional polyaniline. Similarly, Olad and Rashidzadeh (2008) prepared two types of nanocomposites, PANI/Na-MMT and PANI/O-MMT by doping polyaniline with hydrophilic and organophilic montmorillonite, respectively. Although these nanocomposites exhibited lower conductivity than pure polyaniline films, both outperformed unmodified polyaniline coatings in protecting iron samples from corrosion, highlighting the effectiveness of clay-based nanocomposites in corrosion inhibition applications.

In particular, clay-based composites, such as those derived from Ukpok clay, combined with conductive polymers like polyaniline, offer a promising and environmentally friendly approach to corrosion inhibition. These composites capitalize on the synergistic effects of clay's barrier properties and the electroactive nature of polyaniline, enabling the development of materials with tailored properties capable of performing effectively in harsh and aggressive environments. Despite the significant advantages of incorporating clay into polyaniline for corrosion protection, there remains limited research focused on optimizing the inhibition efficiency of such composite systems. Specifically, while previous research has shown that such composites can improve barrier properties and corrosion resistance, there is limited understanding of how to tailor and maximize their performance through controlled modifications, processing parameters, or composite formulations. Therefore, this manuscript aims to enhance the understanding of this approach by developing and characterizing polymeric composites based on Ukpok clay and polyaniline, with the goal of optimizing their corrosion inhibition performance and contributing to sustainable, effective corrosion control solutions.

2. Materials and Methods

2.1 Materials

Aniline and ammonium persulfate (APS) ($(\text{NH}_4)_2\text{S}_2\text{O}_8$), along with 10-camphorsulfonic acid (CSA), were purchased from Madus Great Chemicals, Lagos, and used as received. CSA served as a dopant in the synthesis of polyaniline (PANi) and the nanocomposites. Ukpok clay was collected from Ukpok, Anambra State, and characterized by the following composition: SiO_2 (53.07%), Al_2O_3 (31.51%), CaO (0.18%),



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Fe₂O₃ (0.87%), MgO (0.16%), and loss on ignition (LOI) (14.21%). Aluminium metal is examined in this study because of its widespread use, attributed to its strength, lightweight properties, and corrosion resistance. However, it is susceptible to corrosion in acidic environments such as HCl. Therefore, investigating methods of corrosion protection for aluminium is crucial to guarantee its durability and safety in practical applications. The aluminum metal, with a composition of Si (0.25%), Fe (0.02%), Zn (0.07%), Mn (0.14%), Mg (0.03%), V (0.04%), Ti (0.12%), Cu (0.03%), and 99.3% Al, was obtained from Montech Research and Development Ltd, Enugu State.

2.2 Methods

2.2.1 Preparation of clay and its characterization

The sample was washed thoroughly with water. Washing of clay with water helps in removing unwanted materials from the clay (Azinta et al, 2021). Then, the clay sample was heated in the furnace at 600°C for 2 hours. After cooling in desiccators, the weighed clay was stored in nylon bags for use in the synthesis of the inhibitor.

2.2.2 Synthesis of polyaniline clay Nanocomposites

Inhibitors of Ukpo clay/polyaniline composite (UCPC) were synthesized using the method employed by Zhu (2003). The in-situ polymerization technique was employed in the synthesis of the nanocomposite. An adequate quantity of aniline was dissolved in distilled water to make a solution of 0.2M. 200mls of 0.2M aniline and 200g of samples (Ukpor/Clay) were mixed to form a solution with vigorous stirring for 4 hours. An ultrasonic bath was used to distribute the clay throughout the solution. The suspension was left in the air for about 30 minutes for the clay to swell. 5% Ammonium persulfate ((NH₄)₂S₂O₈) was added to the aniline-sample mixture in a drop-wise manner and stirred for 48 hours before filtration. The precipitated powder was collected with a Buchner funnel and rinsed with 1000 mL distilled water to remove residual oxidant. The final composite was crushed, weighed, and placed in vials for subsequent use after being vacuum-dried to a consistent weight at 100°C. Then, various concentrations of the inhibitor (Ukpo clay/polyaniline composite (UCPC)) were made for the experiment. A total of 10 grams of the inhibitor was dissolved in one litre of the acid solution. Using this stock solution (which has a concentration of 10 g/l), test solutions were then made at various concentrations of 0.1, 0.3, 0.5, 0.7, and 0.9 g/l. The inhibitor was characterized with gas chromatography-mass spectrometry (GC-MS), Fourier transform infrared spectrometry (FTIR) and scanning electron microscopy (SEM) to determine its chemical analysis, functional groups and morphology, respectively.

2.2.3 Metal Preparation

Aluminium is widely used due to its strength, lightweight nature, and corrosion resistance, but it is vulnerable to corrosion in acidic environments like HCl. Studying corrosion protection for aluminium is therefore essential to ensure its durability and safety in practical applications. Aluminium was fashioned into coupons measuring 3 cm by 3 cm with an initial weight of 0.338g. These coupons underwent cleaning



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with distilled water, followed by polishing with emery paper of varying grit sizes, starting with coarse, then semi-fine, and finally fine to expose a bright, polished surface. To eliminate any oils and organic impurities, the coupons were degreased using acetone, then rinsed with distilled water, air-dried, and stored in desiccators. The initial weight of each coupon was precisely measured using an electronic balance, and these measurements were recorded.

2.2.4 Weight Loss (Gravimetric) Method of the Corrosion Inhibition Study

The corrosion inhibition tests were performed using the weight loss method over a range of temperatures, exposure durations, and inhibitor concentrations. Metal coupons with known initial weights were individually immersed in 250 ml open beakers containing 200 mL of 1 M HCl (serving as the control). Separate coupons were also placed in beakers with 200 mL of 1 M HCl plus different concentrations of inhibitors. The weight loss was periodically measured at temperatures between 303 K and 343 K, both without and with inhibitors at concentrations from 0.1 g/l to 0.9 g/l. At each sampling point, coupons were removed, immersed in acetone to clean, scrubbed gently under running water, dried, and then reweighed. The weight loss was evaluated as the difference between the initial and final weights in grams. The collected data were used to compute the weight loss (Δw), corrosion rate (CR), inhibition efficiency (IE), and surface coverage, using Equations (1), (2), (3), and (4), respectively (Onukwuli and Omotoma, 2019).

$$\Delta w = w_i - w_f \quad (1)$$

$$CR = \frac{w_i - w_f}{At} \quad (2)$$

$$IE (\%) = \frac{CR_0 - CR_1}{CR_0} * 100 \quad (3)$$

$$\theta = \frac{CR_0 - CR_1}{CR_0} \quad (4)$$

w_i and w_f represent the initial and final weight of aluminium coupons; CR_1 and CR_0 (9.389mg/cm²hr) stand for corrosion rate with or without inhibitor. A represents the surface area of the aluminium, and t denotes the immersion duration. θ indicates the extent of surface coverage.

2.2.6 Optimization of inhibition efficiency using response surface methodology

The experimental design, centred on a weight loss approach, was developed using Response Surface Methodology (RSM) implemented through Design Expert Software.



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Inhibition efficiency served as the primary response variable, with key factors including inhibitor concentration, temperature, and duration. The design matrix and corresponding response data are presented in Table 1. RSM analysis was employed to interpret these responses, following procedures similar to those used in previous studies (Omotiomomo and Onukwuli, 2016; Anadebe et al., 2018). Both ANOVA and graphical analyses were conducted to evaluate inhibition efficiency, leading to the development of mathematical models expressed with coded variables—where high levels are denoted as +1 and low levels as -1. These models facilitated the identification of optimal conditions for inhibition and enabled predictions of responses at specific factor levels. The effects of inhibitor concentration, temperature, and time on efficiency were examined through graphical representations and the mathematical models derived from the RSM approach. This method effectively optimized the process by analyzing the combined influence of multiple variables on the response. Data analysis included three-dimensional surface plots that depicted the relationships between inhibition efficiency and the studied factors. The resulting mathematical model offered valuable insights into how temperature, time, and concentration interactively influence the process, highlighting their combined effects.

Table 1: Design matrix and response for the inhibitive effect of UCPC on corrosion the Aluminum in HCl

Run	A: Inhibitor conc. (g/L)	B: Temp. (K)	C: Time (hr)	Weight loss (g)	CR (mg/cm ² hr)	Inhibition efficiency (%)
1	0.7	313	4	0.029001	0.805576	91.42
2	0.9	303	5	0.077775	2.160409	76.99
3	0.9	323	3	0.134424	3.734005	60.23
4	0.5	323	3	0.182387	5.066304	46.04
5	0.5	303	3	0.137838	3.828834	59.22
6	0.9	313	4	0.042893	1.191464	87.31
7	0.5	303	5	0.127292	3.535897	62.34
8	0.7	313	4	0.029001	0.805576	91.42
9	0.7	323	4	0.077673	2.157592	77.02
10	0.7	313	3	0.046171	1.282537	86.34
11	0.7	313	4	0.029001	0.805576	91.42
12	0.9	303	3	0.107857	2.99603	68.09
13	0.7	313	5	0.046171	1.282537	86.34
14	0.7	313	4	0.029001	0.805576	91.42
15	0.7	303	4	0.039039	1.08443	88.45
16	0.5	313	4	0.071893	1.99704	78.73
17	0.9	323	5	0.075679	2.102197	77.61
18	0.5	323	5	0.16863	4.684172	50.11
19	0.7	313	4	0.029001	0.805576	91.42
20	0.7	313	4	0.029001	0.805576	91.42

3. Results and Discussions

3.1 GC-MS results of the sample

GC-MS chromatograms of UCPC are presented in Figure 1. Chemical constituents of the UCPC were revealed as aniline, isobutyl chloroformate, 9,12-octadecadienoic acid, 9,17-octadecadienal, 1h-indene, cyclopropane carboxamide, 2-cyclopropyl-2-methyl-n-(1-cyclopropylethyl), 2-bromo-4-fluorophenyl ester, bis(2-ethylhexyl) phthalate, piperidine-4-carbonitrile, 1,1-diisobutoxy-butane, 3,4-octadiene, 19,19-dimethyl-eicosa-8,11-dienoic acid, 6-methyl-3,4-octadiene and pregnenolone. The structural nature of the chemical species shows that the UCPC is a potential corrosion inhibitor (Anadebe et al, 2018).

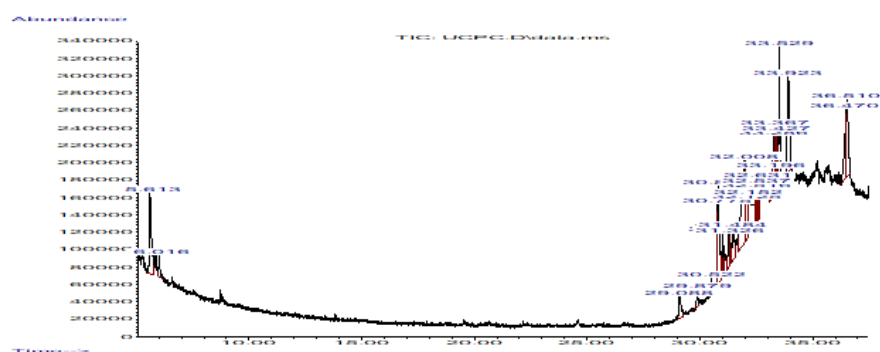


Table 1: FTIR absorption peaks and functional groups of the samples

Peak position (cm ⁻¹)		Peak assignment
Ukpor clay	Ukpor clay-PANi Composite	
678.0 - 693		=C-H bend, Silica Si-O bond stretching and Al-O bending
752.9 - 797.7		CH out of plane bending
872.2	-	-
909.5 - 1118.2		Silicate Si-O bond stretching, C-O stretch
1457.4	-	-
1971.8	-	N=B=N benzenoid ring stretching
2009.0 - 2158.1	-	CH ₂ asymmetric and symmetric stretchings
3203 - 3697.5		N-H stretch, OH bending stretching
		N-H stretch, Secondary amine

3.3 Morphology analysis

Microstructures of the Ukpor clay, pure PANi and Ukpor/PANi as observed by SEM are presented and compared in Figures 2a to 2c, respectively. The coarse structure of Ukpor is clearly observed in Figure 2a, and the lumped structure is observed in pure PANi (Figure 2b). In the polyaniline composites of Ukpor/PANi with increasing PANi content (Figure 2c), the structure changes from coarse and lumped structures to a slight globular structure, pointing out that at a higher monomer/filler ratio, the polymerization is not limited only to the filler's galleries. The PANi partially coats the clay surface, forming a plate-like layer due to electrostatic interactions between the positively charged nitrogen atoms in PANi and the negatively charged surface of the clay. Additionally, when there is an excess of monomer, some of it remains unreacted in the reaction mixture, allowing polymerization to occur in the bulk phase. This results in free polymer chains that are not anchored to the clay surface.

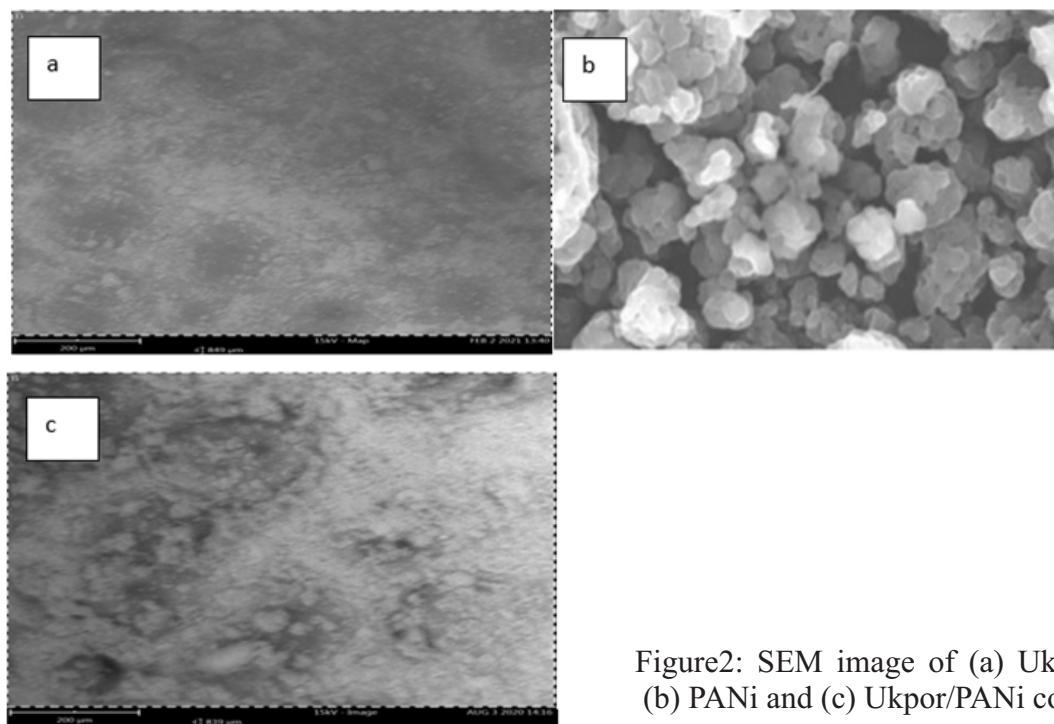


Figure2: SEM image of (a) Ukpok clay, (b) PANi and (c) Ukpok/PANi composite.

3.4 Response surface methodology (RSM) results

The experimental data obtained from the RSM are summarized in Table 1. According to the table, the highest inhibition efficiency recorded was 89.97%. This elevated IE indicates that the inhibitor is effective in preventing corrosion of aluminium in an HCl environment. The table includes inhibition efficiency results for 20 experimental runs. Analysis of the interactions between inhibitor concentration, temperature, and time showed that the maximum IE was achieved at the mid-range levels of these factors. This finding suggests that the relationships among concentration, temperature, and time follow a parabolic pattern (Ezeugo et al., 2018; Anadebe et al., 2018).

Table 2 displays the ANOVA results for the quadratic model of inhibition efficiency (IE) of aluminium in HCl with UCPC. The model's F-value of 237.28 indicates it is highly significant, with only a 0.01% probability that such an F-value could occur by chance due to noise. P-values below 0.0500 confirm that the terms A, B, C, AB, AC, BC, A², B², and C² are statistically significant. The predicted R² of 0.9629 closely aligns with the adjusted R² of 0.9911, with a difference of less than 0.2, demonstrating good model reliability. Adequate precision measures the signal-to-noise ratio, and a value above 4 is considered acceptable (Omotioma and Onukwuli, 2015). Hence, the ratio is 46.386, indicating an adequate signal. This model can effectively guide exploration within the design space.

Table 2: ANOVA of quadratic model of the IE for Al in HCl with UCPC

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	4184.28	9	464.92	237.28	< 0.0001	significant
A-Inhibitor concentration	495.33	1	495.33	252.81	< 0.0001	
B-Temperature	177.16	1	177.16	90.42	< 0.0001	
C-Time	154.37	1	154.37	78.79	< 0.0001	
AB	21.13	1	21.13	10.78	0.0082	
AC	27.68	1	27.68	14.13	0.0037	
BC	10.44	1	10.44	5.33	0.0436	
A ²	367.03	1	367.03	187.32	< 0.0001	
B ²	382.11	1	382.11	195.02	< 0.0001	
C ²	115.75	1	115.75	59.08	< 0.0001	
Residual	19.59	10	1.96			
Pure Error	0.0000	5	0.0000			
Cor Total	4203.87	19				
Std. Dev.	1.40		R ²		0.9953	
Mean	75.48		Adjusted R ²		0.9911	
C.V. %	1.85		Predicted R ²		0.9629	
			Adeq Precision		46.3857	

Figures 3 through 4 present graphical analyses of the results for aluminium in HCl. In Figure 3, the plot comparing predicted versus actual inhibition efficiency of UCPC displays a linear relationship, with data points closely aligned along the line of best fit. This suggests that the developed model effectively captures the corrosion inhibition process. This finding aligns with previous studies (Omotioma and Onukwuli, 2015; Ezeugo et al., 2018; Anadebe et al., 2018). Figure 4a illustrates the combined influence of UCPC concentrations and temperatures on inhibition efficiency, indicating that IE increases with higher inhibitor concentrations up to a maximum point, then a decrease is observed. The same trend is observed in Figure 4b, which examines the combined influence of inhibitor concentration and time on IE. The interaction between temperature and time on UCPC's inhibition efficiency for protecting aluminium in HCl is also depicted in Figure 4c, showing that IE decreases as temperature rises but increases with longer exposure time, reaching an optimal point where inhibition efficiency is maximized.

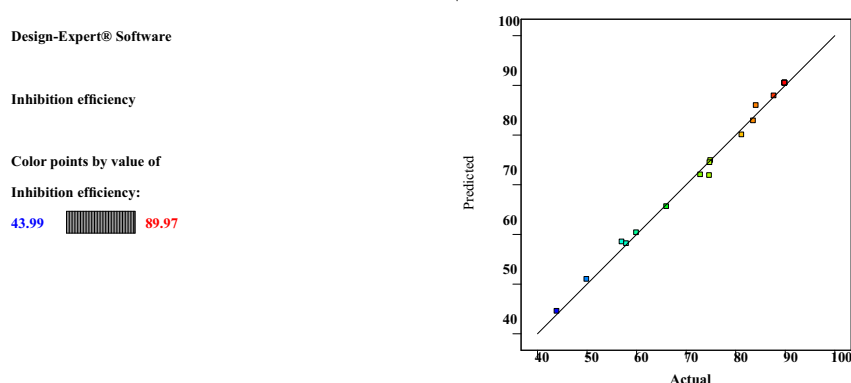


Figure 3: Predicted versus actual inhibition efficiency of UCPC for Al in HCl

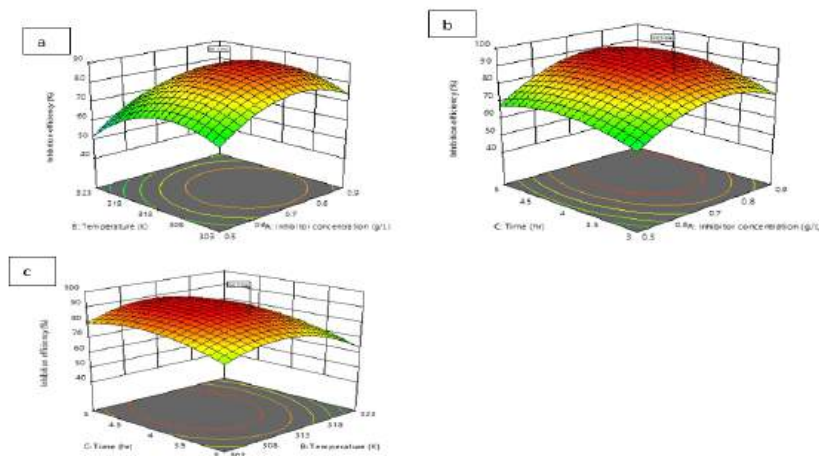


Figure 4: IE versus (a) inhibitor conc. and temperature (b) inhibitor conc. and time (c) temperature and time for Al in HCl with UCPC.

3.5 Optimization and Validation of Results

The optimal conditions of the concentration, temperature and time and the corresponding predicted inhibition efficiencies are displayed in Table 3. The optimal conditions were validated by comparing the experimental results with the predicted ones using the statistical tool of percentage deviation. The experimental data closely matched the predicted values, with percentage deviations remaining below the critical threshold of 5%. This indicates that the models effectively captured the interaction of inhibition efficiency with the concentration of inhibitor, temperatures, and duration (Omotioma and Onukwuli, 2015; Udeh et al., 2021). It shows that RSM was appropriate for optimizing the corrosion control process.

Table 3. Validation of result of the inhibition efficiency

Media	Inh. conc. (g/L).	Temp. (K)	Time (hr)	Predicted IE (%)	Experimental IE (%)	Percentage Deviation (%)
Al in HCl with UCPC	0.72	312.55	3.60	88.54	87.18	1.56

3.6 Characterization of Corrosion Product

3.6.1 FTIR of the corrosion products

Functional groups of the corrosion products are presented in Figure 7. Comparing the functional groups of the corrosion products with the corresponding inhibitors, there were shifts in the intensities of the peaks. These shifts in peaks suggest that there were interactions between the metals and some molecules of the inhibitors. The variation of the number and the nature of the shifts indicates that there is synergy among the functional groups in the corrosion inhibition process. It is in line with observation that interaction may exist among the chemical compositions of the inhibitor (Onukwuli and Omotioma, 2016). From the figure, O-H stretch, C=O stretch, C-F stretch and =C-H stretch are the dominant reactive groups in UCPC involved in the inhibition of the degradation of aluminium in hydrochloric acid.

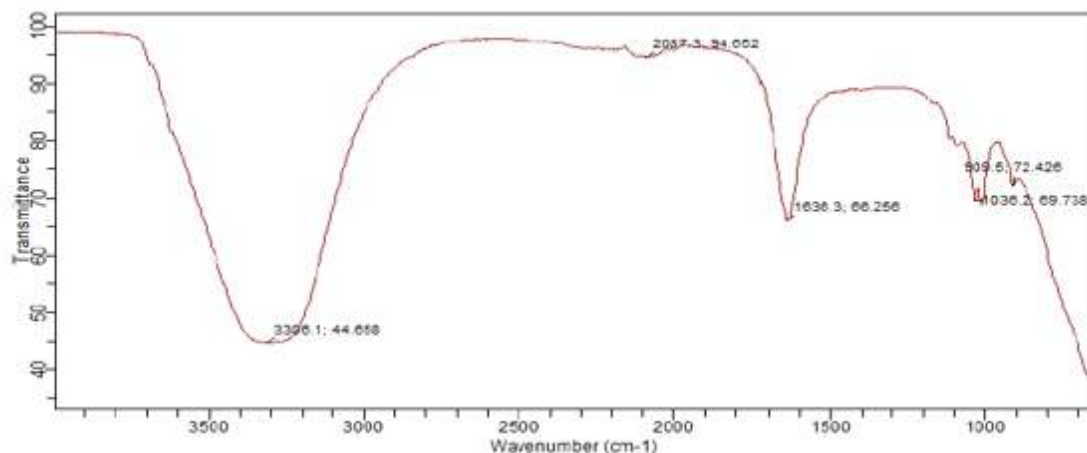


Figure 5: Reactive groups of corrosion products of aluminium in HCl with UCPC.

3.6.2 SEM Analysis of Corrosion Products

The micrographs of the corroded aluminium in the corrosive media in the presence and absence of the inhibitor are presented in Figures 6a & 6b. Considering corroded Al for the HCl medium, there were differences in the morphology of the metal's surface in the presence and absence of the inhibitors. SEM images of the Al (in the absence and presence of the inhibitors) revealed the porosity and surface texture. Figure 6a presents surface morphologies of Al in HCl. The merit of using SEM analysis is the possibility of pointing out cracks on the metal surface (Loto and Popoola, 2012; Onukwuli and Omotioma, 2016; Anadebe et al., 2019). In Figure 6b, the surface of the metal was covered by the adsorbed molecules of the inhibitor. Changes in the surface composition and texture of the metal may be due to interactions between the metal/inhibitor interface. The micrographs demonstrated that the surface was severely corroded when the inhibitor was not present, but the surface was significantly less damaged when the inhibitor was present. The development of a strong protective layer on the metal surface is responsible for this. The micrographs support the findings from the gravimetric technique.

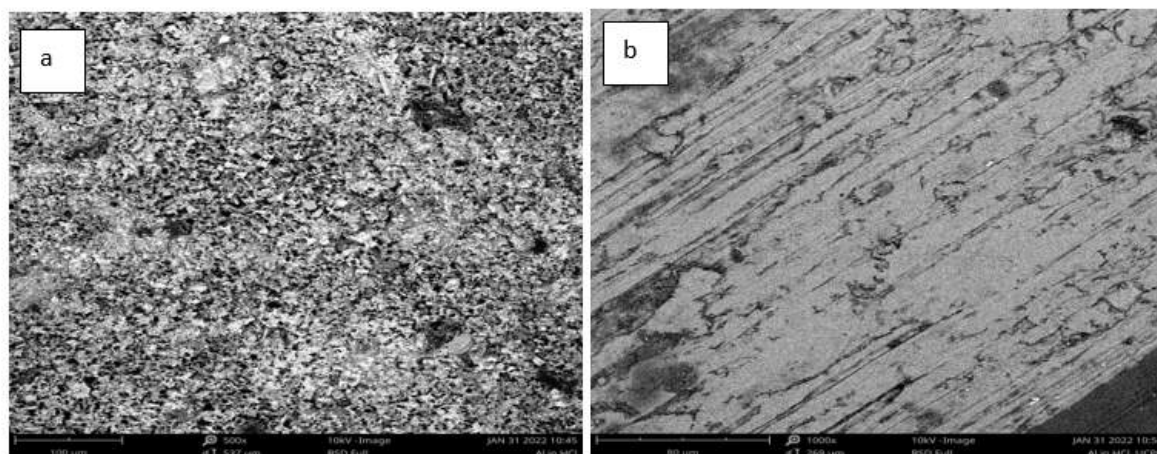


Figure 6: Surface morphology of (a) Al in HCl (b) Al in HCl with UCPC.



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4. Conclusion

The optimization of the inhibition process of aluminium in HCl using Ukpo/PANi composite inhibitor was investigated, and the study showed that Ukpo clay/polyaniline composite was successfully formulated as corrosion control inhibitors. Chemical species, functional groups and surface morphologies of the Ukpo clay/polyaniline composite showed that they are suitable corrosion inhibitors. Heteroatoms (such as nitrogen and oxygen) that aid the corrosion control process are contained in the inhibitors. The optimal conditions are inhibitor concentration of 0.72 g/L, temperature of 312.55K and time of 3.6h with inhibition efficiency of 88.54%. FTIR spectrophotometric analysis of the reactive groups of the corroding product and the inhibitor showed that there was synergy among the functional groups in the corrosion inhibition process. SEM results of the metals (in the absence and presence of the inhibitors) revealed varied porosities and surface textures of the metals. The SEM images confirmed that the Ukpo clay/polyaniline composite efficiently inhibited the corrosion of aluminium in HCl.



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Optimization of mild steel corrosion inhibition in H_2SO_4 solution with expired Gestid as inhibitor and comparative analysis of RSM and ANN modelling

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Abstract

This study considered the effectiveness of expired Gestid as an inhibitor for mild steel (MS) corrosion in H_2SO_4 solution through experimental design. Response surface methodology (RSM) was used to optimize the inhibition process. The inhibitor and the corrosion products were characterized with Fourier Transform Infrared Spectroscopy (FTIR). The results revealed that the inhibitor contains heterocyclic constituents with shifts noticed in the FTIR peaks of the corrosion products. RSM modelling results indicated an optimum Gestid efficiency of 85.28% at a concentration of 0.68 g/L, temperature of 315.24 K, within 4.49 hours. A comparative modelling between RSM and artificial neural network (ANN) indicated that ANN performed better than RSM in terms of predictive ability. Surface morphology examination of the mild steel (MS) sample in sulphuric acid media showed more damage to the MS surface compared to the surface morphology analysis of the MS sample in the inhibited media. Hence, Gestid proves to be a suitable inhibitor for mild steel corrosion.

Keywords: Inhibition efficiency, RSM, ANN, FTIR, Optimization

1. Introduction

Corrosion science and the development of inhibitors represent a key area of research aimed at protecting metals from various corrosive environments. Due to its excellent mechanical and structural properties, mild steel is extensively deployed in many industrial processes. However, in acidic media, mild steel can suffer corrosion and degradation. Various acidic and basic solutions are broadly deployed in many petrochemical and chemical industries for efficient acid pickling treatment. As a consequence of the pickling process, unwanted scales are removed, coupled with the significant damage caused to the mild steel (MS) substrate by the acid. This has orchestrated the high global demand for corrosion reduction and method development for corrosion prevention. Several methods have been explored for reducing metal corrosion. The use of a small amount of organic compounds has been identified to exhibit desirable efficiency for corrosion control. In general, organic compounds that contain π -electrons (O, N, and S) and various heteroatoms act as effective inhibitors in various aggressive solutions due to their strong adsorptive ability on the metallic surfaces (Prashanth et al., 2021).

Many organic compounds have been reportedly deployed as corrosion inhibitors in various environments. It has also been demonstrated that corrosion rate can be averted by forming donor-acceptor complexes of the



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inhibitor and the metal surface. Therefore, the effectiveness of corrosion inhibition is closely linked to the electron density, presence of functional groups, and the electronic configuration of the inhibitor molecules (Prashanth et al., 2021). In several industrial processes, acid solutions are generally deployed for removing undesirable scale and rust. One of the most practical methods of protection against corrosion is the use of inhibitors, mainly in acid solutions, to forestall acid consumption and metal dissolution. Organic compounds have been widely recognized for their effectiveness as corrosion inhibitors. Nevertheless, their toxicity poses risks to both human health and the environment. As a result, attention has shifted toward using alternative substances, particularly those derived from natural sources, as safer corrosion inhibitors. Compounds containing sulphur and nitrogen are more effective as corrosion inhibitors (Quraishi et al., 2010).

Mild steel is an iron and carbon alloy with a maximum carbon concentration of 2% (though it can have more carbon). It is the material of choice for constructing the world's industries and infrastructure since it is so widely available; anything from oil tankers to sewing needles can be made with it. Steel is also used to make the tools needed to construct and produce these items. However, exposure to a hostile environment could lead to the corrosion of steel. Hence, there is a need to develop effective inhibitors to mitigate the effect of corrosion on its application in critical infrastructure (Ezeamaku et al., 2023). According to Yurt et al. (2004), effective corrosion inhibitors for metallic materials must meet several key criteria: they should provide significant protection even at low concentrations, shield all exposed areas of the component from corrosive damage, and retain their efficiency under harsh operating conditions (high velocity and temperature), not form any deposit on the surface metal especially at regions of heat transfer, mitigate both localized and uniform corrosion, maintain long range of effectiveness, must be environmentally friendly, and during application, its over or under dosage must not drastically increase the rate of corrosion.

Several authors have worked on the application of drugs as inhibitors for mild steel corrosion. Alamry et al (2023) studied the use of ampicillin as an inhibitor for mild steel corrosion in hydrochloric acid solution. The study of the inhibitive ability of ampicillin was carried out via weight loss, surface analytical and electrochemical measurement techniques. The result obtained indicated an inhibition efficiency of less than 95% at 55 °C. Impedance analysis revealed that introducing the inhibitor enhanced the charge transfer resistance at the interface between mild steel and the solution. The potentiodynamic polarization result showed that the drug reduced the corrosion current density and behaved as a mixed-type inhibitor. The adsorption study carried out indicated that the Langmuir isotherm gave the best fit to the data from the experiment, and also indicated a combination of chemical and physical mechanisms. The above results were corroborated by the scanning electron microscopy-energy dispersive spectroscopy, and contact angle measurements.

Tsygankova et al. (2024) studied the application of expired drotaverine as an inhibitor for carbon steel



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corrosion in 1 M hydrochloric acid solution. The studies were performed with gravimetry, impedance spectroscopy, and potentiodynamic polarization, in addition to scanning electron microscopy. The Electrochemical diffusion technique was deployed to estimate the effect of Drotaverine on the diffusion of hydrogen released in the corrosion process. An inhibition efficiency of 82% was recorded at room temperature, while at 80 °C, the inhibition efficiency increased to 96%. Drotaverine slows down both hydrogen diffusion and partial electrode reactions deep into the mild steel. The adsorption of the drug on the metal followed the Langmuir isotherm.

Sheit et al. (2024) studied the efficacy of the active components of expired propranolol drug as an inhibitor for mild steel corrosion in 1 M HCl medium. AC-electrochemical impedance spectroscopy, weight loss method, potentiodynamic polarization, energy-disperse X-ray spectroscopy, scanning electron microscopy and atomic force microscopy (AFM) were applied to study the inhibitive capacity of propranolol drug. A maximum inhibition efficiency of 89.81% was obtained at 0.01 M inhibitor concentration at 303 K. The inhibitor followed Temkin's model, as demonstrated by the adsorption study. The AFM and SEM-EDX images indicated the formation of a protective layer on the mild steel against attack by the acid. The result of the potentiodynamic polarization study reveals a mixed-mode inhibition mechanism, which was mainly controlled by the cathodic reaction. The Gibbs free energy value obtained indicated an exothermic and spontaneous process.

Afzalkhah et al. (2024) considered the efficiency of 2-(4-methoxyphenyl)-benzothiazole as a novel inhibitor for mild steel in hydrochloric acid solution through the design of experiments and electrochemical impedance spectroscopy (EIS). The data obtained from the EIS study were evaluated to model the inhibition process. An experimental design was deployed in this work due to the complex nature of the process and to help control the number of main factors. Optimum values obtained from the design include a temperature of 25 °C, inhibitor concentration of 0.001 M and acid concentration of 2 M, giving an inhibition efficiency of 97.8%. Molecular dynamics simulations and quantum calculations were also deployed to investigate the adsorption and inhibitory properties of the 2-(4-methoxyphenyl)-benzothiazole molecules. The results of the quantum calculations show that the inhibitor demonstrated suitable intrinsic molecular properties. Good adsorption energy and parallel orientation of the inhibitor on the Fe (110) surface were predicted from the molecular dynamics simulations.

Corrosion inhibition efficiency is influenced by several interacting parameters, including inhibitor concentration, temperature, and immersion time. Since these relationships are often complex, non-linear, and multi-factorial, they are not easily captured by simple linear models. **Response Surface Methodology (RSM)** is a statistical tool used to evaluate and optimize processes influenced by multiple variables. It enables the identification of both main and interaction effects, develops polynomial models to approximate the response surface, and determines the optimal conditions within the experimental range. In contrast,

Artificial Neural Networks (ANNs) excel in handling highly non-linear systems, offering flexible and accurate predictions when polynomial-based approaches are insufficient. When employed together, RSM and ANN complement each other: RSM provides interpretability and structured optimization, while ANN offers data-driven predictive capability. Their combined application not only enhances optimization reliability but also reduces the number of experimental trials by estimating inhibition efficiency under unexplored conditions (Onukwuli et al., 2024).

In our previous publication, Gestid was applied as an inhibitor for aluminium corrosion in sulphuric acid solution (Nnanwube et al., 2025). Other studies on the application of drugs such as ampicillin, drotaverine, propranolol, and 2-(4-methoxyphenyl)-benzothiazole as corrosion inhibitors, as highlighted above, showed impressive performance. To our knowledge, there has not been any reported work on the optimization of mild steel corrosion inhibition in H_2SO_4 solution using Gestid as an inhibitor; hence, the need to fill this gap. In the present study, expired Gestid was used as an inhibitor for mild steel corrosion in sulphuric acid solution. The parameters, such as temperature, Gestid concentration, and time, were optimized to determine the optimum inhibition efficiency using response surface methodology. The predicted inhibition efficiency was also modelled with an artificial neural network, followed by a comparison of the two modelling techniques.

2. Experimental

2.1 Gestid Preparation

In this study, a stock solution was prepared by dissolving 10 grams of the inhibitor in 1 litre of H_2SO_4 . From this 10 g/L stock, working solutions with concentrations ranging from 0.1 to 0.9 g/L were subsequently prepared (Omotioma et al., 2024).

2.2 Mild Steel Preparation and Characterization

A mild steel sample with (3 cm x 3 cm) dimensions was cut out. The mild steel is composed of C (0.24%), Mn (0.13%), S (0.12%), Si (0.05%), Ni (0.07%), Cr (0.02%), P (0.22%), and Fe (99.15 %). The procedure for metal preparation has been reported. A scanning electron microscope was used to characterize the mild steel after contact with the uninhibited and inhibited media.

2.3 Characterization of the Inhibitor

FTIR was used to identify the inhibitor's functional groups (FGs) as well as the corrosion products. Comparative examination of diverse peaks generated from the FTIR result was carried out to identify the fitting FGs of the inhibition process, as previously reported (Nnanwube et al., 2025).



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2.4 Determination of Inhibition Efficiency

The inhibition efficiency was estimated using Equation (1) (Onukwuli et al., 2024).

$$IE\% = \frac{\omega_0 - \omega_1}{\omega_0} * 100 \quad (1)$$

The weight loss in the Gestid-H₂SO₄ and H₂SO₄-only media is symbolised by 1 and 0, respectively.

2.5 Design of Experiment by RSM

The experiment was structured using the central composite design approach within the framework of response surface methodology (RSM), with the inhibition efficiency as the response, while the factors considered were Gestid concentration, time, and temperature. The RSM design used for this study is shown in Table 1.

Table 1 Variable range and levels used in the RSM design

Independent variable	Unit	Symbol	Levels of coded variables		
			-1	0	+1
Inhibitor concentration	g/L	A	0.5	0.7	0.9
Temperature	K	B	303	313	323
Time	H	C	3	4	5

$$RMSE = \left(\frac{1}{n} \sum_{i=1}^n (Y_{pred,i} - Y_{exp,i})^2 \right)^{1/2} \quad (2)$$

$$SEP = \frac{RMSE}{Y_{exp,ave}} * 100 \quad (3)$$

$$MAE = \frac{1}{n} \sum_i^n |Y_{exp,i} - Y_{exp,i}| \quad (4)$$

3. Results and Discussion

3.1 Infrared Spectroscopy of Gestid

The relevant functional groups found in the inhibitor (Gestid) include NH₂, NH₃⁺, NO₂, CF₃, C-O-C, Si-O-Si stretches (anti-symmetrical); C-H anti-symmetrical and symmetrical stretching; C=O, C-S, Si-C, C-N, C=N, C-Cl stretches. Figures 1 and 2 describe the infrared spectral result of Gestid and that of the corrosion products. Deviations were noticed in certain peaks after contact with a 1 M H₂SO₄ medium. It was noticed from Figures 1 and 2 that the C=O stretch at 1662.4 cm⁻¹ moved to 1636.3 cm⁻¹, while the C-O and C-N stretches at 1241.2 cm⁻¹ moved to 1080.9 cm⁻¹ in the products of corrosion. The effectiveness of Gestid in checkmating MS corrosion is due to heterocyclic constituents in the Gestid (Nnanwube et al., 2025).

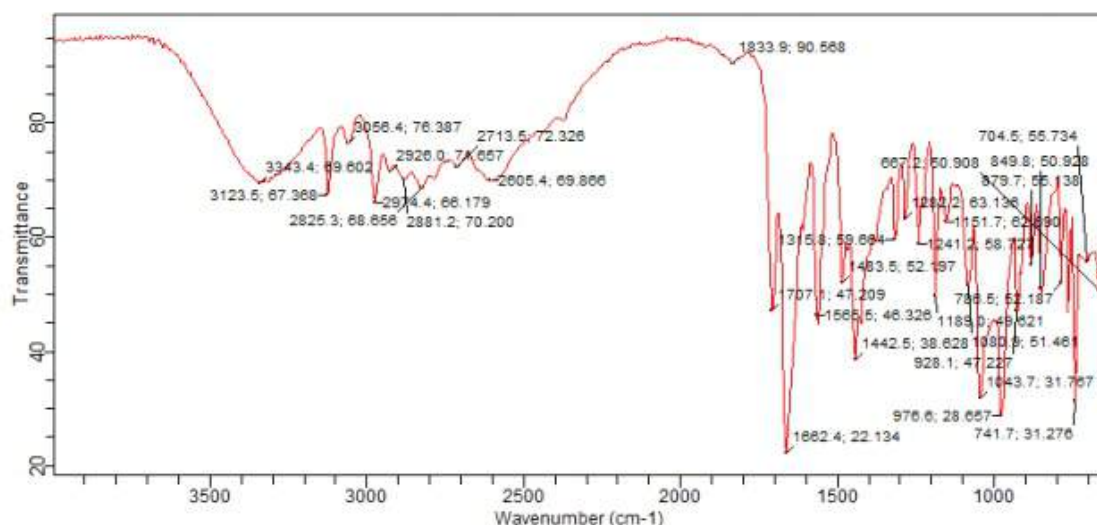


Fig. 1: FTIR spectrum of Gestid.

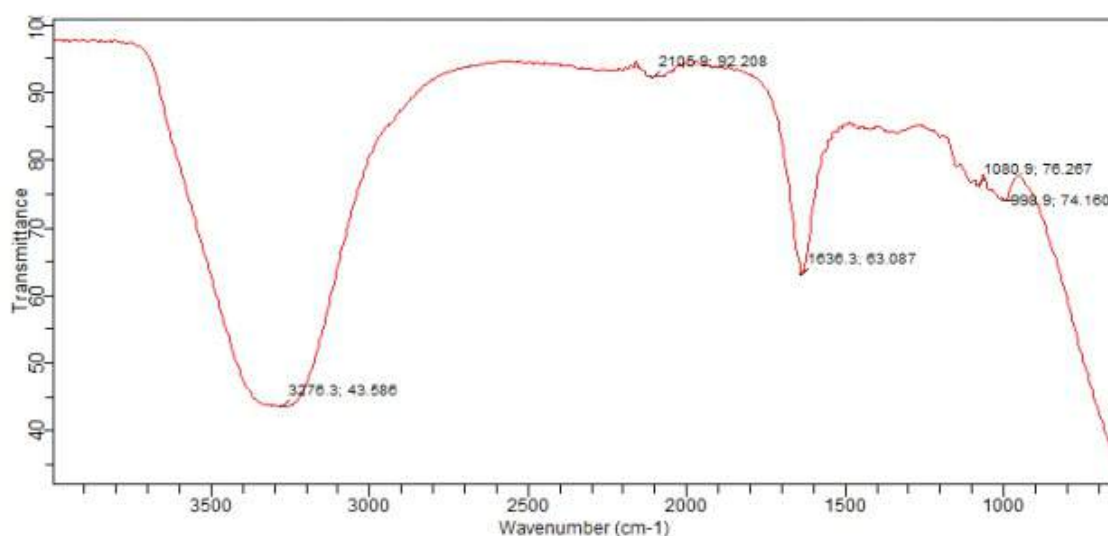


Fig. 2: FTIR spectrum of corrosion products

3.2 RSM Results for Mild Steel in Sulphuric Acid Media

As shown in Table 2, Gestid deployed for MS corrosion inhibition in H₂SO₄ has a maximum IE of 86.02% at a temperature of 313 K, IC of 0.7g/L, and corrosion time of 4 hours. The high IE value shows that Gestid is fitting for inhibiting MS corrosion in H₂SO₄ media. An increase in IE was observed as the IC increased.

Table 2 RSM design, experimental and predicted results for curbing mild steel corrosion in sulphuric acid with Gestid.



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Std	Run	IC g/L	Temp. K	Time h	IE %	
					Experimental	Predicted
2	1	0.9	303	3	68.72	67.79
1	2	0.5	303	3	53.74	55.24
7	3	0.5	323	5	55.6	57.10
9	4	0.5	313	4	76.69	73.45
12	5	0.7	323	4	75.56	73.18
14	6	0.7	313	5	85.31	85.41
5	7	0.5	303	5	72.23	71.73
10	8	0.9	313	4	84.14	85.10
20	9	0.7	313	4	86.02	86.78
3	10	0.5	323	3	47.21	47.95
11	11	0.7	303	4	80.99	81.08
19	12	0.7	313	4	86.02	86.78
18	13	0.7	313	4	86.02	86.78
17	14	0.7	313	4	86.02	86.78
15	15	0.7	313	4	86.02	86.78
16	16	0.7	313	4	86.02	86.78
13	17	0.7	313	3	78.95	76.56
4	18	0.9	323	3	65.56	66.63
6	19	0.9	303	5	76.51	76.34
8	20	0.9	323	5	68.77	67.84

Table 3 shows the analysis of variance for MS corrosion inhibition in sulphuric acid with Gestid as the inhibitor. The data in the table shows parameters such as F-value, P-value, sum of squares, mean square, predicted R^2 and adjusted R^2 . The F-value of 87.54 suggests a significant model since just 1 out of 100 probabilities of an F-value as huge as this could arise owing to noise. Less than 0.0500 P-values suggest significant model terms. Hence, the important model terms in this case are A^2 , B^2 , C^2 , A, B, C, AC, BC, and AB. There is proximity between R^2 (predicted) of 0.8967 and R^2 (adjusted) of 0.9762; i.e. the variance is < 0.2 . A ratio of 29.584 for the adequate precision implies an acceptable signal. (Onukwuli et al., 2024; Edoziuno et al., 2020).

Table 3 Quadratic model for MS corrosion control in H_2SO_4 with Gestid.

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	2714.76	9	301.64	87.54	< 0.0001	significant
A-Inhibitor concentration	339.07	1	339.07	98.40	< 0.0001	
B-Temperature	155.95	1	155.95	45.26	< 0.0001	
C-Time	195.72	1	195.72	56.80	< 0.0001	
AB	18.79	1	18.79	5.45	0.0417	
AC	31.52	1	31.52	9.15	0.0128	
BC	26.94	1	26.94	7.82	0.0189	
.	155.08	1	155.08	45.01	< 0.0001	
B^2	256.06	1	256.06	74.31	< 0.0001	
C^2	92.34	1	92.34	26.80	0.0004	
Residual	34.46	10	3.45			
Lack of Fit	34.46	5	6.89			
Pure Error	0.0000	5	0.0000			
Cor Total	2749.22	19				
Std. Dev.	1.86		R^2		0.9875	
Mean	75.30		Adjusted R^2		0.9762	
C.V. %	2.47		Predicted R^2		0.8967	
			Adeq Precision		29.5840	

3.3 Mathematical Equations of the IE

Equations (5) and (6) represent the coded and actual factors for the inhibition efficiency. The coded factor equation can be applied to predict the response for certain levels of the factors.

$$IE = +86.78 + 5.82A - 3.95B + 4.42C + 1.53AB - 1.99AC - 1.84BC - 7.51A^2 - 9.65B^2 - 5.79C^2 \quad (5)$$

$$IE = -9555.60545 + 91.81284 * \text{Inhibitor concentration} + 60.20888 * \text{Temperature} + 115.16336 * \text{Time} + 0.766250 * \text{Inhibitor concentration} * \text{Temperature} - 9.92500 * \text{Inhibitor concentration} * \text{Time} - 0.183500 * \text{Temperature} * \text{Time} - 187.73864 * \text{Inhibitor concentration}^2 - 0.096495 * \text{Temperature}^2 - 5.79455 * \text{Time}^2 \quad (6)$$

3.4 Graphical Interpretation of IE

The plots of IEs of Gestid for curbing MS corrosion in H_2SO_4 solution are displayed in Figure 3(a-d). The plot of predicted versus actual inhibition efficiency (IE) (Figure 3a) shows a straight-line trend, with data points closely aligned along the line, suggesting strong agreement between the experimental results and the predicted values.

The 3-D plots showed the joint effects of IC, time, and temperature on the inhibition efficiency of gestid on MS in H_2SO_4 medium. The 3-D plots of Figures 3(b-d) show optimum IE of Gestid as 85.28 % at IC of 0.68 g/L, temperature of 315.24 K and immersion time of 4.49 hours. This high value of IE indicated that Gestid is suitable for impeding MS corrosion in H_2SO_4 medium.

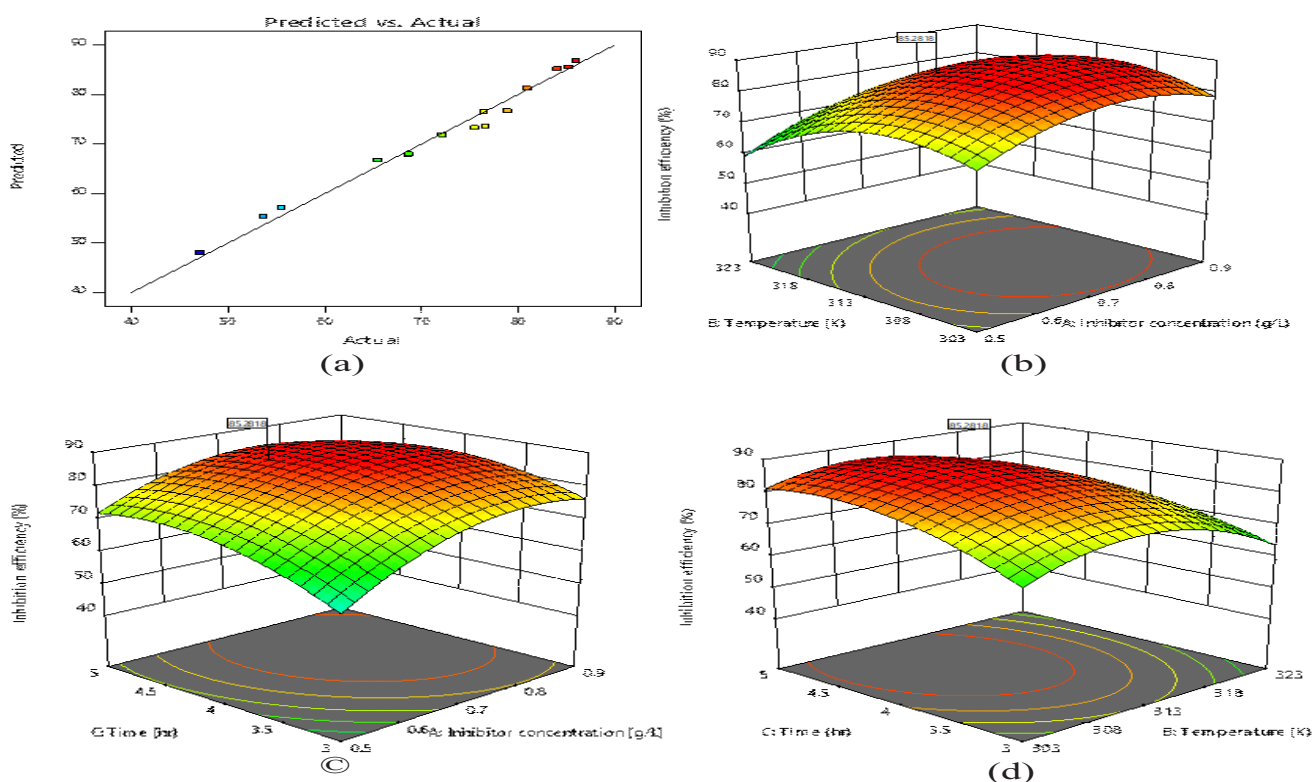


Fig. 3. (a) RSM predicted against experimental IE, (b) IE vs inhibitor concentration and temperature, (c) IE vs inhibitor concentration and time, (d) IE vs temperature and time.

3.5 ANN Modelling

ANN was used to predict and model the inhibition efficiency of gestid using the experimental values obtained from the RSM design. ANN often achieves higher predictive accuracy than traditional regression models. They can learn directly from experimental or simulation data, making them suitable for systems where the mechanism is not fully understood (Nnanwube et al., 2025).

The ANN's best performance plot for inhibiting MS corrosion in H_2SO_4 with Gestid is presented in Figure 4. 70%, 20%, and 10% of the results obtained from the experiment were respectively deployed for training, validation, and testing, using the algorithm developed by Levenberg-Marquardt. The graph illustrates four training epochs, with the optimal value of 10.4351 achieved at the second epoch, indicating that the ANN model is well-suited for predicting inhibition efficiency. Figure 5 shows the graphs of regression.

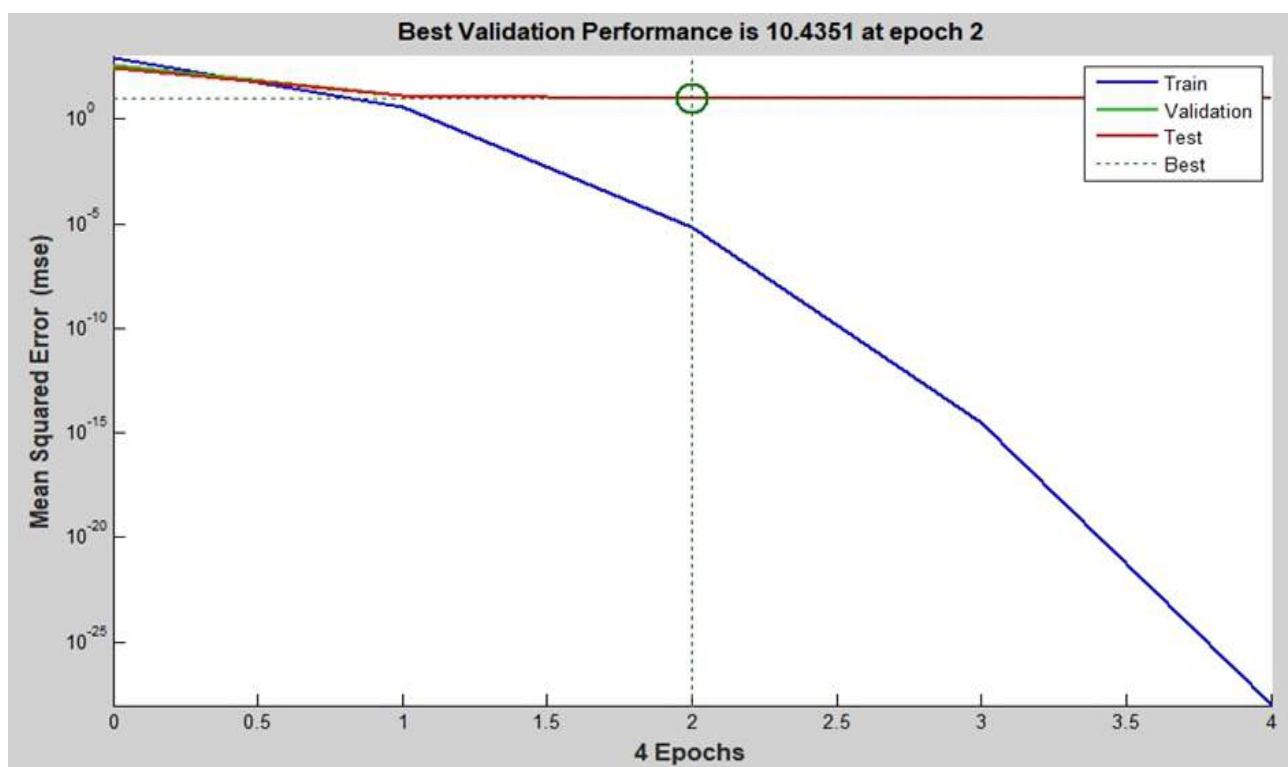


Fig. 4. Plot of best validation performance

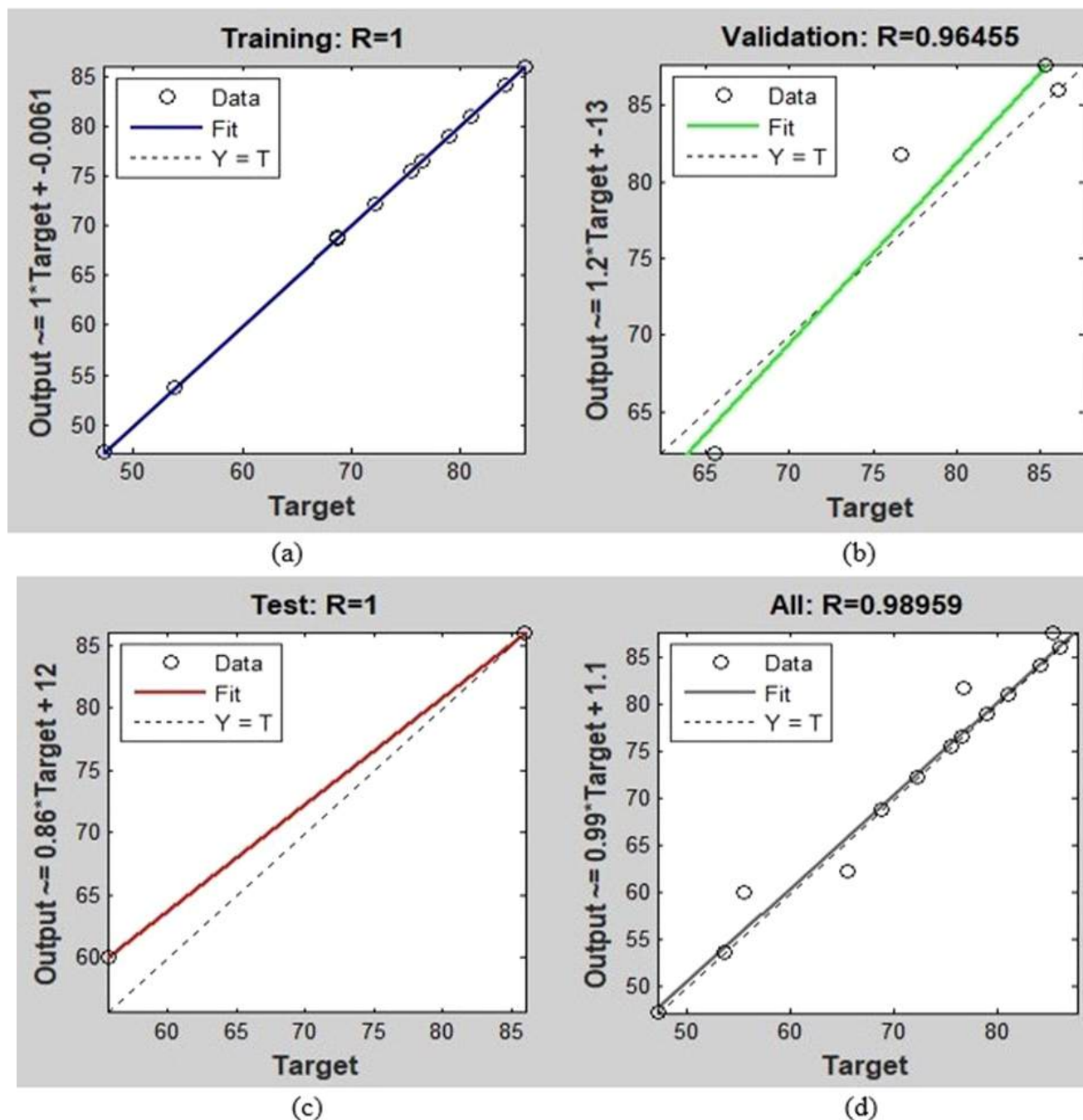


Fig. 5. Plots of output versus target for training (a), validation (b), testing (c), and all plots (d).

3.6 Assessment of RSM and ANN Predicted Values

The predicted values of RSM and ANN are presented in Table 4. Statistical tools used to compare the two predictions indicate that ANN performed better than RSM in terms of predicted IE, as indicated by the statistical parameters such as RMSE (1.3130 (RSM), 0.0061 (ANN)), SEP (1.7436 (RSM), 0.0081 (ANN)), MAE (1.0530 (RSM), 0.0061 (ANN)), where ANN gave lower error values.

Table 4 ANN and RSM predicted values for curbing MS corrosion in H_2SO_4 using Gestid.



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Std	Run	Inhibitor conc. g/L	Temp. K	Time h	IE %		
					Experimental	RSM Predicted	ANN Predicted
2	1	0.9	303	3	68.72	67.79	68.7139
1	2	0.5	303	3	53.74	55.24	53.7339
7	3	0.5	323	5	55.6	57.10	55.5939
9	4	0.5	313	4	76.69	73.45	76.6839
12	5	0.7	323	4	75.56	73.18	75.5539
14	6	0.7	313	5	85.31	85.41	85.3039
5	7	0.5	303	5	72.23	71.73	72.2239
10	8	0.9	313	4	84.14	85.10	84.1339
20	9	0.7	313	4	86.02	86.78	86.0139
3	10	0.5	323	3	47.21	47.95	47.2039
11	11	0.7	303	4	80.99	81.08	80.9839
19	12	0.7	313	4	86.02	86.78	86.0139
18	13	0.7	313	4	86.02	86.78	86.0139
17	14	0.7	313	4	86.02	86.78	86.0139
15	15	0.7	313	4	86.02	86.78	86.0139
16	16	0.7	313	4	86.02	86.78	86.0139
13	17	0.7	313	3	78.95	76.56	78.9439
4	18	0.9	323	3	65.56	66.63	65.5539
6	19	0.9	303	5	76.51	76.34	76.5039
8	20	0.9	323	5	68.77	67.84	68.7639

3.7 Effect of Temperature, Acid Concentration, Inhibitor Concentration, and Time on inhibition Efficiency

The performance of corrosion inhibitors is strongly governed by operational variables such as temperature, medium acidity, inhibitor concentration, and exposure duration. Temperature rise generally diminishes inhibition efficiency, primarily due to enhanced desorption of inhibitor molecules from the metallic substrate, which reduces surface coverage. Such temperature-dependent behaviour is typically associated with physisorption, where adsorption forces are relatively weak and unstable at elevated conditions. In contrast, if high efficiency is retained under thermal stress, this is more suggestive of chemisorption, involving the formation of stronger, more persistent chemical interactions with the substrate (Onukwuli et al., 2024; Sheit et al., 2024).

The aggressiveness of the corrosive environment, particularly acid concentration, is another decisive factor. Higher concentrations of protons accelerate metal dissolution and often

disrupt the protective film established by the inhibitor. Compounds that maintain notable efficiency even in strongly acidic solutions generally indicate robust adsorption strength and resilience against ionic attack. Inhibitor dosage also plays a key role. Increasing concentration typically enhances performance owing to improved surface coverage and the development of a denser protective barrier. Nevertheless, once adsorption sites are saturated, further increases produce negligible benefits and may induce aggregation phenomena. Immersion time further influences inhibitor effectiveness. While adsorption is initially rapid, prolonged exposure can result in partial desorption or gradual film degradation. Inhibitors capable of generating stable, adherent films demonstrate superior long-term efficiency, highlighting the importance of durability in assessing their practical application (Omotioma et al., 2024; Tsygankova et al., 2024).

3.8 Optimum Conditions and Validation

Table 5 shows the optimal IC, temperature, time and inhibition efficiency of Gestid for mild steel in H_2SO_4 . The optimum inhibition efficiency value of Gestid was estimated as 85.28 %, which is close to a value of 92.01 % obtained when Gestid was used as an inhibitor for aluminium corrosion in sulphuric acid solution, as previously reported (Nnanwube et al., 2025). This IE value recorded indicates that gestid is a proper inhibitor for curbing MS corrosion in H_2SO_4 solution. The optimum parameters were validated with a deviation obtained as 0.57%.

Table 5 Optimum conditions by RSM.

Media	IC (g/L).	Temp. (K)	Time (h)	IE (%)
Mild steel in H_2SO_4 with Gestid	0.68	315.24	4.49	85.28

3.9 Surface Morphology of MS in Sulphuric Acid Media

SEM analyses of the MS sample in H_2SO_4 solution are displayed in Figure 6(a, b). Less damage was noticed on the metals in the Gestid-inhibited solution compared to those in the free solution. It indicates that the adsorption of the inhibitor on the surface of the metal controls the corrosion process.

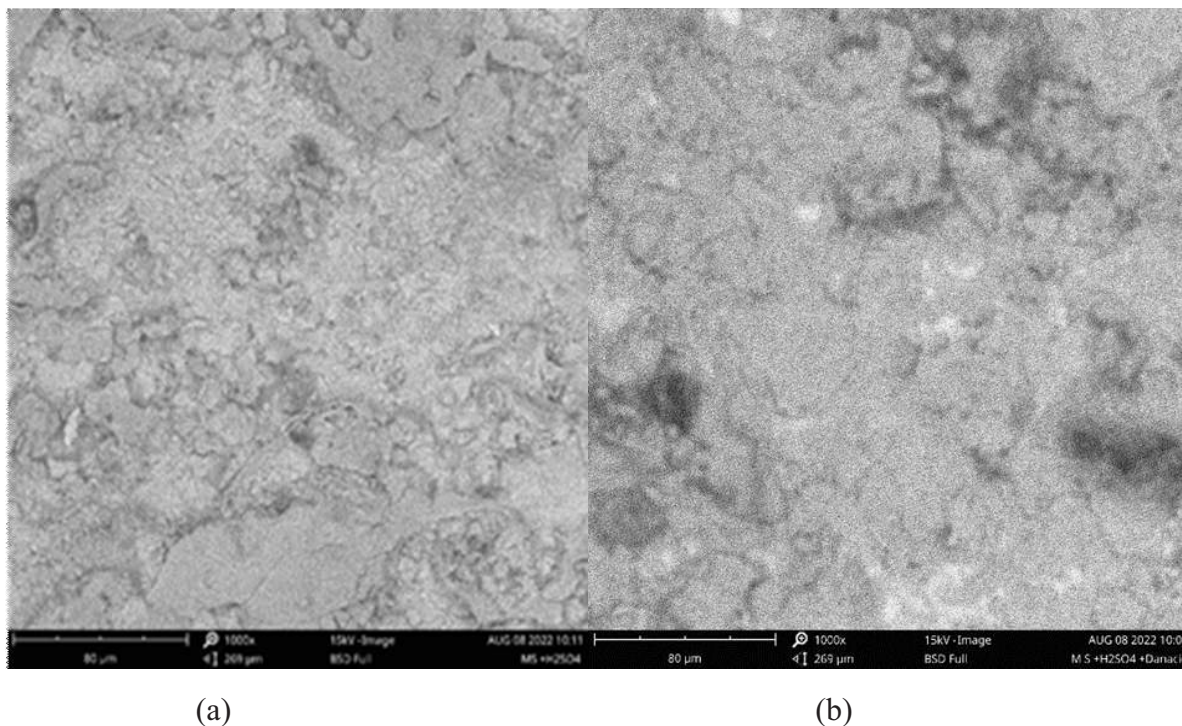


Fig. 6. SEM micrographs of Mild Steel in H_2SO_4 (a) SEM micrograph of MS in H_2SO_4 (b).

4. Conclusion

This study explored the optimization of mild steel corrosion prevention in H_2SO_4 using Gestid as the inhibiting agent. Response surface methodology was deployed for the optimization study. The inhibitor and corrosion products were characterized with Fourier Transform Infrared Spectroscopy (FTIR). An optimum inhibition efficiency of 85.28% was obtained from response surface methodology (RSM) optimization. The experimental data were further modelled using an artificial neural network (ANN) to predict the inhibition efficiency of Gestid, after which a comparison of the two techniques was done. ANN gave a better prediction of the inhibition efficiency as indicated by the statistical parameters such as root mean square error, mean absolute error, and standard error of prediction. The surface morphology of mild steel, after exposure to both inhibited and uninhibited solutions, was examined using a scanning electron microscope (SEM). The result revealed greater damage to the mild steel surface in the uninhibited solution compared to the inhibited solution. Hence, it can be concluded that expired Gestid is a viable inhibitor for mild steel corrosion.



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Improving the Mechanical Strength and Water Resistance of Polyethylene Composites Via Reinforcement with Chemically Treated Natural Fibres-19

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Abstract

The effects of alkaline treatment on the strength and hydrophilicity of pineapple leaf fibre-reinforced polyethene (PLF-P) and local sponge fibre-reinforced polyethene (LSF-P) composites were investigated. Composite plates (10–50 wt% fibre) were produced using the hand lay-up method and analyzed for water absorption, density, tensile, compressive, and impact strength. Water absorption increased with fibre content, and the PLF-P exhibited higher absorption than the LSF-P. The composite density also increased, reaching 1.561 g/cm³ (PLF-P) and 1.906 g/cm³ (LSF-P). Tensile and compressive strength peaked at 30 wt% for PLF-P (~60 MPa) and 40 wt% for LSF-P (~60.24 MPa). However, impact strength declined after alkali treatment due to reduced fibre pull-out, as it decreased by 21.46% (PLF-P) and 16.24% (LSF-P) at 30 wt%. SEM and FTIR analyses confirmed improved composite properties.

Keywords: Pineapple-leaf-fibre; Local-sponge-fibre; Natural-fibre; Reinforced-composites

1. Introduction

A Composite consists of two or more materials that give better properties than those of the individual components when used alone and whose properties are a function of the strength of the reinforcement material (Egbo, 2021). Among the arrays of composites is the fibre-reinforced plastic (FRP), formed as a product of a reinforcing polymer matrix with either a synthetic or natural fibre –(Aniagor et al., 2025). Recently, the suitability of natural fibres as suitable reinforcements in composite development has been underscored (Elfaleh et al., 2023). This is due to their cheap availability, positive functional properties, and eco-friendliness. Furthermore, unlike other synthetic reinforcing fibres, they are biodegradable and non-abrasive (Kamarudin et al., 2022). Despite the numerous merits of natural fibres, they still face challenges such as poor adhesive interaction with polymer matrices and relatively high hydrophilicity (Islam et al., 2024). Natural fibers' hydrophilicity coupled with the presence of pectin and wax, hinders their effective bonding with the matrix. This necessitates the need for fibre treatment to entrench enhanced interfacial bonding.



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In an attempt to reduce hydrophilicity and enhance their adhesion to polymeric matrices, natural fibres have been subjected to numerous treatment techniques. Physical methods have been extensively studied and reported to yield fibres with enhanced strength and hardness, but the binding interaction of these fibres within the polymer matrix is still a challenge (Cruz & Fanguero, 2016). Similarly, the chemical treatment technique targets an improved fibre structure and crystallinity via the elimination of hemicellulose and lignin from the biomass using various chemicals (Koohestani et al., 2019). Notably, different chemical fibre treatment techniques exist, including alkaline, silane, benzylation, peroxide, and acetylation treatment (Rippon & Evans, 2020). Alkalization is a means of fibre chemical treatment which intends to modify the fibre surface by improving the adhesion between the fibre surface and polymer matrix, in addition to increasing fibre strength. According to Raghu and Goud (2020), alkaline treatment is the most widely adopted chemical treatment technique for natural fibres, as the treatment enhances the fibre's strength, hardness, and thermal stability. Similarly, Rokbi et al. (2020) reported that alkaline treatment also improves the filler/polymer matrix adhesion, leading to better interfacial bonding.

This study investigates how alkaline treatment influences the hydrophilicity and functional properties of natural fibres when used in reinforced composites. Locally sourced sponge fibres (LSF) from *Luffa cylindrica* and pineapple leaf fibres (PLF), an agricultural byproduct, were chosen due to their abundance, sustainability, and strong mechanical properties. LSF is lightweight, biodegradable, and tensile-resistant, while PLF has high cellulose content, excellent tensile strength, and low density. Their use not only reduces agricultural waste but also creates economic benefits for farmers and industries. By examining morphological, chemical, and mechanical changes in composites with varying fibre proportions before and after alkali treatment, the study highlights the potential of these renewable, cost-effective fibres as sustainable reinforcements in polymeric materials.

2. Materials and Methods

2.1. Material collection and treatment

This research utilizes pineapple leaves and local sponge fibre, as precursors, as well as LDPE resin, acetic acid, sodium hydroxide, and distilled water as reagents. The details of the sourcing and processing of the precursor materials are detailed in our previous work (Agbo et al., 2025). In a nutshell, the precursor materials were impregnated in a suitable volume of 5% NaOH for 2 h to remove hemicellulose and lignin. The alkaline system was subsequently neutralized with acetic acid, rinsed with distilled water to pH 7.0, and sun-dried. Figures 1 and 2 illustrate the extraction process for PLF and LSF, respectively.

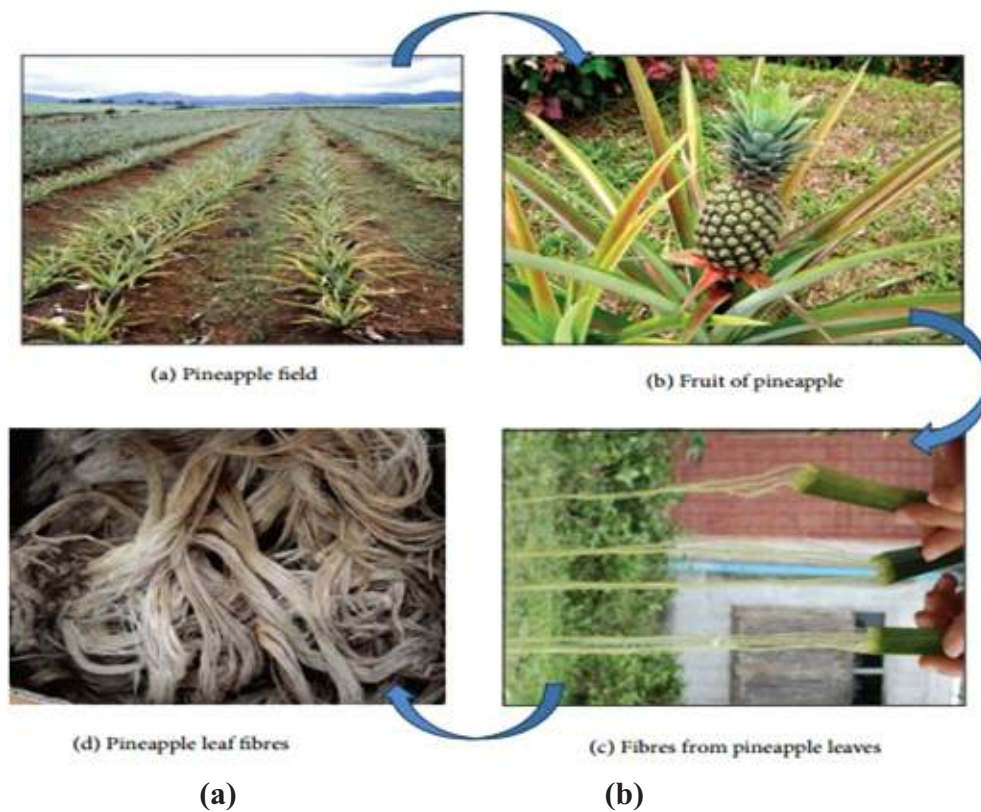


Figure 1: Sequential arrangement of the production of PLF (a) pineapple plantation, (b) pineapple fruit, (c) fibres extraction from pineapple leaves, and (d) extracted PLF



Figure 2: (a) Local sponge tree (b) Local sponge fibre after processing

2.2. Fabrication of the fibre-reinforced composites

In line with the hand lay up technique earlier proposed by Kim et al. (2014), a suitable mass of the extracted natural fibres (5mm long) and polyethylene resin was complexed at varying weight ratios (Table 1) and cast in 150 mm × 65 mm × 5 mm metal mould lined with an aluminium release sheet. The excess polymer was managed, and after 15 - 20 min, the samples were removed, trimmed, and stored airtight for further testing. Further details on the fabrication protocol can be obtained from our previous work (Agbo et al., 2025). The fabricated composite was further characterized using standard American Society for Testing and Materials (ASTM) procedures (Kodur et al., 2022).

Table 1: The varying fibre weight ratios adopted in this study

Code name	% Compositions of PLF composite			Code name	% Compositions of LSF composite		
	PLF _{untreated}	PLF _{Treated}	LDPE		LSF _{Untreated}	LSF _{Treated}	LDPE
Blank	0.0	0.0	100.0	Blank	0.0	0.0	100.0
UPLF-P ₁₀	10.0	0.0	90.0	ULSF-P ₁₀	10.0	0.0	90.0
UPLF-P ₂₀	20.0	0.0	80.0	ULSF-P ₂₀	20.0	0.0	80.0
UPLF-P ₃₀	30.0	0.0	70.0	ULSF-P ₃₀	30.0	0.0	70.0
UPLF-P ₄₀	40.0	0.0	60.0	ULSF-P ₄₀	40.0	0.0	60.0
UPLF-P ₅₀	50.0	0.0	50.0	ULSF-P ₅₀	50.0	0.0	50.0
TPLF-P ₁₀	0.0	10.0	90.0	TLSF-P ₁₀	0.0	10.0	90.0
TPLF-P ₂₀	0.0	20.0	80.0	TLSF-P ₂₀	0.0	20.0	80.0
TPLF-P ₃₀	0.0	30.0	70.0	TLSF-P ₃₀	0.0	30.0	70.0
TPLF-P ₄₀	0.0	40.0	60.0	TLSF-P ₄₀	0.0	40.0	60.0
TPLF-P ₅₀	0.0	50.0	50.0	TLSF-P ₅₀	0.0	50.0	50.0

NB: UPLF-P = Composite reinforced using untreated PLF; TPLF-P = Composite reinforced using alkaline-treated PLF; ULSF-P = Composite reinforced using untreated LSF; TLSF-P = Composite reinforced using alkaline-treated LSF

3. Results and Discussions

3.1. Water absorption test

To determine the quantity of water absorbed by the untreated and alkaline-treated PLF-P and LSF-P composites, the swelling capacity was investigated under 24 h immersion and the results obtained for both composites are shown in Figure 3. According to the result, the water uptake for the untreated fibre composite (UPLF-P and UTSF-P) increased within the first 72 h of water immersion and further equilibrated at 192 h, where very little or no water was further imbibed. Although both UPLF-P and UTSF-P composites absorbed a significant volume of water, the UPLF-P had a comparatively better water absorption capacity than the UTSF-P. This could be due to the high availability of polar functional groups, with high affinity for water (Sayeed et al., 2023). Meanwhile, the composites developed in the alkaline-treated fibres (TPLF-P and TTSF-P) showed a slightly decreased water absorption capacity. For instance, the maximum water absorption capacity for the UPLF-P and TPLF-P are 21.62 % and 11.90 %, respectively, at 30 wt % fibre loading. Similarly, the UTSF-P and TTSF-P respectively, showed water absorption capacities of 21.47% and 19.67% at the same 30 wt% fibre loading. The lower percentage of water absorption recorded for the TPLF-P and TTSF-P is attributed to the hydrophobicity introduced to the fibres due to their alkalization.

Praveena et al. (2021) explored the functional properties of sisal/pineapple leaf/polyester composite. The study demonstrated that enhanced fibre content in the polyester composites (up to 50 wt%) results in composites with better mechanical and hydrophobic properties. It was also noted that the hydrophobic behaviours of the polypropylene hybrid composites reinforced with jute, kenaf, and pineapple leaf fibre (PALF) improved through the hybridization (Feng et al., 2020). Daramola et al. (2017) also reported that the amount of water absorbed by treated pineapple leaf fibre (PALF) reinforced polyester composites increased with an increase in fibre loading.

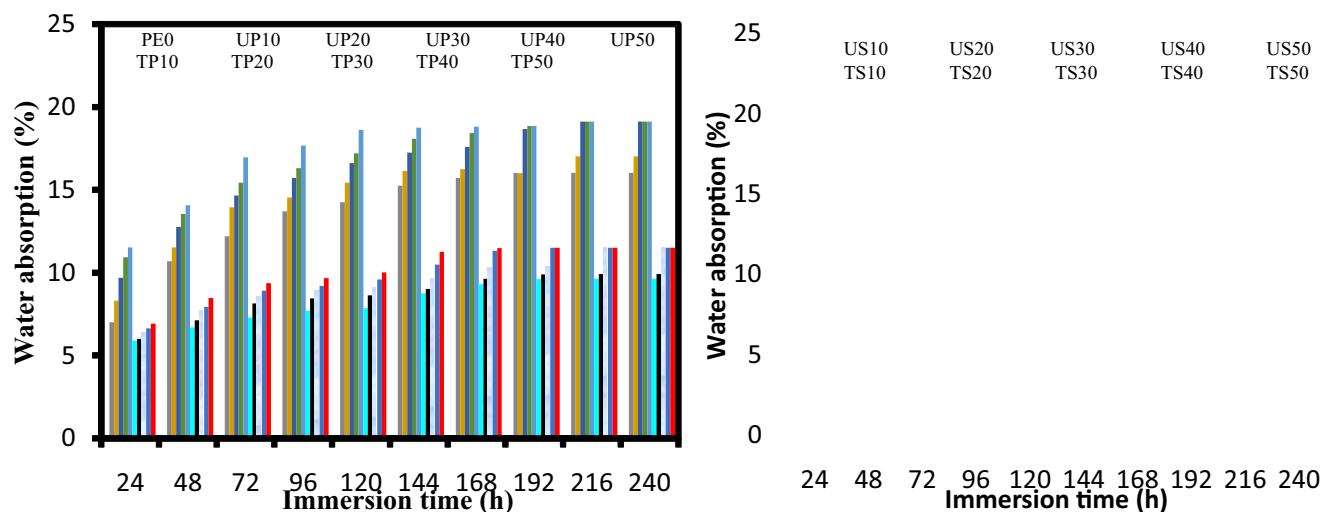


Figure 3: Swelling behaviour of (a) the PLF-P composites and (b) the LSF-P composites

3.2. Composite density analysis

The result shown in Figure 4 shows that the raw LDPE sample had a density value of 0.935 g/cm^3 . However, after reinforcement with both untreated and alkaline-treated fibres, the resultant composites showed a significant density increment. For the untreated PLF composite (UPLF-P), the density at 10 wt% and 30 wt% fibre loading, respectively, increased from 1.053 to 1.561 g/cm^3 . Similarly, the density of the alkaline-treated PLF composite (TPLF-P) at 10 wt% and 30 wt% fibre loading, respectively, increased from 1.005 g/cm^3 to 1.518 g/cm^3 . It was observed that further increments in the fibre loading, beyond 30 wt%, negatively impacted the density of the resultant composites. For the untreated LSF composite (ULSF-P), the density increased from 1.511 g/cm^3 with 10 wt% fibre to 1.906 g/cm^3 with 40 wt% fibre. Similarly, the density of the alkaline-treated LSF composite (TLSF-P) increased from 1.192 g/cm^3 at 10 wt% fibre loading to 1.816 g/cm^3 at 40 wt% fibre content. It was observed that further increments in the fibre content, beyond 40 wt%, negatively impacted the density of the resultant composites. It is thus concluded that the untreated and alkaline-treated versions of both composites show that fibre weight varies directly as the density of their composites up to a certain benchmark. However, the PLF-P composites generally showed less density compared to the LSF-P composites.

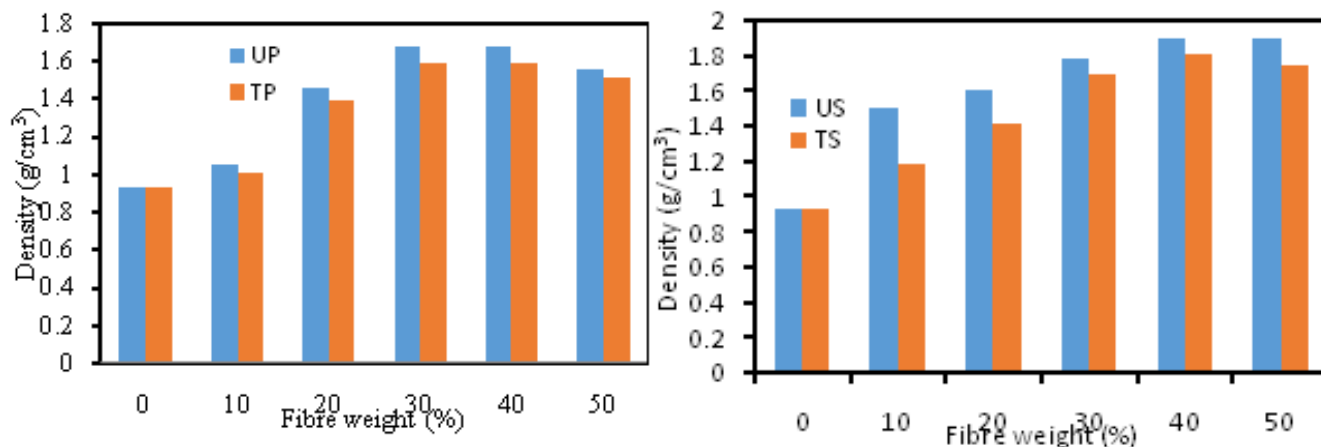


Figure 4: Fibre weight variation vs density for (a) PLF-P and (b) LSF-P composites

3.3. Analysis of the tensile strength of the composites

The tensile strength measures the force required to break a composite specimen. Results for untreated (UPLF-P, ULSF-P) and alkaline-treated (TPLF-P, TLSF-P) composites generally increased with fibre content. For PLF-P-based composites, at 50 wt% fibre loading, Young's modulus reached 1980.09 MPa (UPLF-P) and 2550.01 MPa (TPLF-P), compared to 1240.02 and 2150.13 MPa at 10 wt%. Corresponding tensile strengths were 46.14 MPa (UPLF-P) and 57.12 MPa (TPLF-P), against 31.13 and 44.02 MPa at 10 wt%. Thus, higher fibre content improved fibre–matrix interaction, stress transfer, and overall strength. Treated fibres (TPLF-P) outperformed untreated ones due to improved interfacial bonding, reduced defects, and enhanced properties.

In contrast, LSF-P composites showed maximum tensile strength at 40 wt%. At this point, ULSF-P and TLSF-P recorded 55.06 and 60.24 MPa, respectively, compared to 47.04 and 50.22 MPa at 10 wt%. However, increasing fibre to 50 wt% reduced tensile strength by ~2% in both cases, likely due to fibre agglomeration, poor stress transfer, and voids. The Young's modulus at 50 wt% was 2200.21 MPa (ULSF-P) and 2400.32 MPa (TLSF-P), up from 1900.12 and 2010.03 MPa at 10 wt%, showing that stiffness still increased with fibre loading. This indicates an optimum fibre content around 40 wt% for strength, while modulus benefits persist at higher levels. These findings align with the literature. Aliyu et al. (2022) reported tensile strength gains in polyester composites with newspaper particulate up to 20 wt%, beyond which strength declined. Öztürk (2010) observed that fibre type, loading, and hybridisation strongly affect hybrid composites, with tensile and flexural strengths peaking at 36 vol.% fibre. Similar trends were reported for polylactic acid/kenaf composites (Ismail & Ishak, 2018) and banana fibre/epoxy composites (Raghavendra et al., 2024).

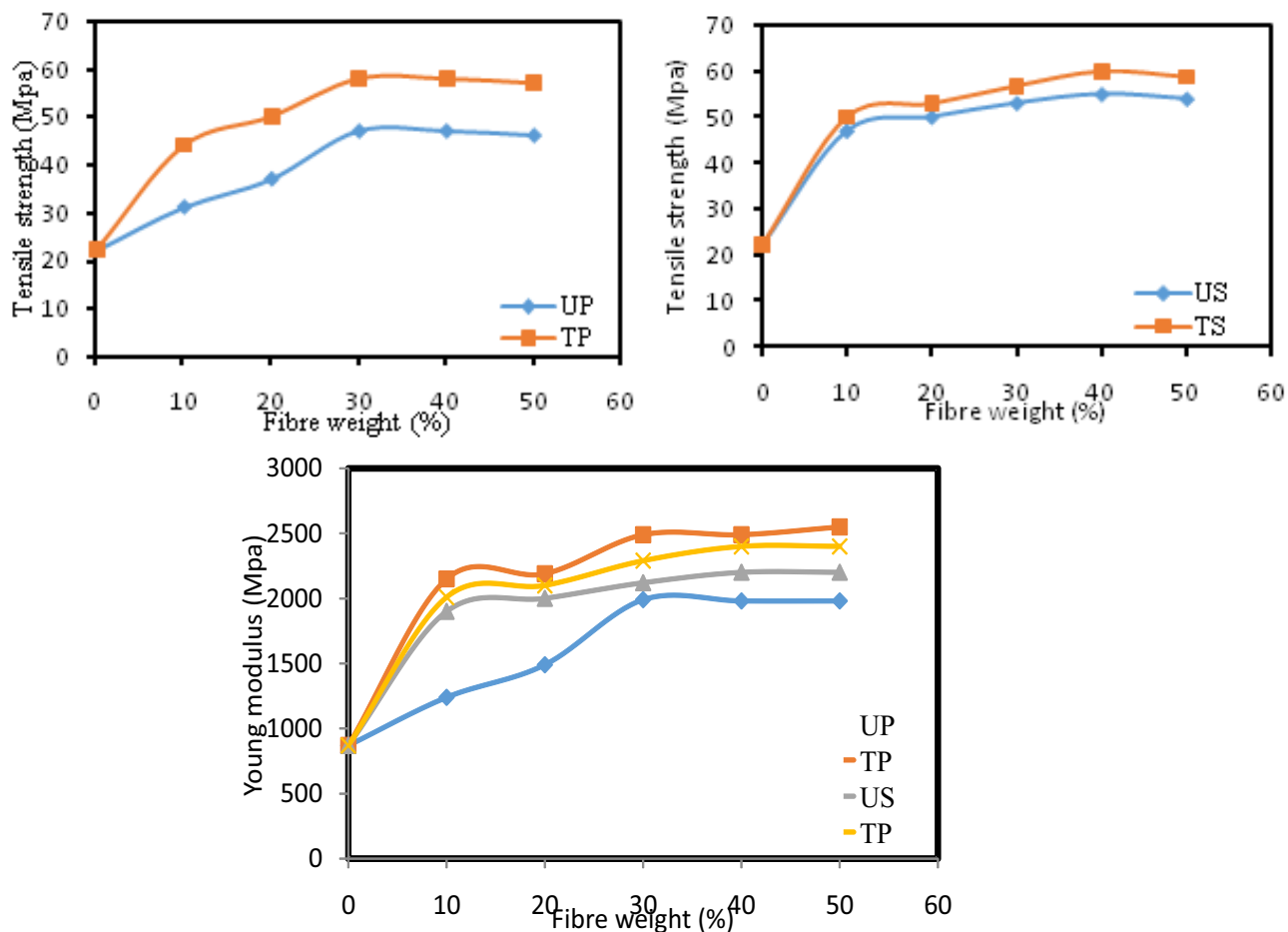


Figure 5: (a) Tensile strength plot for UPLF-P and TPLF-P (b) Tensile strength plot for ULSF-P and TLSF-P composites (c) Young modulus plots for UPLF-P, TPLF-P

3.4. Compressive test

The compressive strength of both untreated (UPLF-P, ULSF-P) and alkaline-treated (TPLF-P, TLSF-P) composites increased steadily with fibre content, reaching peak values at 30 wt% for UPLF-P and TPLF-P, and 40 wt% for ULSF-P and TLSF-P, as illustrated in Figure 6. Beyond the aforementioned benchmarks, the change in compressive strength was very marginal. Notably, the compressive strength of the TPLF-P varies from 28.05 to 38.21 MPa, while that of the TLSF-P varies from 30.24 MPa to 40.04 MPa. Daramola et al. (2017) observed that incorporating fibre into polyester enhances hardness up to 30 wt%, beyond which further fibre loading (40 wt%) leads to a decline in hardness. A similar trend was reported by Uzun et al. (2011), where high-density polyethylene composites reinforced with chicken feather and cow hair fibres exhibited reduced mechanical properties at higher fibre weight fractions.

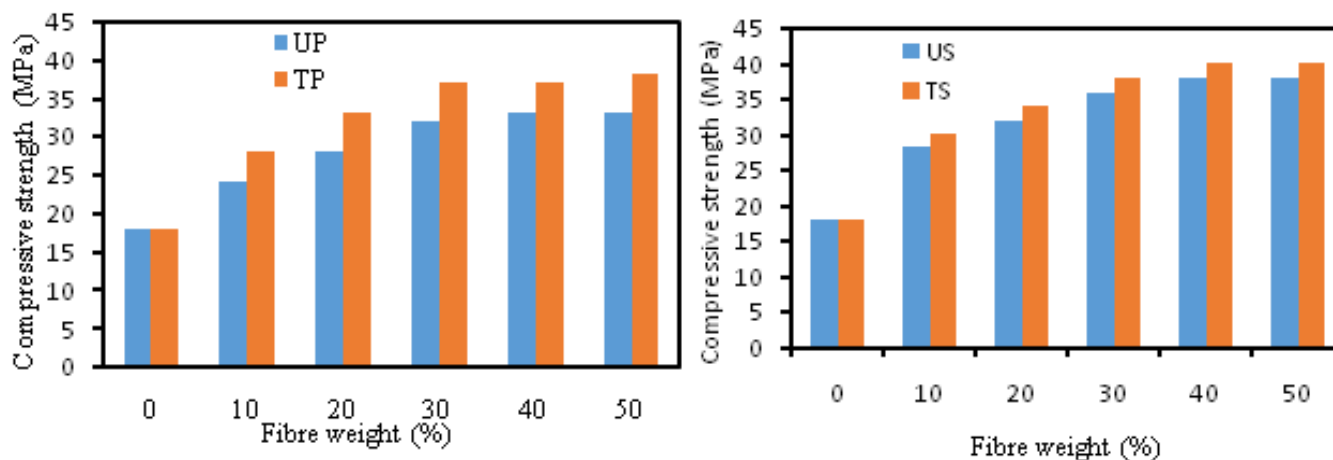


Figure 6: Plot of compressive strength for (a) UPLF-P and TPLF-P and (b) ULSF-P and TLSF-P composites

3.5. Analysis of the impact strength of the composites

This analysis indicates the overall material toughness and the results for untreated (UPLF-P₃₀ and ULSF-P₄₀) and alkali-treated (TPLF-P₃₀ and TLSF-P₄₀) pineapple and local sponge fibre polyethylene composites at optimum fibre loading are shown in Figure 7. Notably, the result for both composites increased as the fibre content increased until 30 wt% and 40 wt%, for PLF-P and LSF-P composites, respectively. Furthermore, the highest impact strength of 28.556 and 25.53 kJ/m² was respectively recorded for UPLF-P₃₀ and ULSF-P₄₀ composite. This value was subsequently reduced to 22.43 KJ/m² for TPLF-P₃₀ and 22.23 KJ/m² for TLSF-P₄₀ composite after alkali treatment. Beyond the respective optimum fibre loadings, there was a decrease of 21.46 % for the TPLF-P₄₀ composite and 16.24% for the TLSF-P₅₀ composite. The primary reason for this is that during impact, a significant portion of energy absorption occurs through the fibre pull-out process (Rahman et al., 2018). Notably, the post-alkali-treated fibre showed improved fibre - matrix binding, which is synonymous with reduced fibre pull-out. This development consequently results in a decrease in impact strength.

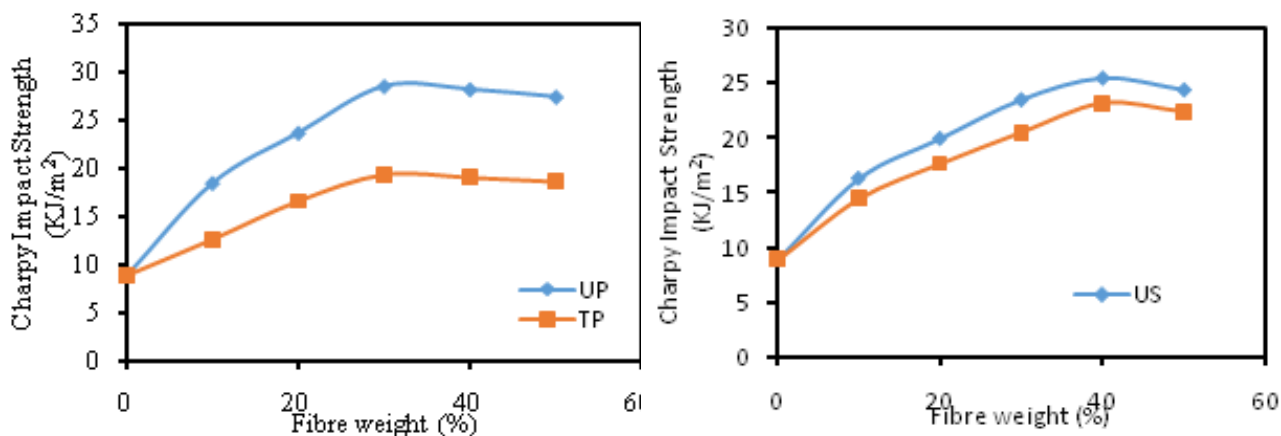


Figure 7: Plot of impact strength for (a) UPLF-P₃₀ and TPLF-P₃₀ and (b) ULSF-P₄₀ and TLSF-P₄₀ composites

3.6. Scanning electron microscopy (SEM)

The tensile failure of polyethylene composites reinforced with pineapple leaf fibre (PLF) and local sponge fibre (LSF), both untreated and alkaline-treated at their optimum fibre loading (UPLF-P₃₀, TPLF-P₃₀, ULSF-P₄₀, TLSF-P₄₀), is shown in Figures 8(a–d). For UPLF-P₃₀ (Figure 8a), the micrograph reveals a rough, non-uniform structure with visible voids and fibre pull-outs, indicating weak fibre/matrix adhesion. This is attributed to the hydrophilicity of PLF and the inability of the non-polar polyethylene to interact strongly with the unmodified fibre.

In contrast, TPLF-P₃₀ (Figure 8b) exhibits improved surface morphology with reduced voids and fewer fibre pull-outs. Alkaline treatment removes impurities and increases fibre roughness, enhancing wettability and interfacial bonding. This facilitates better load transfer between fibre and matrix, thereby improving tensile properties.

For ULSF-P₄₀ (Figure 8c), the SEM image shows a porous and rough surface with poor interfacial adhesion. The absence of chemical treatment leaves waxes, lignin, and other impurities on the fibre surface, hindering bonding with the matrix. Additionally, at 40 wt% fibre loading, fibre agglomeration occurs, creating stress concentration points and interfacial debonding under stress. These defects reduce both tensile and impact strength.

TLSF-P₄₀ (Figure 8d) presents a more compact, integrated morphology with fewer voids. Alkaline treatment eliminates non-cellulosic materials, improving adhesion. The reduced fibre pull-outs suggest stronger bonding and enhanced stress transfer, resulting in superior mechanical performance compared to the untreated counterpart.

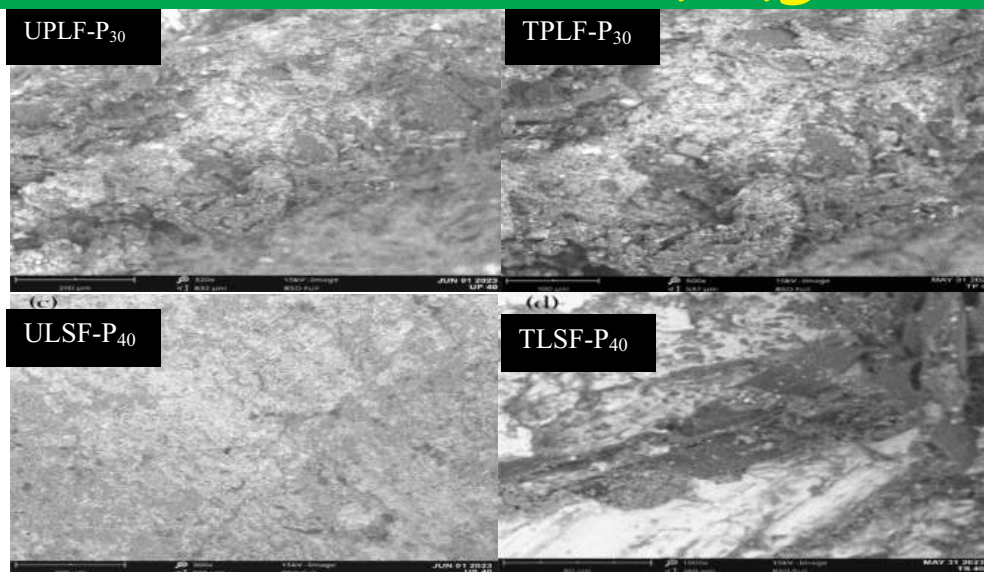


Figure 8: SEM result of the composite at optimum values (a) UPLF-P₃₀ (b) TPLF-P₃₀ (c) ULSF-P₄₀ (d) TLSF-P₄₀

3.7. Fourier transform infrared (FTIR) spectroscopic analyses

The Fourier transform infrared (FTIR) spectroscopy of polyethene composites reinforced with PLF and LSF, both in untreated and alkaline-treated states at their respective optimum fibre loading (UPLF-P₃₀, TPLF-P₃₀, ULSF-P₄₀ and TLSF-P₄₀), is presented in Figures 9 (a-d) and Table 2.

The FTIR analysis of untreated fibre composites (UPLF-P₃₀ and ULSF-P₄₀) in Figure 9(a & c) reveals characteristic peaks of lignocellulosic components. The broad hydroxyl (O-H) stretching peak at 3300 cm⁻¹ confirms the presence of cellulose and hemicellulose, while the 2900 cm⁻¹ peak indicates aliphatic C-H bonds in cellulose (Hashem et al., 2021). The carbonyl (C=O) stretch at 1800 - 1900 cm⁻¹ suggests hemicellulose and lignin content (Mohamed et al., 2021), and peaks between 1600-1500 cm⁻¹ correspond to aromatic C=C vibrations in lignin. The 1200-1000 cm⁻¹ region shows C-O-C stretching from cellulose and hemicellulose backbone structures (Vârban et al., 2021).

For alkali-treated composites (TPLF-P₃₀ and TLSF-P₄₀) in Figure 9 (b & d), spectral changes demonstrate successful fibre modification. The O-H peak becomes sharper and less intense, indicating hemicellulose removal and reduced hydroxyl groups. Similarly, the C-H

stretching persists at 2900 cm⁻¹, with a slightly altered intensity, a reflection of lignin dissolution. The diminished C=O peak (1800 - 1900 cm⁻¹) and reduced aromatic C=C vibrations (1600-1500 cm⁻¹) confirm substantial hemicellulose and lignin removal (Roman Maldonado et al., 2024). The retained but modified C-O-C peaks (1200-1000 cm⁻¹) verify cellulose preservation with structural alterations.

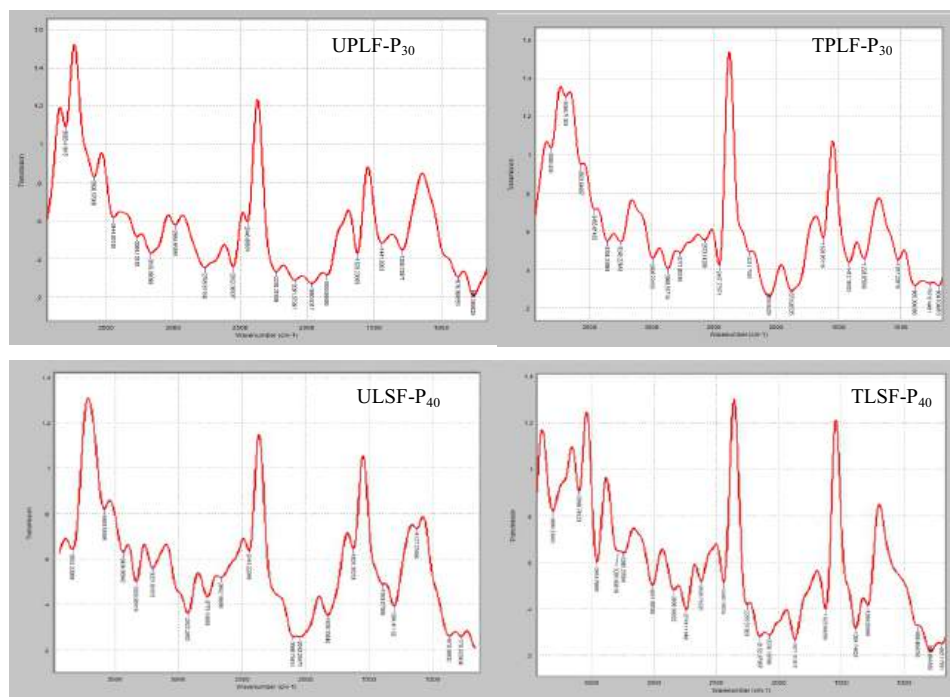


Figure 9: FTIR spectra of (a) UPLF-P₃₀ (b) TPLF-P₃₀ (c) ULSF-P₄₀ (d) TLSF-P₄₀ at composite at optimum values

Table 2: The recorded wavenumbers and transmittance for the optimal composite samples

UPLF-P ₃₀		TPLF-P ₃₀		ULSF-P ₄₀		TLSF-P ₄₀	
W (cm ⁻¹)	T(-)	W (cm ⁻¹)	T(-)	W (cm ⁻¹)	T(-)	W (cm ⁻¹)	T(-)
3803	1.1	3808	1.03	3832	0.63	3809	0.82
3590	0.82	3688	1.33	3583	0.82	3598	0.96
3444	0.61	3563	0.97	3434	0.63	3454	0.6
3269	0.51	3455	0.74	3329	0.5	3285	0.65
3165	0.43	3354	0.57	3201	0.57	3240	0.64
2984	0.58	3248	0.56	2925	0.37	3011	0.52
2765	0.36	2990	0.44	2773	0.42	2838	0.5
2552	0.34	2868	0.40	2663	0.56	2741	0.399
2446	0.60	2771	0.50	2445	0.63	2620	0.54
2230	0.35	2573	0.57	2090	0.24	2440	0.56
2091	0.30	2457	0.42	2042	0.24	2255	0.42
1965	0.28	2211	0.5	1828	0.26	2152	0.28
1850	0.32	2056	0.28	1625	0.66	2076	0.29
1625	0.43	1873	0.3	1393	0.49	1871	0.28
1441	0.48	1620	0.38	1304	0.399	1625	0.4
1289	0.44	1412	0.425	1127	0.765	1384	0.3
-	-	-	-	870	0.245	1289	0.41
-	-	-	-	776	0.243	888	0.34



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3.8 Comparison of functional properties of the developed composite with a synthetic counterpart

The comparative analysis of the functional properties of alkaline-treated pineapple leaf fibre (TPLF-P₃₀) and alkaline-treated local sponge fibre (TLSF-P₄₀) reinforced polyethene composites against the E-glass reinforced LDPE composite (Table 3) reveals notable differences in their mechanical and physical characteristics. In terms of density, moisture regain, and mechanical strength, the E-glass LDPE composite exhibits superior performance compared to TLSF-P₄₀ and TPLF-P₃₀. Although the synthetic fibre (E-glass) reinforced LDPE composite demonstrates higher mechanical properties than its natural fibre counterparts, there is a close correlation between their functional properties.

Given the similarities in performance, natural fibre-reinforced composites can be adopted in place of synthetic composites. They offer advantages in terms of bulkiness and eco-friendliness, as they are lighter than the E-glass LDPE composite, making them more suitable for applications in the manufacturing and packaging industries. Additionally, natural fibre-based composites are biodegradable and have lower production-related emissions compared to synthetic fibres, contributing to environmental sustainability. Furthermore, the production of natural fibres is labour-intensive, thus fostering job creation and supporting poverty alleviation programs. The cost of producing synthetic fibers is significantly higher than that of natural fibres, making natural fibre-reinforced composites a more economical option. As a result, these composites are gaining prominence as a sustainable and cost-effective trend in material science and engineering.

Table 3: Comparative evaluation of the functional properties of the composite developed at optimum conditions with a synthetic composite

Properties	TPLF-P ₃₀	TLSF-P ₄₀	E-glass LDPE composite
Density (g/cm ³)	1.244	1.466	1.501
Moisture regain (%)	11.51	19.67	1.8
Tensile strength (MPa)	47.01	55.24	86.24
Young modulus (MPa)	1990.0	2200.0	2400.0
Compressive strength (MPa)	37.05	40.12	54
Impact strength (KJ/m ²)	22.43	22.23	25.01



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4. Conclusion

This study demonstrates that alkali treatment significantly enhances the performance of pineapple leaf fibre (PLF) and local sponge fibre (LSF) composites by improving their mechanical properties and resistance to water absorption. The treatment effectively reduces moisture absorption while optimizing fibre-matrix adhesion, as evidenced by mechanical testing and SEM analysis. Although a slight reduction in impact strength was observed, the overall improvements in tensile and compressive strength, coupled with reduced hydrophilicity, make the composites reinforced with treated fibre highly suitable for varied applications. The removal of non-cellulosic components through alkali treatment creates a cleaner fibre surface that promotes stronger interfacial bonding with the polymer matrix. These findings highlight the crucial role of fibre modification in developing sustainable, high-performance biocomposites that can compete with conventional materials in industries requiring durable and environmentally friendly solutions. Ultimately, this research provides valuable insights for advancing natural fibre composite technology toward more practical and wide-ranging industrial applications.



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Kinetics and Thermodynamics Evaluation of Activated *Mucuna Pruriens* Seed Shell Properties on Aqueous Chlorpyrifos

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Abstract

The excessive use of pesticides (chlorpyrifos) in modern agriculture has increased the level of chlorpyrifos (CLPF) residues in water. Hence, there is a need for imperative attention on alleviation of these negative impacts. Therefore, this study evaluated the likely use of *Mucuna Pruriens* seed shell (MPSS) as a bio-sorbent. MPSS was treated and activated by adding one mole of sulphuric acid (H_2SO_4) before it was characterized with analytical techniques using Fourier Transform infrared (FTIR), Scanning electron microscopy and Energy Dispersive X-ray (SEM-EDX), and Brunauer-Emmet-Teller (BET). The efficiency of MPSS with respect to CLPF adsorption under optimum conditions was observed. The best kinetic model and thermodynamic studies were studied. From the results obtained, the optimum sorption of CLPF onto MPSS was 94.43% at optimum condition: 30mg/l, pH 6, MPSS 0.5g/100ml. Pseudo-second order best described the kinetics study with $R^2(0.9987)$. Thermodynamic parameters ΔH° , ΔS° and ΔG° values at optimum temperature 40 °C obtained are -0.008 kJ/mol, -0.441 kJ/Kmol and +0.134 kJ/mol, respectively. The adsorption process was feasible and spontaneous in nature, with cation exchange between chlorpyrifos and *Mucuna* shell as the rate-limiting phase. Experimental results illustrate that the adsorption capacity increased with pH, adsorbent dosage and concentration. Conclusively, MPSS is an efficient adsorbent for removing chlorpyrifos.

Keywords: Chlorpyrifos, *Mucuna Pruriens* Seed Shell (MPSS), Adsorption, Thermodynamics

1.0 Introduction

Chlorpyrifos (O, O-diethyl-O-3,5,6-trichloro-2-pyridylphosphorothioate) ($C_9H_{11}Cl_3NO_3PS$) is an organophosphorus pesticide (OPP), colourless to white crystal solid, with mild mercaptan (thiol) odour, and having a similar smell with sulphur, is a widely used active insecticide that is effective by ingestion and contact (Zalat *et al.*, 2014).

Chlorpyrifos is usually mixed with oily liquid before being used in crops and animals, but it is more complicated when mixed with other pesticides, which may lead to serious toxic formulation (Iwuzor *et al.*, 2023). Today, chlorpyrifos has been reported to be used unchecked in excess all over the world, causing high contaminations of a lot of natural elements (Joshi *et al.*, 2023; Iwuzor *et al.*, 2023; Saloko *et al.*, 2012; Igwe *et al.*, 2018). For these reasons, research has been ongoing in order to provide a low-cost method to mitigate their side effects.

The treatment technologies that have been in use for a long time in the removal of pollutants in wastewater generally include photocatalytic methods, nano-filtration, membrane bioreactor and activated sludge. Although recent technologies are gaining more attention, such as biochar, microalgae, bioremediation, precipitation, ion exchange, chemical oxidation and adsorption methods and many more (Nitin *et al.*, 2023).



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The agricultural sources, residues, waste materials and by-products form abundant sources of sustainable adsorbents (Dai *et al.*, 2018). They are highly helpful over synthetic adsorbent, since they are abundantly available, economic, environmentally friendly, biodegradable and cost-effective (Kyzas and Kostoglou 2014; Omo-Okoro *et al.*, 2018). Among the most used biomass as adsorbents by many researchers are peels, husks, stocks, starch, fibre, leaves, corks, and shells, etc. They are naturally equipped with good adsorption potentials. This study helps to bridge the gap of exploring lower cost and available agricultural waste that are not commonly used by researchers for the conduct of agro-runoff wastewaters, such as velvet beans identified as *Mucuna Pruriens seed shell* (MPSS), that can easily be sourced locally.

Some related literatures review on the use of MPSS as an adsorbent and the use of agro-waste in the treatment of CLPF are as follow:

MPSS was reported to be a useful adsorbent for the adsorption of dyes by Igwegbe *et al.* (2016).

Suo *et al.* (2018) treated water polluted with chlorpyrifos using activated cellulose/graphene oxide, achieving a removal efficiency of 90.0% and their analysis indicated that the Langmuir isotherm model best represented the experimental results. Likewise, ul Haq *et al.* (2015) treated water polluted with chlorpyrifos using ZnO and NPs impregnated pea peels, achieving an appreciable amount of CLPF removal of 47.85 mg/g at 305.5 K and pH 2. Ghati (2017) reduced chlorpyrifos to an acceptable level using Barley husks at optimum pH 7.3, discovering that there was a high affinity between sorbate and sorbent in well-diluted solution.

Adsorption isotherms are vital for the description of how molecules or ions of adsorbate interact with adsorbent surface sites and are critical in optimizing the use of adsorbents (Igwe *et al.*, 2018). The successful representation of the constant change in adsorptive separation of solute from solution onto an adsorbent hinge on a good description of the equilibrium separation sandwiched between the two phases (Igwe *et al.*, 2018).

Kinetics study is also important for designing sorption systems since rapid kinetics mostly facilitate smaller reactors because of the lower retention time for effective adsorbate uptake, whereas a slow rate of uptake necessitates long columns or series of columns to utilize maximum potential of the biosorbent (Igwe *et al.*, 2018).

Hence, in this study, the results of activation of the adsorbents and the adsorption of chlorpyrifos onto MPSS are reported. The effect of adsorption contact time, adsorbent dosage, temperature, initial concentration of pesticide and pH was investigated. An adsorption isotherm study was carried out. The kinetics of adsorbate sorption were also used to determine the uptake capacity of the sorbent, the rate of uptake of the adsorbate by the MPSS. The thermodynamics study was also carried out from the results obtained.

2.0 Materials and Methods

2.1 Materials and Chemicals Used

High-grade Chlorpyrifos (pesticide) powder, HCl, NaOH, H₃PO₄, distilled water, filter paper and a pH 7 capsule were purchased from a standard substance vendor at Onitsha head bridge in Anambra state, Nigeria. The adsorbent (Velvet beans seed) with botanical name *Mucuna pruriens seed*, locally known as (*Okobo*), was purchased from the new market in Enugu state, Nigeria. Figures 1(a and b) showed *Mucuna pruriens* seed and *Mucuna pruriens* seed shell, respectively.



Fig.1a: *Mucuna pruriens* seed



Fig.1 b: *Mucuna pruriens* seed shell

2.2 Preparation of Adsorbent

The sample of *Mucuna pruriens* shells was collected and separated from the seed, washed thoroughly, sundried for 5 hours before being milled with a silver crest Sc -1588 5000W blender. The ground sample was sieved to get the desired particle size (450 μm) and carbonized in a muffle furnace at (350 $^{\circ}\text{C}$) for 1 hour before activating with one mole of orthophosphoric acid (H_3PO_4). The impregnation ratio, which is referred to as chemical activation, was used in the ratio of 2:1, which is the mass of activation agent divided by amount of adsorbent (Obiora - Okafo and Onukwuli., 2013). The impregnation (IR) is calculated thus as shown in “Eq. (1)”,

$$IR = \frac{V_{\text{H}_3\text{PO}_4}}{V_{\text{mpss}}} \quad (1)$$

The impregnated sample was stirred at 600 rpm for 60 min and then allowed for 24 hours. After that, the stirring was repeated before filtering (Uchechuku *et al.*, 2015; Tchatchounang *et al.*, 2022). The activated sample was carefully washed with distilled water till the desired pH between 6.76-7.0 was obtained, then the sample was dried in a Memmert Oven (Din 400050-Ip20) at a moderate temperature of 50 $^{\circ}\text{C}$ for 30 minutes and then stored in a polythene bag for further use (Igwegbe *et al.*, 2016).

2.3 Preparation of Chlorpyrifos

The adsorbate (CLPF) was simulated by dissolving 1g of CLPF powder in 1000ml of distilled water, the mixture was stirred vigorously for about 3 hours, then kept for 24 hours to ensure proper dissolution, after which the mixture is stirred properly till a homogeneous solution is formed. Hence different concentrations were prepared from the stock solutions of 1000mg/l, to obtain initial concentration (10, 20, 30, 40, 50 and 60) mg/l, by measure out various aliquots (10, 20, 30, 40, 50 and 60) cm^3 into 1000 cm^3 beakers and made up to the mark of 1000 cm^3 volume with distilled water (Uchechuku *et al.*, 2015). These concentrations are higher than the maximum allowable limit (MRL) of 0.03mg/l for chlorpyrifos according to (Arain *et al.*, 2018). Hence, there is a need for treatment of the contaminated water before discharge into the environment.

2.4 Physicochemical and Instrumental Characterization of the Adsorbent

Physicochemical properties describe the suitability of an adsorbent for an adsorption process according to (Igwegbe *et al.*, 2016; Evwierhoma *et al.*, 2018). The physicochemical samples characterized in this analysis are moisture content, ash content, bulk density, pH, and surface area using BET and the reference methods, is as shown in Table 1 (Evwierhoma *et al.*, 2018, Mayakaduwa *et al.*, 2015).



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Table 1: Physicochemical Characterization

Samples	Reference method
Moisture content (%)	Igwegbe <i>et al.</i> , 2016
Ash content (%)	Verla <i>et al.</i> , 2012
Bulk density (g/cm ²)	Igwegbe <i>et al.</i> , 2016
pH	Madu and Lajide, 2013, Idriset <i>al.</i> , (2011)
BET Surface area (m ² g ⁻¹)	Mayakaduwa <i>et al.</i> , 2015

2.4.2 Instrumental Characterization

SEM is the technique used to investigate the shape and the surface texture morphology of *MPSS* which promotes binding Yuan *et al.*, (2022): EDX plot on the other hand is a plot done before adsorption that display the elemental composition of *MPSS* such as; carbon, oxygen and then followed by calcium as the major elemental constituents, identified by the sharpness of their peaks: FTIR analysis also was used to examine the surface functional groups of the adsorbent (*MPSS*) and to identify those groups such as OH, C-C, O=C=O, Si-O-Si which are responsible for CLPF adsorption: BET is used for analysis of surface area adsorbent (Mayakaduwa *et al.*, 2015). In this study, the BET model version (Asap 2021 v4.02 (V4.02 H)) was used to analyse and determine *MPSS* surface area.

2.5 Experimental Procedure

Activated *Mucuna pruriens seed shell* was used as an adsorbent for treating CLPF-contaminated wastewater solution. 250 mL beakers containing 100ml of 30mg/l CLPF concentration in five different ranges with *MPSS* (0.5g) dose were set at different temperatures of 27±1°C, 30°C, 35°C, 40°C, and 45°C on hot plates with magnetic stirrers. The beakers containing the solute and the solvent were stirred using a magnetic stirrer at a speed of 100 rpm for 50 min. At the end of each set time, 10ml solution is withdrawn and filtered using Whatman filter paper. The filtered samples (treated) were placed one after another in a UV spectrophotometer (model ASUV-6300PC) and the reading was taken from the absorbance-concentration profile. This was done after taking the reading of the untreated solute sample, which was set at wavelength $\lambda_{\max} = 505$ nm according to (Joshi *et al.*, 2023). The effects of pH, adsorbent dosage, solute concentration, time, and temperature were studied using a batch adsorption process with one-factor-at-a-time (OFAT) technique (Igwegbe *et al.*, 2016; Igwe *et al.*, 2018). For each run, 100ml of prepared pesticide key sample at pH 6 was treated with 0.5 g of adsorbents (*MPSSAC*) at temperature 27 ±1°C for a specific time interval between 10 to 50min placed on the magnetic hot plate agitated/stirred with magnetic stirrer at the speed of 100 rpm, at end of each time interval, about 5ml sample is withdrawn, filtered and the filtrate analysed subsequently for residual CLPF concentration willpower by means of UV/Visible spectrophotometer model ASUV-6300PC, then the amount (q_t) adsorbed per unit mass of adsorbents at the time (t) and the percentage removal of chlorpyrifos is determined using the following Eq. “(2)” and “(3)” according to (Tchatchouang *et al.*, 2022):

$$Q_t \left(\frac{mg}{g} \right) = \frac{C_0 - C_t}{MAC} \times V_s \quad (2)$$

$$Re \% = \frac{C_0 - C_e}{C_0} \times 100 \quad (3)$$

where C_t , C_0 and C_e (mg/l) are the concentration at time 't', initial concentration and equilibrium concentration, respectively, V_s is the volume of the solute, and MAC is the mass of the adsorbent (Joshi *et al.*, 2023). Furthermore, the tentative adsorption data were modelled using the dedicated equations presented in Tables 2, 3 and 4 (Igwegbe *et al.*, 2016; Mayakaduwa *et al.*, 2015).

Table 2: Adsorption kinetics models applied (Mahmood *et al.*, 2022).

Kinetic mode	Linear Equations	Plots Made	Equation No.
PFO	$\ln(q_e - q_t) = \ln q_e - K_1 t$	$(q_e - q_t) \text{ vs } t$	(9)
PSO	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$	$\frac{1}{q_t} \text{ vs } t$	(10)
IPD	$q_t = k_{id} t^{1/2} + 1$	$q_t \text{ vs } t^{1/2}$	(11)
Elvoch	$q_t = E_0 + E_1 \ln(t)$	$q_t \text{ vs } \ln t$	(12)

Where, q_e is Quantity of Glyphosate/chlorpyrifos rejected at Equilibrium, q_t is Quantity of Glyphosate/chlorpyrifos rejected at time (t), k_1 -pseudo first order constant, k_2 -pseudo second order constant, k_{id} -intraparticle model constant, E_0 and E_1 are Elovich constants.

Table 3: Thermodynamic Equations applied in this study

Thermodynamic mode	Linear Equation	Plot made	Equation No.
Thermodynamics	$\ln K_{eq} = \frac{\Delta S_0}{R} - \frac{\Delta H_0}{R} \times \frac{1}{T}$	in K_{eq} vs $1/T$	(13)

Where 'T' is temperature, K_{eq} - thermodynamic constant

3.0 Results and Discussion

3.1 The Physiochemical Properties of the Adsorbent

The result of the physicochemical properties of *Mucuna pruriens seed shell* is shown in Table 4:

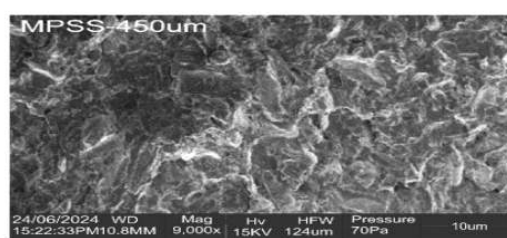
Table 4: Physiochemical properties of *Mucuna pruriens seed shell*

Samples	MPSS
pH	6.7
Surface area	770.550
Moisture content %	4.0
Ash content %	5.6
Bulk density g/cm ²	0.61

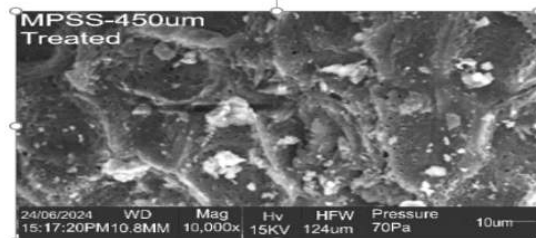
3.2 Instrumental Characterization Result

3.2.1 SEM characterization of MPSS before and after treatment of CLPF

The shape and the surface texture morphology of *Mucuna pruriens seed shell* were investigated by the SEM technique for MPSS before the adsorption of CLPF, is as shown in Plate 1: (a), (b) and (c). There are pronounced features of an irregular, rough surface with substantial layers of rough heterogeneous pores, cavities and saddles, which are favourable properties that increased the adsorption of chlorpyrifos. Igwegbe *et al.*, (2016), obtained similar results.



(a) Before adsorption with 10 μ



(b) After adsorption with 10 μ

Plates 1 a and b: Shape and the surface texture morphology of *Mucuna pruriens* seed shell(10 μ m) obtained before adsorption(a) and after adsorption (b).

3.2.2 Fourier transform infrared spectroscopy (FTIR) analysis result

The FTIR plots of %Transmittance vs wave number for MPSS before activation are presented in Fig. 2. Peak 3419.00cm⁻¹ showed the presence of a strong, broad O–H stretch and H–bond signifying the presence of alcohol and phenol, C=C 1636.47cm⁻¹ stretching in alkenyl, medium C–H 1466.81cm⁻¹ bend in alkane, medium bonded C–N 1103.00 stretching in aliphatic amines, medium C–Br 1028.00cm⁻¹ stretching in alkyl halide.

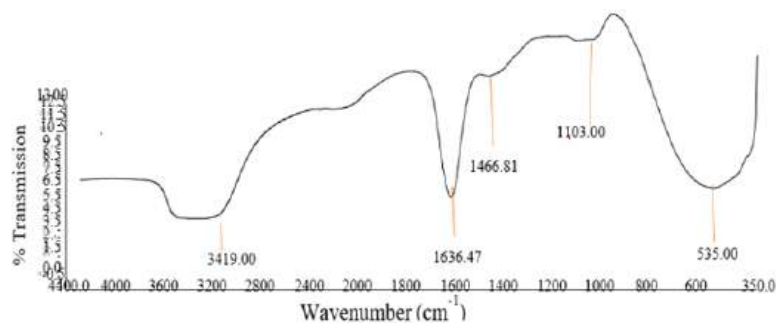


Fig.2: FTIR plots of MPSS %Transmittance vs wave number before activation

The FTIR plots of %Transmittance vs wavenumber for MPSS after activation as presented in Fig. 3. showed strong peaks at 3690.76cm⁻¹ due to O–H stretching of particle water and ROH at 2930.12cm⁻¹ due to C–H stretching, 2372.33cm⁻¹ C–C stretching in nitriles, 1934cm⁻¹ due to C=C=C stretching, 1826.60cm⁻¹ due to C=O carboxylic acid anhydrides, 759.00cm⁻¹ due to C–H strong aromatics and C–X (haloalkanes) stretching of 686.69 cm⁻¹, 545.00cm⁻¹ and 460.29 cm⁻¹. Kamala *et al.* (2013) obtained similar results to this. Thus, the FTIR spectra show that the surface of MPSS after activation was rich in hydroxyl and carboxylic groups, which act as proton donors to bind the ions along with the other medium and weak functional groups participating in the adsorption process (Saga and Isra'a, 2021).

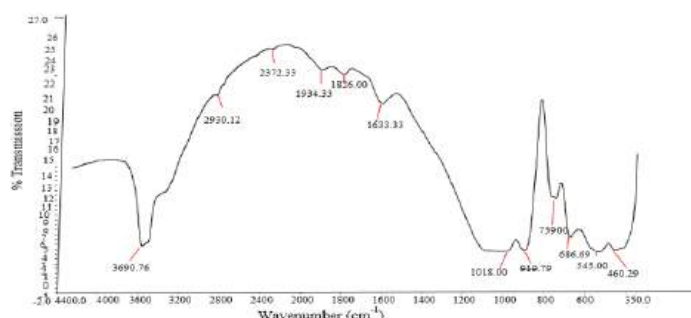


Fig.3: FTIR plot of percentage transmittance of MPSS against wavenumber(cm⁻¹) after activation



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3.2.3 The BET analysis result

The results of the surface of the BET surface area before treatment and after are: $770.550 + 3.2220 \text{ m}^2/\text{g}$, and $965.450 + 5.2220 \text{ m}^2/\text{g}$, respectively. This indicates that after activation of *MPSS*, more and larger pores are created, hence, a specific surface area, the adsorption cumulative surface area of pores was between 15,000A and 30,000.00 and width: $52.330 \text{ m}^2/\text{g}$, with total pore volume of $0.584000 \text{ cm}^3/\text{g}$, and adsorption average pore width of 27.4400 nm. These results implied that the *MPSS* composite has a high relative capacity and can accommodate the adsorbed CLPF molecules (Aniagor and Menkiti, 2024). Langmuir correlation coefficient (R^2) of the sorbent was dictated by the BET analysis to be 0.9996000, which agreed with the experimental Langmuir correlation coefficient $R^2 = 0.9995$. Joshi *et al.* (2023) obtained similar results with Langmuir giving the highest R^2 value above 90% although the value is less than what was obtained in this study with some fractions.

3.3 Batch Adsorption Capacity

3.3.1 Effect of pH and adsorbent dose on adsorption capacity

The pH of CLPF was adjusted with either 0.1 M NaOH or 0.1 M HCl, and a pH value range of 2 to 10 was obtained, and each sample labelled and placed in a series of 250 ml beakers (Joshi *et al.*, 2023). The investigation was carried out on 30 mg/l CLPF concentration with 0.5 g *MPSS* at room temperature $27 \pm 1^\circ\text{C}$, for a time interval of 10 to 50 min, at the end of each set time, about 5 ml of the filtrate is measured out, and the absorbance is checked in the UV-spectrophotometer. The quantity adsorbed is determined from the calibration curve. The maximum removal of CLPF occurred at optimum pH 6, where 94.23% was obtained within the first 20 min into the process, as shown in Fig. 4. It was observed that above this pH, percentage removal decreased, the reason could be because chlorpyrifos ions become more negatively charged, resulting in a reduction of adsorption due to repulsion between the anionic ion and the surface layer.

The optimum dose of an adsorbent is a very important factor in an adsorption study since it defines the adsorption capacity of an adsorbent in each initial concentration (Cara and Jitareanu, 2015). The effects of adsorbent dose on the adsorption of CLPF onto *MPSS* were investigated under controlled conditions, room temperature $27 \pm 1^\circ\text{C}$, adsorbate concentration 30 mg/l, pH 6. The experiment was done altering the adsorbent dose from (0.3 to 0.7 g) at different time interval range (10-50 min), the rate of sorption is recorded and the graph of percentage removal against dosage is used to explain the impact of dosage variation as shown in Fig.5. The adsorption percentage increased rapidly as the adsorbent dose was greater than before to 0.5 g where maximum removal was achieved to be 93% before it dropped. The increase in percentage removal is because an increase in adsorbent dosage increases the number of active sites available for adsorption (Suo et al., 2019b).

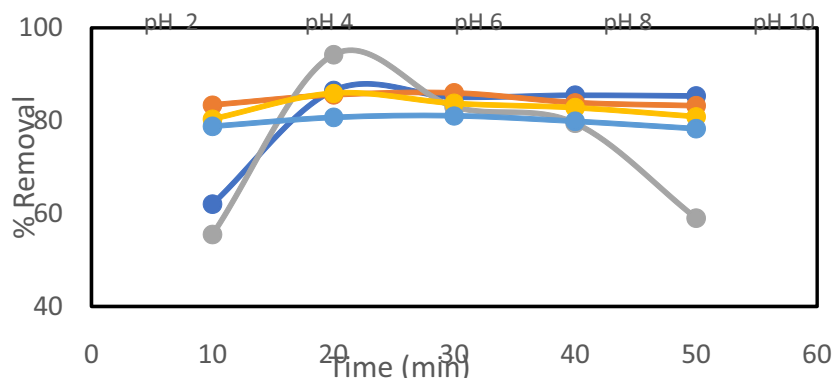


Fig. 4: Effect of pH variation vs contact time on the treatment of CLPF onto MPSS

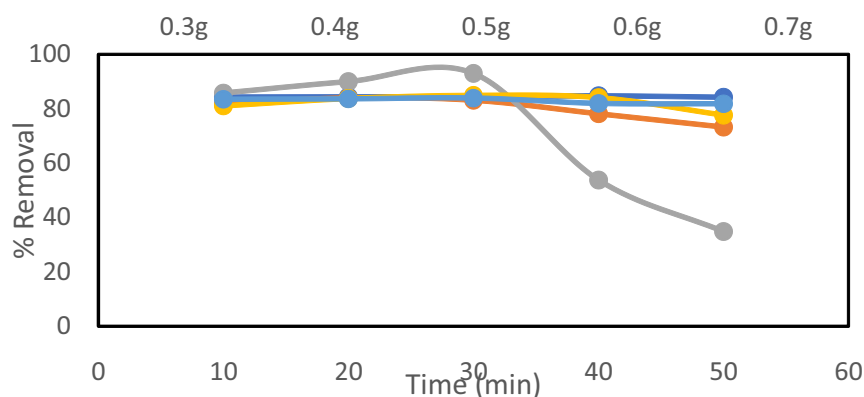


Fig. 5: Effect of MPSS dosage on treatment of CLPF

3.3.2 Effect of concentration and time on adsorption capacity

The nature of the adsorption of chlorpyrifos on the adsorbent is illustrated in Fig. 6. As the initial concentration and time changes, readings were taken, and the percentage removal is plotted against time. It could be seen from the graph that the percentage removal of CLPF decreased as the initial concentration was increased, but greater than before, as time increased, with the highest percentage removal above 95% realized within the first 30 min of agitation. Rissoulli *et al.* (2017) obtained similar results with the decontamination of water polluted with pesticides using biopolymers. The decrease in percentage removal could be explained on the basis that the sorption sites were already saturated, leaving little or no available sites to accommodate more sorbate molecules. This also suggests that for a greater proportion of removal to be realized within the same period, the sorbent dose may be increased. Joshi *et al.* (2023) reported that the amount adsorbed augmented with increasing sorbate concentration for the adsorption of chlorpyrifos onto boiler fly ash and maize and Igwe *et al.* (2018) reported that the concentration gradient between adsorbate (chlorpyrifos) onto lemon peel in solution (bioadsorbent) surface decreases as time passes. The Temperature variation effect was also studied with temperature variations of 27 ± 1 , 30, 35, 40 and 45°C under a controlled environment. The percentage yield of activated MPSS on CLPF at different temperatures is shown in Fig.7. As can be seen, maximum percentage removal of above 80% was realized at the room temperatures $27\pm 1^\circ\text{C}$ which decreased as the temperature increased from (30-45) $^\circ\text{C}$. Joshi *et al.* (2023) and Igwe *et al.* (2018) got similar results on the treatment of CLPF with lemon peel and fly ash, respectively.

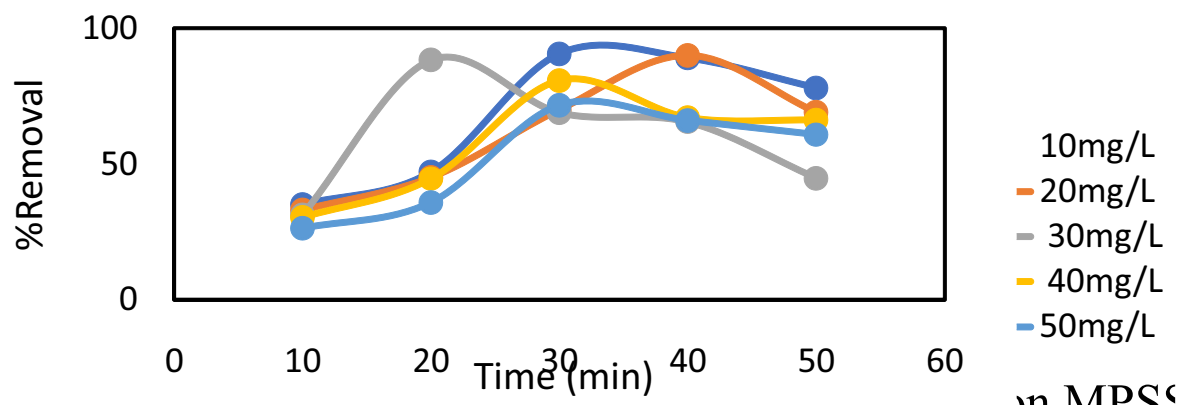


Fig.6: Effect of CLPF initial concentration on MPSS against time

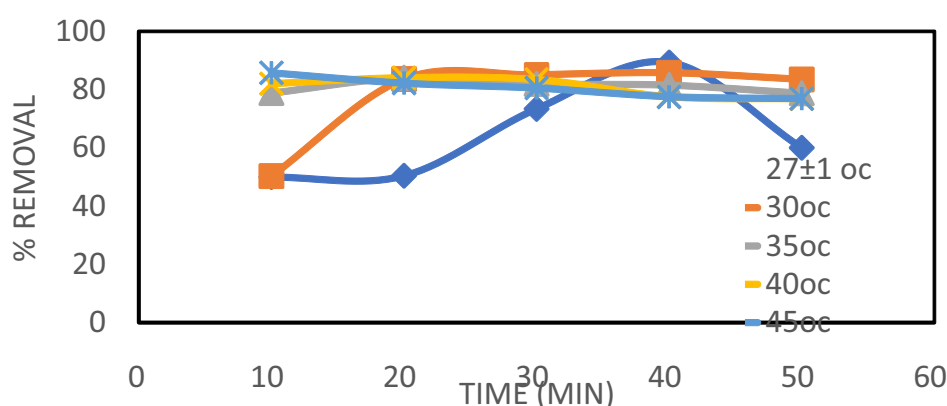


Fig. 7: Effect of chlorpyrifos temperature variation on MPSS

3.4 Adsorption Kinetic Studies of Chlorpyrifos on MPSS.

The kinetic data obtained from experimental results after treatment of 30 mg/l CLPF solution with 0.5 g MPSS at different contact time ranges (10-50) min and temperatures 30 °C, 35 °C, and, 40 °C were used to predict the behaviour of the adsorption process. Four different kinetic models were used to investigate the processes: First Order, PFO, PSO, Elovich and Intra-particle diffusion model. The kinetic parameters and coefficient (R^2) were lifted from the kinetic plots shown in Figs. (12 to 16) and the data listed in Table 5. The best fitted kinetic model is the pseudo-second order (PSO) with a correlation coefficient (R^2) above 97% at all the temperatures. Joshi et al. (2023) obtained similar results on the treatment of chlorpyrifos with lemon peel. The calculated q_e at the temperatures of 30, 35 and 40 °C were 5.8139mg/g, 4.6129mg/g and 4.6904 mg/g, respectively. They were all close to the tentative data in the PSO model, thereby validating the model. Hence, the PSO model is the best fit kinetics that describes the kinetic behaviour more accurately than the other four models. It was also observed that the increase in rate *was* stable in all the models, including the PSO model, was not consistent, instead of increasing with respect to temperature increase, most of them decreased as the temperature increased beyond the previous level. This could be because the kinetic complexity of CLPF molecules with the MPSS ions in the aqueous phase got distorted by temperature increase, thereby reversing rapidly the entire process. The electrostatic attraction between the ions and the neutral molecules became inert as the temperature exceeds 30 °C. Hence, room temperature could be recommended for most favourable result in this process.

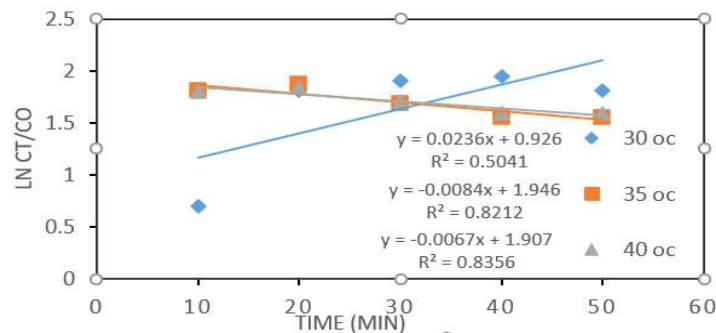


Fig. 8: First Order kinetic plot for the adsorption of CLPF onto *MPSS*

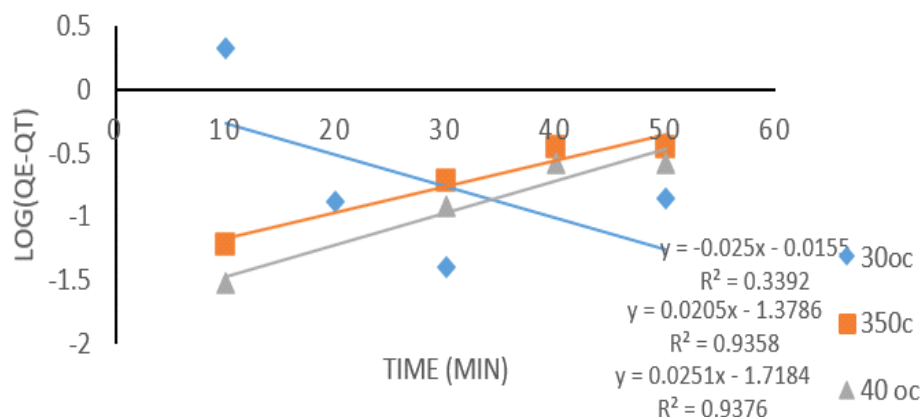


Fig. 9: Pseudo-first order kinetic plot for the adsorption of CLPF onto *MPSS*

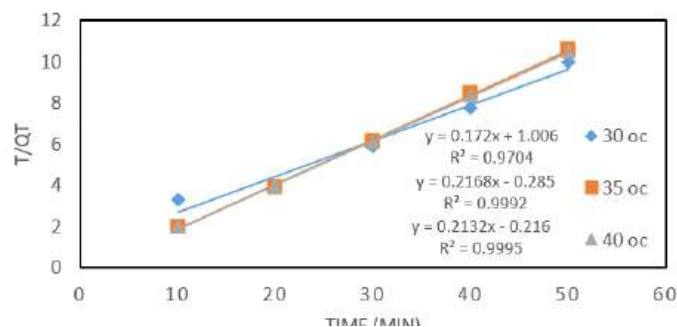


Fig. 10: Pseudo-second order kinetic plot for the adsorption of CLPF onto *MPSS*

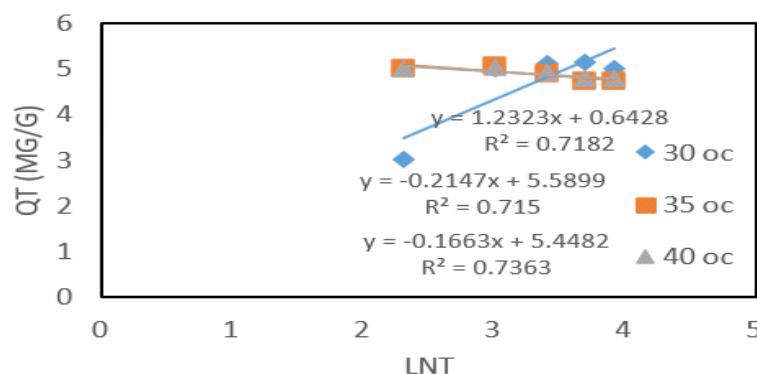


Fig. 11: Pseudo -second order kinetic plot for the adsorption of CLPF onto *MPSS*

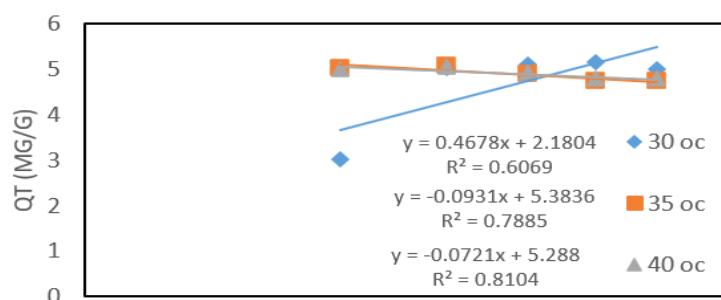


Fig. 12: Intraparticle kinetic order plot for the adsorption of CLPF onto *MPSS*

Table 3: Adsorption kinetics of CLPF onto *MPSS*

Kinetic Model	Temperature		
	303 k	313 k	323 k
First order			
K_1 (min^{-1})	0.0236	0.0084	-0.0067
R^2	0.5042	0.8212	0.8356
Pseudo-first Order			
K_1 (min^{-1})	0.253×10^{-2}	-0.732×10^{-2}	-2.303×10^{-4}
q_e (mg/g)	1.644	0.0202	30.123
R^2	0.6889	0.8424	0.3119
Pseudo-second Order			
K_1 (g/mg/min)	0.9940	-3.5088	-4.6298
q_e (mg/g)	+5.8169	+4.6125	+4.6904
R^2	0.9704	0.9992	0.9995
Elovich			
K_1	+0.8115	-4.6577	-6.0132
Intercept	0.6428	5.5899	5.4482
R^2	0.7182	0.715	0.7363
Intra-particle and film diffusion			
K_{pi} ($\text{mg g}^{-1} \text{min}^{-1}$)	-0.086	-0.4892	-0.0777
C_i	+2.098	+4.5169	+2.0461
R^2	0.0804	0.8539	0.2876

3.5 Thermodynamics Study

Thermodynamic studies carried out in this study disclosed the relationship, in the form of heat, because of the energy of interaction between *MPSS* and the CLPF (Iwuozor *et al.*, 2023). At equilibrium, the Van't Hoff reaction isotherm equation tallies with the free energy (ΔG), standard free energy change (ΔG°), and the equilibrium constant (K) at room temperature (T) using Equation (14) (Aniagor and Menkiti, 2024).

$$\Delta G = \Delta G^\circ + RT \ln K_e \quad (14)$$

When ΔG become zero, then Eq. (14) changes to Eq. (15)

$$\Delta G^\circ = -RT \ln K_e \quad (15)$$

Predicting the standard enthalpy change (ΔH°) and standard entropy change (ΔS°), Eq.14 is rearranged into Eq. (15).

$$\ln K_e = -\frac{\Delta G^\circ}{RT} = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (16)$$

The thermodynamic parameters of the adsorption process were calculated using the experimental data at various temperatures (303K, 308K, and 313K). The plot of the thermodynamic study is shown in Fig. 13. The values of ΔG° (standard free energy change) calculated were found to be positive for the adsorption of CLPF onto *MPSS*. The positive value indicates that the adsorption is not spontaneous in nature. The values of ΔG° for CLPF on *MPSS* indicates that it is an ion–dipole and dipole–dipole interaction. The values of ΔH° as shown in Table 6 were negative for the adsorption of CLPF onto *MPSS*, which indicates that the process is exothermic and that adsorption activity took place naturally. Joshi *et al.* (2023) obtained a parallel result. The negative value of ΔS° shows decreasing randomness at the adsorption interface. The low enthalpy of the adsorption of chlorpyrifos on *MPSS* indicates a physisorption process.

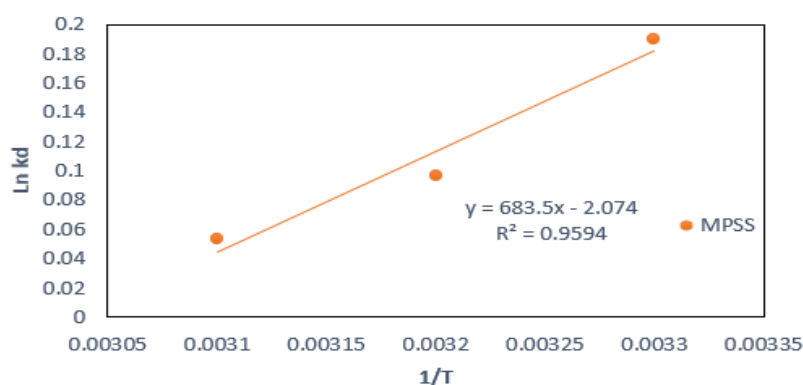


Fig. 13: Thermodynamic plot for CLPF on *MPSS*

Table 4: Thermodynamic parameters for CLPF on *MPSS*

Temp. (k)	ΔG°	ΔH°	ΔS°
303	+0.130	-5.683	-17.243
308	+5.305		
313	+5.391		

Conclusion

From this study, it can be concluded that the activated *MPSS* was successfully utilized to remove Chlorpyrifos from aqueous solution to an appreciable level. Hence, it could be recommended as a good adsorbent for agro-runoff treatment. The percentage adsorbed increased with an increase in pH, adsorbent dose, and initial concentration but decreased with an increase in temperature. From the equilibrium kinetics, pseudo-second order described the sorption process best at all temperatures with R^2 values above 97 %.The sorption process was found to follow a physisorption mechanism, probably through hydrophobic pesticide-pesticide interactions.



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Natural Clay-Based Phillipsite Zeolite: Synthesis and Optimization Study

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Abstract

This study shows Phillipsite zeolite from Ahoko kaolin was synthesized and characterized using XRF, XRD, SEM, and FTIR. Optimization was done considering four factors: crystallization temperature, crystallization time, ageing time and alkaline molar composition. XRF of raw Ahoko kaolin shows a high SiO₂ concentration, which suggests a notable presence of quartz. The reduction in SiO₂ concentration after refinement shows the successful removal of quartz. The optimal sample B1 was synthesized at a crystallization temperature of 150°C, crystallization time of 24hrs, ageing time of 24hrs and 1.5M alkaline molar composition. XRD pattern of sample B1 shows typical of Phillipsite zeolite at 2θ = 9.8°, 16.2°, 21.6°, 27.3°, and 30.9°, having 89.1% crystallinity and crystallite size of 15nm. SEM image of sample B1 shows micrographs of twinned crystals, prismatic aggregates and spherical crystals with some rod-like features interspersed, having a particle size of 1.35 μm.

FTIR spectra of sample B1 show OH-stretch group (3609cm⁻¹ and 3288cm⁻¹), C-CH₂ alkyl chain (2067cm⁻¹), H-O-H (1636 cm⁻¹), asymmetric stretch Si-O-Al / Si-O-Si (1112cm⁻¹) and symmetric stretch T-O-T (723cm⁻¹). According to the findings, Phillipsite can adsorb nutrients like NH₄⁺, K⁺, and PO₄³⁻ and release them gradually because of its porous structure and ion-exchange ability.

Keywords: Phillipsite, Kaolin, Characterization, Optimization and Nutrient Release.

1. Introduction

The growing global population, projected to reach nearly 10 billion by 2050, has created an urgent need to significantly increase food production (Mondal *et al.*, 2021). With limited options to expand arable land, the only feasible solution is to enhance the productivity and efficiency of current agricultural practices (Cataldo *et al.*, 2021). High rates of nutrient input and efficient irrigation are essential for maximizing crop yields. However, if nutrients are rapidly introduced into the soil, a significant portion can be washed away, leading to water contamination and reduced yields (Soltys *et al.*, 2020).

Controlled-release fertilizers have been extensively studied as a promising approach to address the limitations of traditional synthetic fertilizers (Jakkula *et al.*, 2011). By regulating the rate or concentration at which nutrients are made available, controlled-release fertilizers can maintain the presence of essential plant nutrients, such as nitrogen, phosphorus, and potassium, in the soil for an extended period (Ferretti *et al.*, 2024).

Zeolites have been extensively studied for their ability to enhance agricultural efficiency. The exceptional chemical and physical characteristics of natural zeolites, such as their high cationic exchange capacity and strong affinity for ammonium and potassium ions, allow them to be utilized to optimize nitrogen use



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efficiency in agriculture (Bikkinina *et al.*, 2020). Kaolin, a naturally occurring clay mineral composed of aluminosilicates, has been widely investigated for its potential applications in agriculture due to its ample availability, low cost, and diverse properties (Manjaiah *et al.*, 2018).

Therefore, this study presents Phillipsite zeolite synthesized from Ahoko kaolin as a raw material for controlled nutrient release to ensure food sustainability. The structural and surface characteristics were examined by XRD, XRF, SEM, and FTIR to confirm its applicability in controlled nutrient release fertilizers to enhance sustainable food security.

2. Materials and Methods

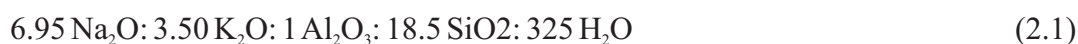
All the chemicals used in this research were of analytical grade with percentage purity in the range of 96 – 99.9%. Ahoko kaolin was sourced from Ahoko town, Kogi State, Nigeria. Deionized water used for this research was obtained from the Chemical Engineering Department Laboratory, Federal University of Technology, Minna, Niger State.

2.1 Preparation of Ahoko Kaolin

The starting material for the synthesis of Phillipsite zeolites was kaolin from Ahoko in Kogi State, Nigeria. The refinement process adhered to Kovo's (2010) methodology. After crushing 1000 g of Ahoko clay with a mortar and pestle, the kaolin was sieved through a 75 μm mesh. A 1000 cm^3 measuring cylinder was used to soak the screened mixture in deionized water in order to beneficiate it. In accordance with Kovo's (2010) methodology, deionized water was poured into the cylinder until it reached the 28 cm^3 mark after the kaolin had been filled to the 2 cm^3 mark. The mixture was then rapidly agitated. The particles settled in 4 minutes (Kovo, 2010). The cleaned clay was oven-dried for two days at 45 $^{\circ}\text{C}$ after the supernatant was decanted into a different container and allowed to settle (Kovo, 2010).

2.2 Synthesis of Phillipsite from Ahoko Kaolin

The synthesis of Phillipsite zeolite was conducted according to the approach of Salako (2021) with modifications. Alumina and silica were obtained from metakaolin, which was produced at 600 $^{\circ}\text{C}$ for three hours. The effects of ageing time, alkaline molar composition, crystallization time, and crystallization temperature were investigated. The molar composition of the reaction mixture was



To create the aluminosilicate gel, 3g of metakaolin was dissolved in 14.40 mL of deionized water with 1.39g of NaOH and varying KOH molarity (1.0–2.0 M) using 0.8g (1 M), 1.21g (1.5 M), and 1.62g (2 M) of KOH

pellets. The mixture was stirred for 0.5 hour at 150rpm and aged for 24–72hours under static conditions. Crystallization was carried out in a 100ml Teflon-lined stainless-steel autoclave at 100–150°C under autogenous pressure for 8–24 hours (Salako, 2021). The products were then cooled, filtered, rinsed with deionized water to pH 7, and dried at 80°C overnight.

2.3 Optimization of Synthesis Parameters

In the synthesis of Phillipsite zeolite, Surface Response Methodology (RSM) with definitive screening design was used to optimize the synthesis parameters, which included alkaline molar composition, ageing time, crystallization temperature, and crystallization time. This resulted in 13 experimental runs. The 13 runs generated through RSM were named Sample B1 to B13 respectively. The Zeolite was characterized using XRD, SEM and FTIR.

3.0 Results and Discussion

3.1 Characterization of Raw and Refined Kaolin

The raw Ahoko kaolin was characterized through XRF to show the elemental composition of the kaolin. After beneficiation of the raw kaolin, the refined kaolin was characterized using XRF. Table 1 shows the XRF of raw and refined Ahoko kaolin. The raw Ahoko kaolin contains a high SiO₂ concentration, which suggests a notable presence of quartz (Kovo,2010). The reduction in the percentage of SiO₂ and increase in Al₂O₃ show that a significant amount of free silica (quartz) has been removed from the raw material (Kovo, 2010). Due to the removal of quartz (SiO₂), the rise in Fe₂O₃, Na₂O, K₂O, MgO and LOI^a is mostly a relative enrichment impact. The aluminosilicate and accessory minerals that bind these oxides become proportionately more prevalent in processed kaolin (Kovo, 2010).

Table 1 XRF of raw and refined Ahoko kaolin

Chemical constituent	Weight % of Raw Kaolin	Weight % of Refined Kaolin
SiO ₂	72.455	54.039
Al ₂ O ₃	18.963	40.827
Na ₂ O	0.021	0.109
K ₂ O	0.431	0.537
Fe ₂ O ₃	1.0471	2.009
MgO	0.132	0.177
LOI ^a	6.170	2.07

3.2 Characterization of Phillipsite zeolite

The synthesized Phillipsite zeolite was characterized using XRD, SEM and FTIR. The XRD patterns acquired were analyzed via tools including OriginPro and X'pert High Score Plus, and compared with JCPDS reference card 96-9007471 for Phillipsite-Na to attain crystallinity. Scherrer's equation was used to calculate the crystallite size. SEM images were used to calculate the particle size of the crystals using ImageJ software and OriginPro. FTIR was used to identify the structural features of Phillipsite zeolite.

3.2.1 X-ray diffraction analysis

The XRD patterns of the synthesized Phillipsite zeolite samples B compared with JCPDS (Joint Committee on Powder Diffraction Standards) reference card 96-9007471 for Phillipsite-Na are in Figures 1 to 3. All synthesized samples have diffraction peaks in the range of $2\theta^\circ = 7^\circ$ to 35° , which is typical of the Phillipsite crystallographic planes (Salako, 2021). Sample B1 had the strongest and widest peaks in Figure 1, indicating multiple crystallographic domains and high crystallinity; samples B5 to B8 had sharper and more defined peaks from Figure 2, suggesting a more organized framework structure and enhanced crystallinity; and samples B9 to B13 had a sharp peak at $2\theta^\circ = 26.8^\circ$ in Figure 3, almost matching the reference pattern, but with fewer peaks than the standard. The successful synthesis of Phillipsite was confirmed by the overall close match between the reference peaks and the XRD patterns of B1 and B6. These findings were corroborated by crystallinity calculations, which showed that B1 was 89.1% and B6 was 93.1%. In accordance with B1, the reference pattern displayed prominent peaks at $2\theta^\circ = 9.8^\circ, 16.2^\circ, 21.6^\circ, 27.3^\circ$, and 30.9° . Crystallite sizes of 15 nm (B1) and 21 nm (B6) were determined using the Scherrer equation; a smaller crystallite size in B1 indicates a larger surface area.

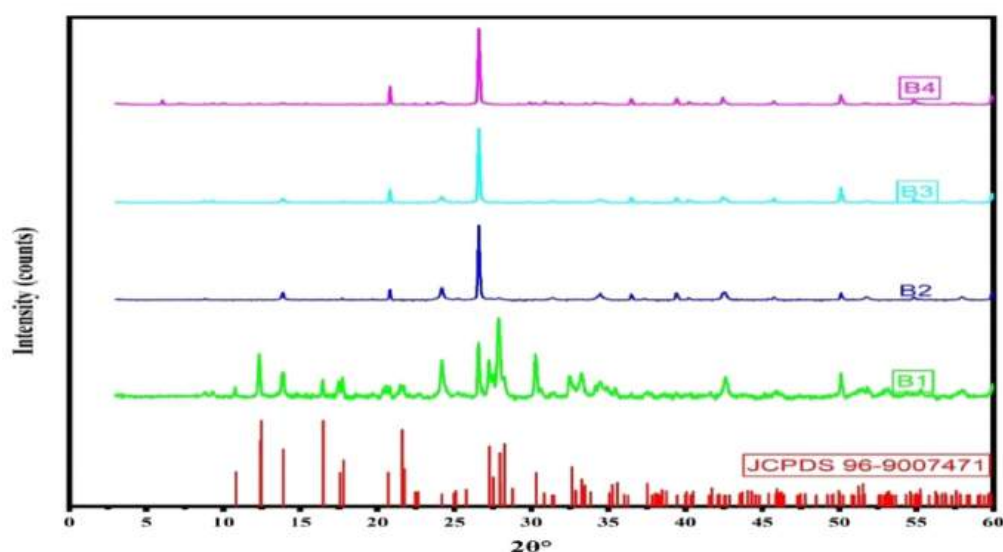


Fig 1 XRD Pattern of synthesized Phillipsite sample B1-B4 compared with JCPDS 96-9007471

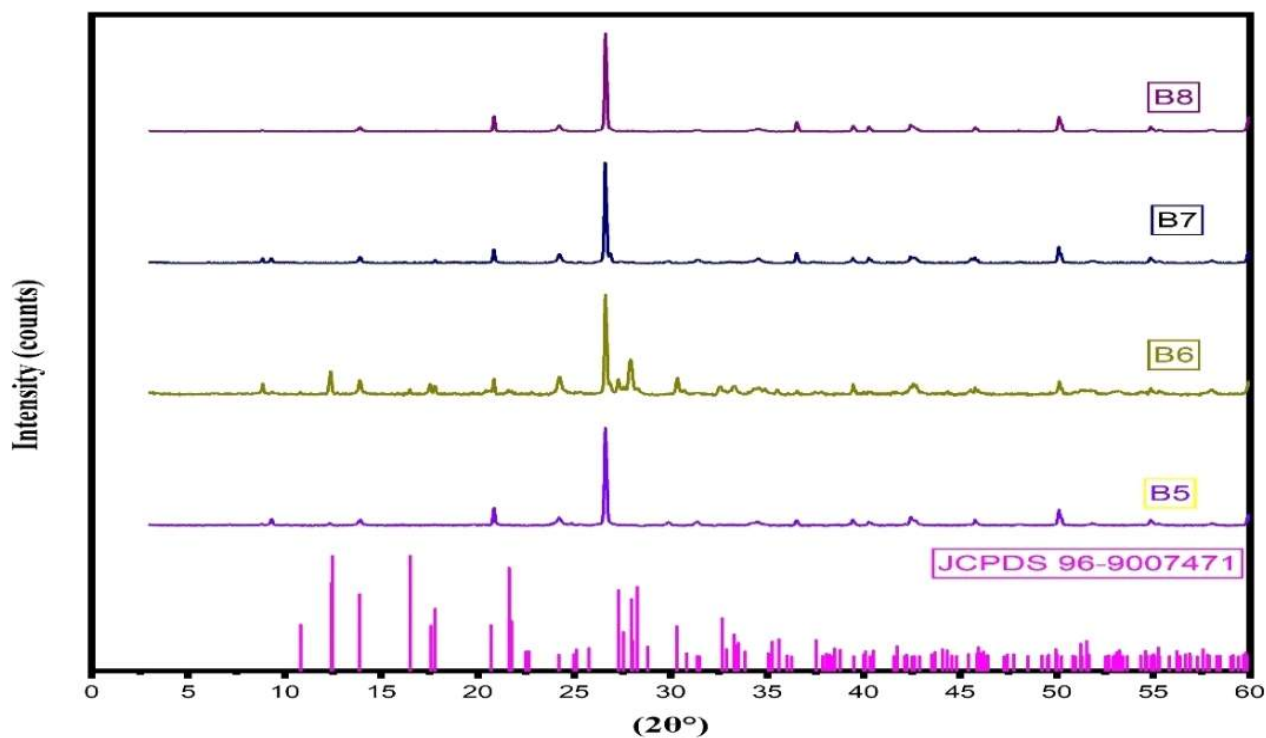


Fig 2 XRD pattern of synthesized Phillipsite samples B5-B8 compared with JCPDS 96-9007471

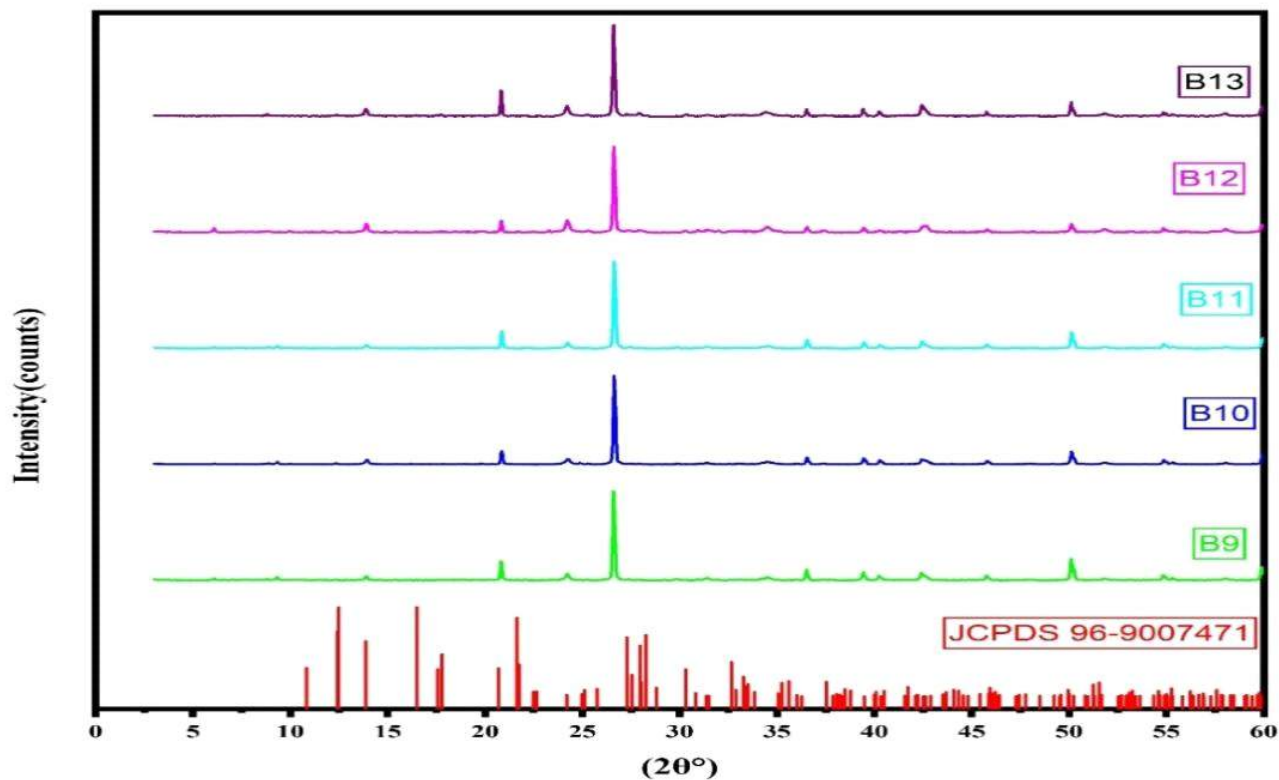


Fig 3 XRD pattern of synthesized Phillipsite samples B9-B13 compared with JCPDS 96-9007471



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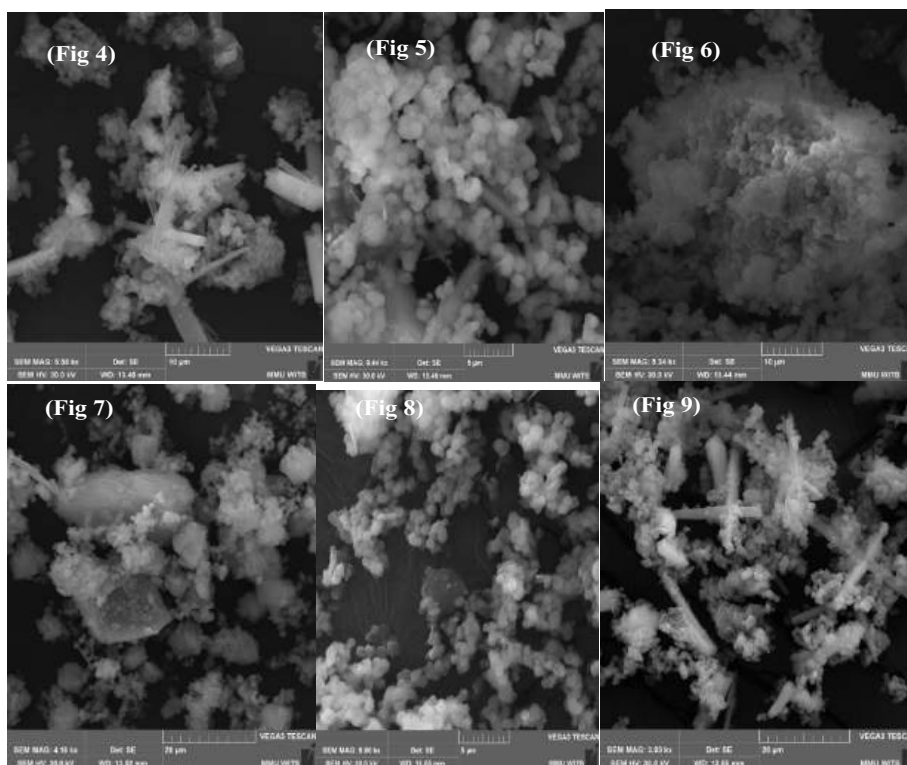
Table 2 shows detailed information about the synthesis of sample B.

Table 2 Synthesis of samples B for Phillipsitezeolite

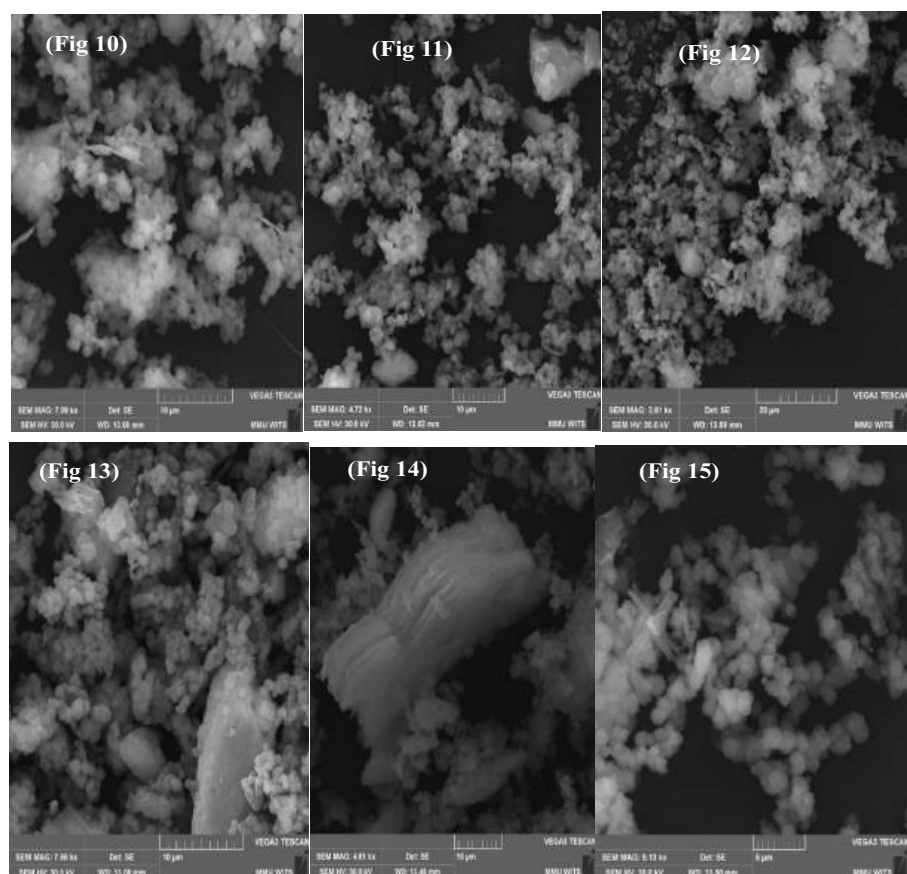
Sample Std Run	Crystallization Temperature	Crystallization Time (Hrs)	Aging Time (Hrs)	Alkaline (M)	Crystallinity Percentage (%)	Crystallite Size (nm)
B1	150	24	24	1.5	89.1	15.5
B2	150	8	48	2	65.2	30.8
B3	125	16	48	1	63.1	27.6
B4	100	16	72	1.5	51.3	28.1
B5	100	8	24	1	65.7	34.2
B6	150	16	24	1.5	93.1	21.3
B7	100	24	24	2	50.7	26.1
B8	125	8	24	2	50.2	34.1
B9	100	24	48	1	69.2	35.7
B10	100	8	72	2	39.4	30.0
B11	100	24	72	2	50.0	31.0
B12	125	24	72	1.5	61.5	30.9
B13	150	8	72	1	74.6	34.8

3.2.2 Scanning electron micrographs for synthesized phillipsite

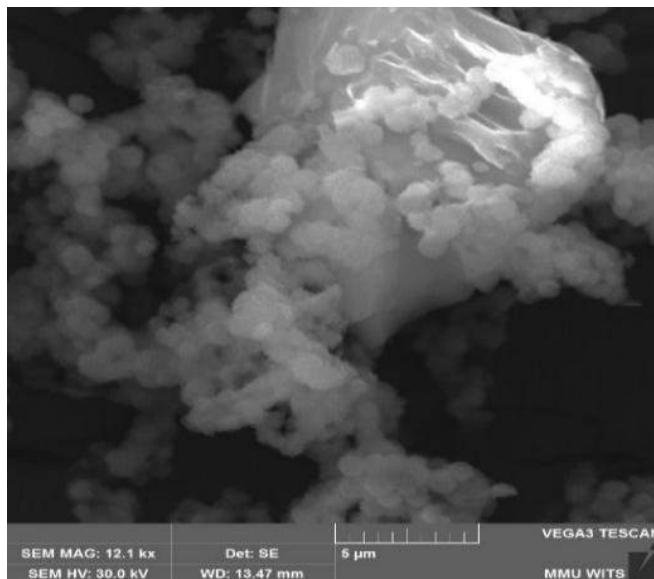
Micrographs of the crystals in the synthesized samples B of Phillipsite are presented in Figures 4 to 16. A report by Längauer *et al.* (2021) states that complex twinned crystals were seen in micrographs of the Phillipsite's crystal development, while smaller crystals typically display simpler shapes like fouling, prismatic, and spherical clusters of these forms. Salako (2021) reported crystals of Phillipsite exhibiting twinned crystals, aggregated and spherical crystals with some rod-like features or needle-shaped crystals interspersed, observed to have characteristics of 25 μ m long and 0.2 μ m thick and have length to width ratios of about 1.5 – 10. SEM image of sample B1 and B6 shows twinned crystals, prismatic aggregates and spherical crystals with some rod-like features or needle-shaped crystals interspersed. SEM image of sample B1 exhibits characteristics of length 16.07 μ m, width of 1.86 μ m, a length to width ratio of 8.6 and a particle size of 1.35 μ m. SEM image of sample B6 exhibits characteristics of length 18.03 μ m, width of 1.26 μ m, a length to width ratio of 14.3, and a particle size of 1.79 μ m. SEM image of samples B2 and B12 have some rod-like features or needle-shaped crystals interspersed with highly aggregated and spherical particles dominating the image, suggesting lower crystallinity. SEM image of samples B3, B5, B7, B8, and B9 exhibits densely packed, highly aggregated spherical crystals, which explain the XRD pattern's decreased crystallinity. SEM image of samples B4, B10, B11 and B13 exhibits a platy crystal, suggesting a layer-by-layer growth mechanism. SEM image of sample B1 and B6 shows the characteristics of Phillipsite, suggesting a high surface area, good channel accessibility and the high crystallinity from the XRD pattern (Salako, 2021).



SEM image of Fig 4, Fig 5, Fig 6, Fig 7, Fig 8 and Fig 9 corresponding for sample B1, B2, B3, B4, B5 and B6.



SEM image of Fig 10, Fig 11, Fig 12, Fig 13, Fig 14 and Fig 15 corresponding for sample B7, B8, B9, B10, B11, and B12.



SEM image of Fig 16 corresponding for sample B13.

Figure 17 below, shows the particle size distribution of sample B1. Sample B1's SEM-derived particle size distribution is unimodal and slightly right-skewed, with an average particle diameter of about 1.3 μm . Good homogeneity is shown by majority of particles falling between 1.0 and 1.5 μm .

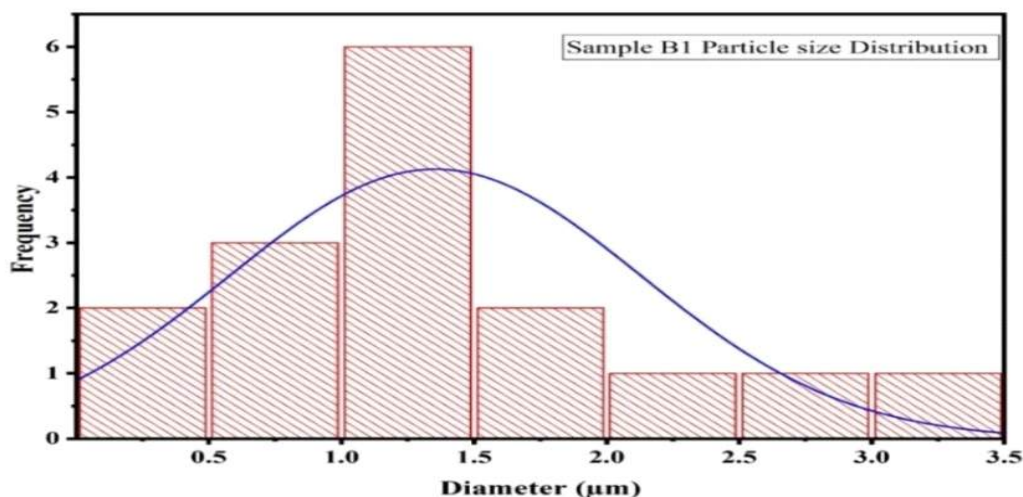


Fig. 17 Particle Size Distribution of Sample B1

3.2.3 FTIR of synthesized phillipsite

Phillipsite production was confirmed by the distinctive vibrational bands found in the FTIR spectra of sample B1 in Figure 18. Asymmetric Si–O–Al / Si–O–Si stretch was detected at 1112 cm^{-1} , symmetric T–O–T stretch at 723 cm^{-1} , O–H stretch at 3609 and 3288 cm^{-1} , C–CH alkyl chain at 2067 cm^{-1} , and H–O–H absorbed water at 1636 cm^{-1} for B1. These bands, in particular O–H stretching (3380 cm^{-1}), asymmetric tetrahedral stretching (950–1250 cm^{-1}), and OH bending (1240–1610 cm^{-1}), agree with values reported in the literature (Salako, 2021). All of the spectra together verify that Phillipsite was successfully synthesized. The XRD, SEM and FTIR of sample B1, conform more to Phillipsite, making

FTIR SPECTRUM OF SAMPLE B1 FOR PHILLIPSITE

Wave length (cm ⁻¹)	Peaks
3609	OH Stretch
3288	OH Stretch
2067	C-CH ₂ alkyl chain
1636	H-O-H adsorbed water
1112	Asymmetric stretch (Si-O-Al / Si-O-Si)
723	symmetric T-O-T

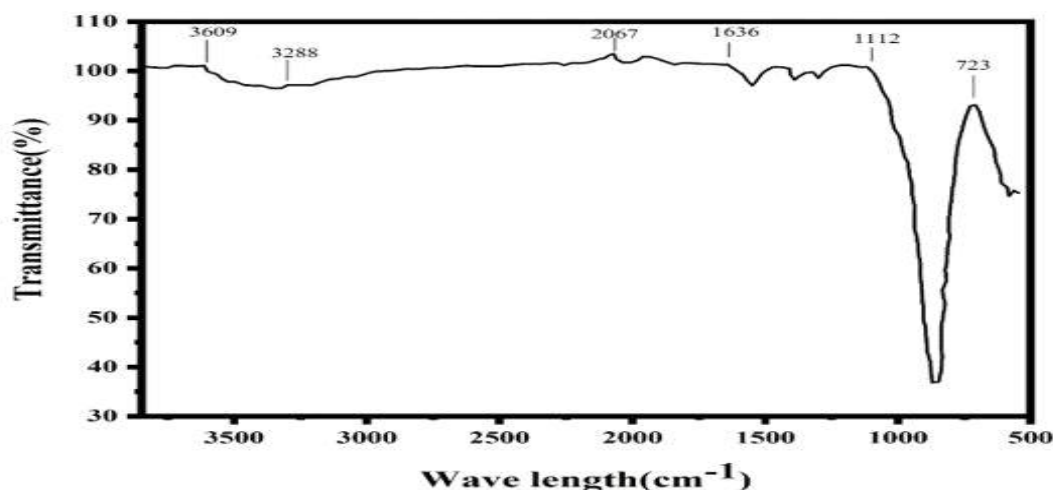


Fig 18 FTIR Spectrum of Sample B1 for Phillipsite

3.3 Optimization study of Phillipsite synthesis

3.3.1 Effect of interactive variables on phillipsite crystallinity percentage

Phillipsite's crystallinity is greatly increased by the interaction of crystallization temperature and time, as seen in Figure 19. Longer periods promoted structural ordering, while higher temperatures supplied more kinetic energy, encouraging nucleation and crystal development. At 150°C and 24 hours, their combined action increased crystal formation to 89.1% crystallinity.

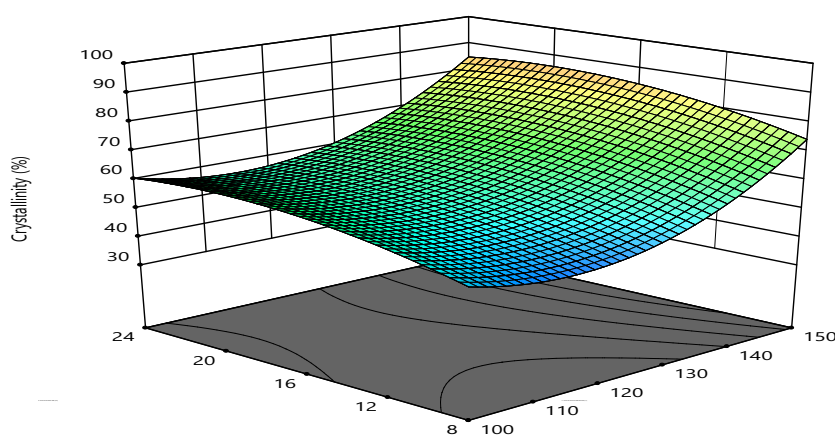


Fig 19 3D plot of interaction of crystallization time and crystallization temperature on percentage crystallinity of Phillipsite

The percentage crystallinity of Phillipsite increases with greater crystallization temperatures but decreases with long ageing times, as seen in Figure 20. Extended ageing (72 hours) decreased crystallinity to 74.6% even at 150°C. According to this inverse relationship, moderate ageing encourages crystal formation, whereas excessive ageing encourages phase change, dissolution, or disordering.

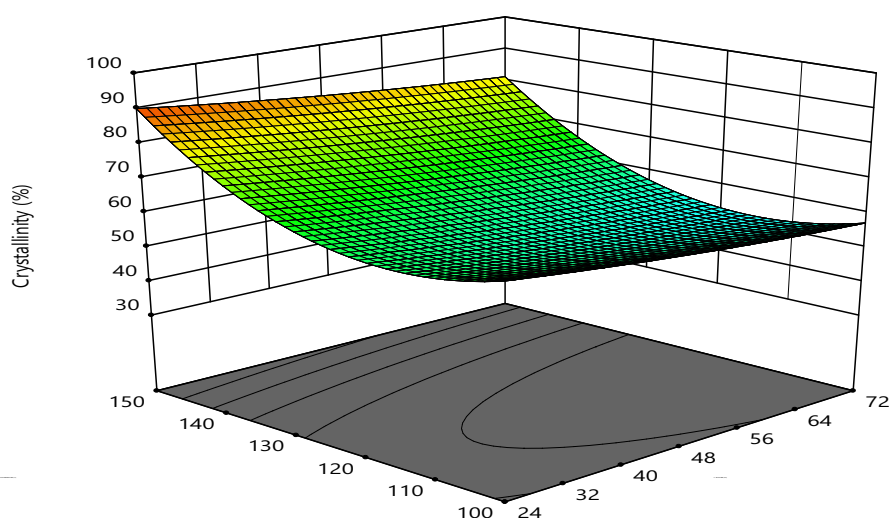


Fig 20 3D plot of interaction of crystallization temperature and aging time on percentage crystallinity of Phillipsite.

At high crystallization temperatures (up to 150°C) and moderate alkaline molar ratios (1.0–1.5M), Phillipsite crystallinity reaches 74–93.1%, as illustrated in Figure 21. Crystallinity, however, drops significantly (64–53%) at increased alkalinity (1.5–2.0M), even at higher temperatures. This implies that excessive alkali promotes amorphous or competing phases, which interfere with ordered crystal formation, whereas high temperatures and moderate alkalinity are ideal for high crystallinity.

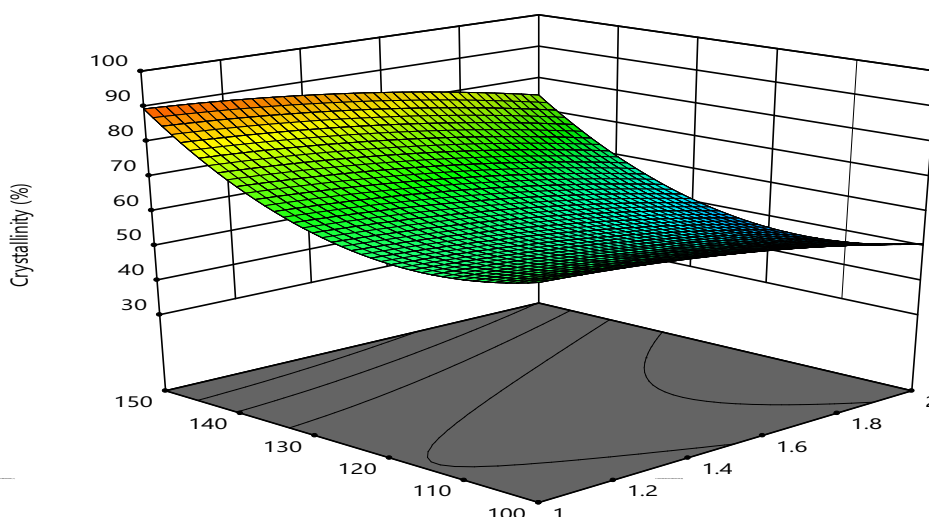


Fig 21 3D plot of interaction of crystallization temperature and alkaline molar composition on percentage crystallinity of Phillipsite

3.3.1.6 Response equation for phillipsite synthesis

The regression equation formulated for the crystallinity of Phillipsite is presented in

Equation 1. The response equation in terms of actual factors is given in Equation 1

$$\text{Crystallinity} = 327.908 - 5.08648A + 3.2283B - 0.341594C + 14.9471D + 0.0222646A^2 - 0.080229B^2 + 0.00166961C^2 - 9.81462D^2 \quad (1)$$

Where A = Crystallization temperature

B = Crystallization time

C = Aging time

D = Alkaline molar composition

4.3.1.7 Test for adequacy of model for phillipsite synthesis

The accuracy and statistical significance of the regression model were estimated using the analysis of variance (ANOVA) (Salako 2021), as shown in Table 3.

Table 3 ANOVA for response surface quadratic model of Phillipsite synthesis

Source	Sum of Squares	Df	Mean Square	F-value	p-value	Coefficient Estimate	Remark
Model	2759.26	8	344.91	46.80	0.0011	58.88	Significant
A- CRYSTALLIZATION TEMPERATURE	974.88	1	974.88	132.28	0.0003	11.99	
B- CRYSTALLIZATION TIME	229.79	1	229.79	31.18	0.0050	5.29	
C-AGING TIME	172.93	1	172.93	23.46	0.0084	-4.35	
D-ALKALINE MOLAR COMPOSITION	353.85	1	353.85	48.02	0.0023	-7.25	
	330.17	1	330.17	44.80	0.0026	13.92	
B ²	44.95	1	44.95	6.10	0.0690	-5.13	
C ²	1.16	1	1.16	0.1569	0.7122	0.9617	
D ²	7.09	1	7.09	0.9616	0.3823	-2.45	
Residual	29.48	4	7.37				
Cor Total	2788.74	12					



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The **Model F-value** of 46.80 implies the model was significant. **P-values** less than 0.0500 indicate model terms were significant. All four parameters are statistically significant ($p < 0.05$) and contribute considerably to the variation in crystallinity percentage. In this case, A, B, C, D, and A^2 were significant model terms.

Table 4 Statistical parameters for the percentage crystallinity of Phillipsite data analysis from model

Std. Dev	Mean	C.V. %	Predicted R^2	Adjusted R^2	R^2	Adeq Precision
2.71	63.02	4.31	0.8530	0.9683	0.9894	23.4481

The Standard deviation of 2.71 shows that there is little variation in the residuals, indicating that the model accurately predicts the actual data. The mean of 63.02 indicates the average percentage of expected crystallinity across experiments. The coefficient of variation (C.V.) of 4.31% indicates high model precision, and dependability is indicated by a low C.V. The **Predicted R^2** of 0.8530 is in reasonable agreement with the **Adjusted R^2** of 0.9683; i.e. the difference is less than 0.2. **Adeq Precision** measures the signal-to-noise ratio. A ratio greater than 4 is desirable. The ratio of 23.448 indicates an adequate signal. Fig 22 shows a linear relationship between the predicted and the actual, indicating that the values that were predicted were very close to the actual values.

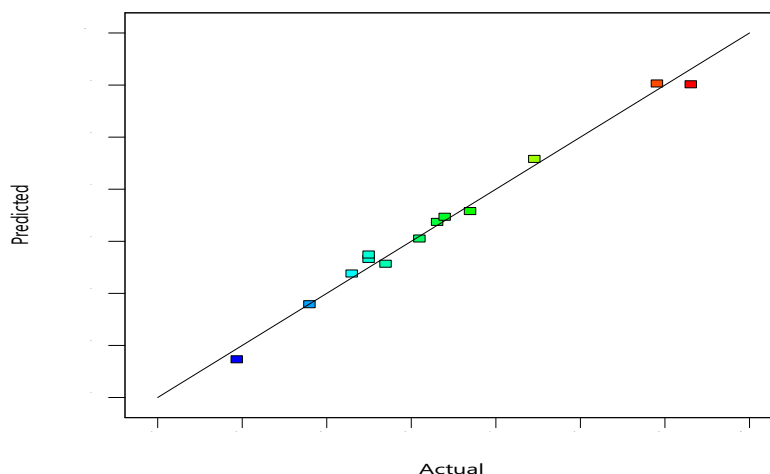


Fig 22 Graph of Predicted values to Actual values

5.0 Conclusion

The ion-exchange potential of Phillipsite from Ahoko kaolin was validated using FTIR, SEM, and XRD investigations. A highly crystalline aluminosilicate structure with negatively charged sites from Al^3 substitution that allowed for cation exchange was shown by XRD. Small crystallite sizes (15–21 nm) and porous shape were shown by SEM, offering a wide surface area and easily accessible exchange sites. The presence of hydrated exchangeable cations was indicated by FTIR, which verified T–O–T vibrations and hydroxyl groups. Phillipsite is suited for controlled-release fertilizers that improve nutrient efficiency and promote sustainable agriculture because of its structural characteristics, which enable it to adsorb and gradually release NH^+ , K^+ , and PO_4^{3-} .

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Diffusion of Dye-Antibiotic Mixtures Adsorption onto *Delonix regia* Pod Copolymeric Hydrogel: Mass Transfer Model Appraisal

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Abstract

The persistence of pharmaceuticals and synthetic dyes in aquatic environments poses critical risks to ecosystems and human health. Conventional treatment technologies are often inadequate for their removal, underscoring the need for sustainable, low-cost alternatives. In this study, a copolymeric hydrogel derived from Delonix regia Pods (DRP) was synthesized and applied for the adsorption of Dye-Antibiotic Mixtures (DAM) from aqueous solutions. Batch adsorption experiments were conducted under varying operational conditions, and the data were fitted to four mass transfer diffusion models: Weber-Morris, Matthew-Weber, Bangham, and McKay film diffusion. The Bangham model exhibited the best correlation ($R^2 \geq 0.95$), indicating pore diffusion as a dominant mechanism, while the McKay film diffusion model also provided an excellent fit ($R^2 \geq 0.94$), suggesting a strong contribution of surface diffusion. In contrast, the Weber-Morris and Matthew-Weber models displayed relatively lower agreement, confirming that intraparticle and external diffusion were not the sole rate-limiting steps. The DRP Copolymeric Hydrogel (DRPCH) demonstrated high adsorption capacities, with maximum removal efficiencies exceeding 95 % across different contaminants and concentrations. The diffusion modelling insights presented here are critical for optimizing adsorbent design, scaling up treatment processes, and advancing the circular bioeconomy in line with the United Nations Sustainable Development Goals.

Keywords: Adsorption, Antibiotic, *Delonix regia* Pod, Dye, Hydrogel

1. Introduction

Water quality is increasingly threatened by anthropogenic discharges, particularly pharmaceuticals and synthetic dyes, which are chemically stable, toxic, and environmentally persistent ([Askalany et al., 2020](#); [Wang et al., 2021](#)). Up to 90 % of antibiotics consumed by humans and livestock are excreted unmetabolized, while synthetic dyes remain resistant to biodegradation (Padder and Bashir, 2023). Their co-occurrence in wastewater creates synergistic risks for aquatic ecosystems and human health (Ferronato and Torretta, 2019). Current wastewater treatment processes rarely achieve complete removal, particularly in resource-limited regions, thereby undermining global water security goals (SDG 6).



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Adsorption has emerged as an effective treatment technology due to its operational simplicity, cost-effectiveness, and high removal efficiency (Babalola *et al.*, 2020). Although activated carbon remains the benchmark adsorbent, its cost restricts large-scale use. Agricultural residues have therefore attracted attention as renewable precursors for low-cost adsorbents (Dada *et al.*, 2020). *Delonix regia* pods, abundant but underutilized, can be valorized into copolymeric hydrogels with strong water affinity and adsorption potential.

Several studies, such as Abiodun *et al.* (2024), Amrutha *et al.* (2024) and Nandiyanto *et al.* (2024), have investigated adsorption kinetics and isotherms; however, limited attention has been paid to mass transfer diffusion modelling, which is essential for understanding rate-limiting steps and scaling up adsorption systems. In this study, the adsorption of dye-antibiotic mixtures onto *Delonix regia* pod copolymeric hydrogel was systematically evaluated through diffusion models, with emphasis on Weber-Morris, Matthew-Weber, Bangham and McKay film transfer mechanisms.

2. Materials and Methods

2.1 Synthesis of Copolymeric Hydrogels from *Delonix Regia* Pod

Delonix regia pods were collected in Ilorin, Nigeria, processed into fine powder, and graft-copolymerized with acrylic acid and acrylamide in the presence of ammonium persulfate (initiator) and N, N'-methylene-bis-acrylamide (crosslinker). The hydrogels were thoroughly washed to remove unreacted monomers and dried to constant mass.

2.2 Characterization of DRP Copolymeric Hydrogels

The synthesized DRP copolymeric hydrogels were crushed and dried at 60 °C for 12 h to remove residual moisture before water absorbency and water retention behaviour tests.

2.2.1 Water absorbency of hydrogels

The water absorbency of DRPCH was assessed by immersing 1.0 g of the dried hydrogel in 1.0 L of distilled water or a 100 mg/L dye solution at room temperature for 24 h. Samples were periodically weighed after blotting until no further weight change was observed, and the equilibrium swelling ratio was calculated as the absorbed mass at equilibrium relative to the initial dry mass Equation (1). (Zhu *et al.*, 2019; Tan *et al.*, 2022).

$$Q = \frac{W_{final} - W_{initial}}{W_{initial}} \quad (1)$$



where $W_{initial}$ and W_{final} are the weights of the swollen hydrogel before and after.

2.2.2 Water retention behaviour

The water retention behaviour of the hydrogels was evaluated at 80 °C using Equation (2). Pre-weighed swollen samples (w_{eq}) were dried in an oven, weighed at 1 h intervals (w_d), and the water retention percentage (w_r %) was calculated accordingly (Zhu *et al.*, 2019).

$$W_R \% = \frac{w_t - w_d}{w_{eq} - w_d} \quad (2)$$

where w_d is the dry weight of the hydrogel sample before swelling

2.3 Batch Adsorption

Batch adsorption experiments were performed by varying initial dye-antibiotic mixtures concentrations (20-100 mg/L), contact times (10-240 min), and adsorbent dosage (1.0 g), at room temperature.

Adsorbate concentrations were measured via UV-Vis spectrophotometry, and the adsorption capacity (q_e) and removal efficiency (R_e) were calculated using Equations (3) and (4) (Dada *et al.*, 2020; Galgano *et al.*, 2023).

$$q_e = \frac{V (C_o - C_e)}{m} \quad (3)$$

$$R_e = \frac{(C_o - C_e)}{C_o} \times 100 \quad (4)$$

2.4 Mass Transfer Diffusion Models

The adsorption data were modelled using Weber-Morris (intraparticle diffusion), Matthew-Weber (external mass transfer), Bangham (pore diffusion), and McKay film diffusion (surface diffusion) Equations (5-8). Model constants and correlation coefficients (R^2) were determined from corresponding plots (Ajani *et al.*, 2022; Alade *et al.*, 2024).

$$q_t = k_{wm} t^{0.5} + C \quad (5)$$

$$\log \frac{C_t}{C_o} = - \frac{K_m A}{2,303} t \quad (6)$$

$$\log (\log) \frac{C_o}{C_o - C_t \cdot m} = \theta \log t + \log \frac{k_b \cdot m}{2.303 \cdot V} \quad (7)$$

$$\ln (1-F) = - k_m t \quad (8)$$

where k_{wm} (mg/gmin^{0.5}) is the intraparticle diffusion rate constant and C (mg/g) is proportional to the boundary layer thickness. where C_t and C_o are the adsorbate concentration at time t and the initial solute concentration (mg/g), k_m is the external mass transfer coefficient (m/h), A is the external surface per unit mass (m²/g), C_t and C_o are the adsorbate concentration at time t and the initial solute concentration (mg/g), V is the volume of the liquid phase, m is the weight of adsorbent per liter of solution g/l, k_b and $\theta < 1$ are constants,

k_m is the diffusion rate constant; F is the adsorption capacity and is obtained as $\frac{q_t}{q_e}$, q_t is the adsorption capacity at each time and q_e is the adsorption capacity at equilibrium.

3. Results and Discussion

3.1 Hydrogel Swelling and Retention Behaviour

The DRPCH exhibited high water absorbency, reaching equilibrium swelling of 288 % in water and 235 % in dye solution, with 80 % of uptake occurring within 2 h, as shown in Figure 1. The hydrogel retained water for up to 7 h, confirming its porous, stable network and suitability for aqueous adsorption applications. The rate at which a polymer expands or swells depends on two coupled processes, the relative rates of polymer-chain relaxation and water penetration into the network. Swelling equilibrium is reached when these two forces are equal (Tan *et al.*, 2022).

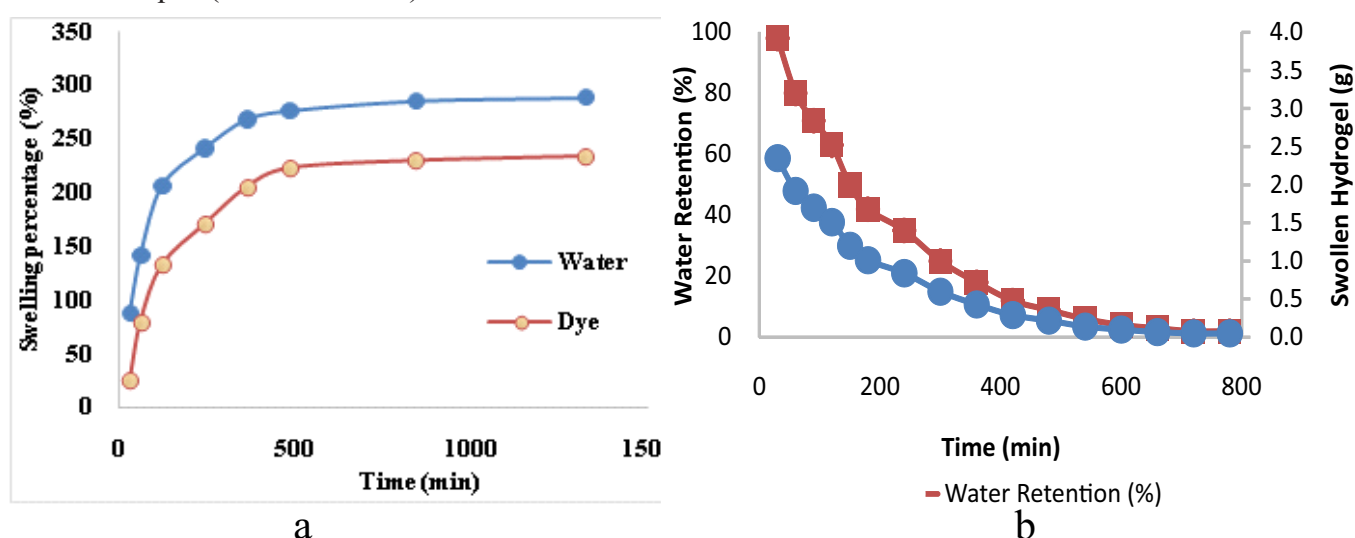


Fig. 1: (a) Water absorbency behavior and (b) Water retention capacity of DRPCH.

3.2 Adsorption of Dye-Antibiotic Mixtures

Adsorption capacity and removal efficiency increased with higher initial concentrations and longer contact times, achieving >95 % removal across contaminants (Figure 2). As contact time increased, percentage removal increased in the first 100 min, but after some time, it gradually approached an almost constant value after equilibrium was reached. This indicated that the surface of the DRPCH was occupied with the pollutants within the first 100 min and there were strong attractive forces between the adsorbate molecules and the adsorbent. The order of affinity was amoxicillin > tetracycline > erythrosine > tartrazine > ampicillin > brilliant blue, consistent with differences in molecular size, charge, and solubility. Previous studies have consistently shown that increasing the initial concentration enhances adsorption (Dada *et al.*, 2020; Asare *et al.*, 2021; Galgano *et al.*, 2023; Rasouli *et al.*, 2024; Alkhaldi *et al.*, 2024).. Based on the results shown in Figure 3, it is possible to conclude that the actual amount of dye-antibiotics mixture adsorbed per unit mass of adsorbent increased with increased concentration. This phenomenon can be explained in terms of available active sites. At low adsorbate concentration, the ratio of surface-active sites to the total dye-antibiotics mixture is high (Galgano *et al.*, 2023). Hence, the antibiotics could interact with the adsorbent to occupy the active sites on the carbon surface, which can be removed from the solution (Dada *et al.*, 2020; Mohamed *et al.*, 2025).

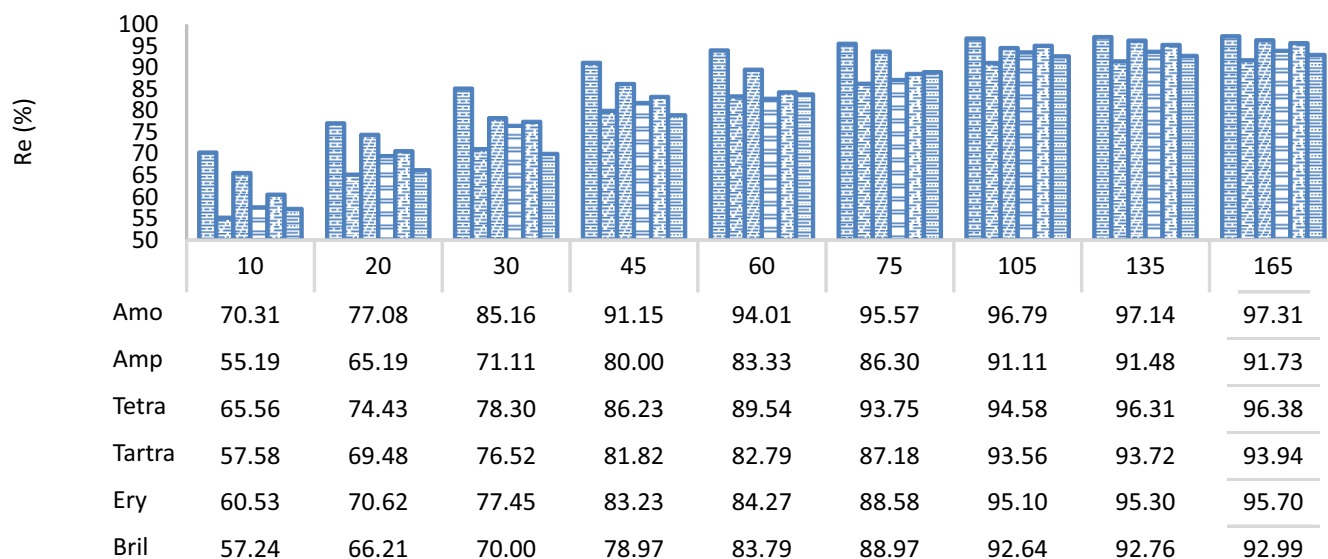


Fig. 2: Adsorption capacity and removal efficiency of DAM on the DRPCH.

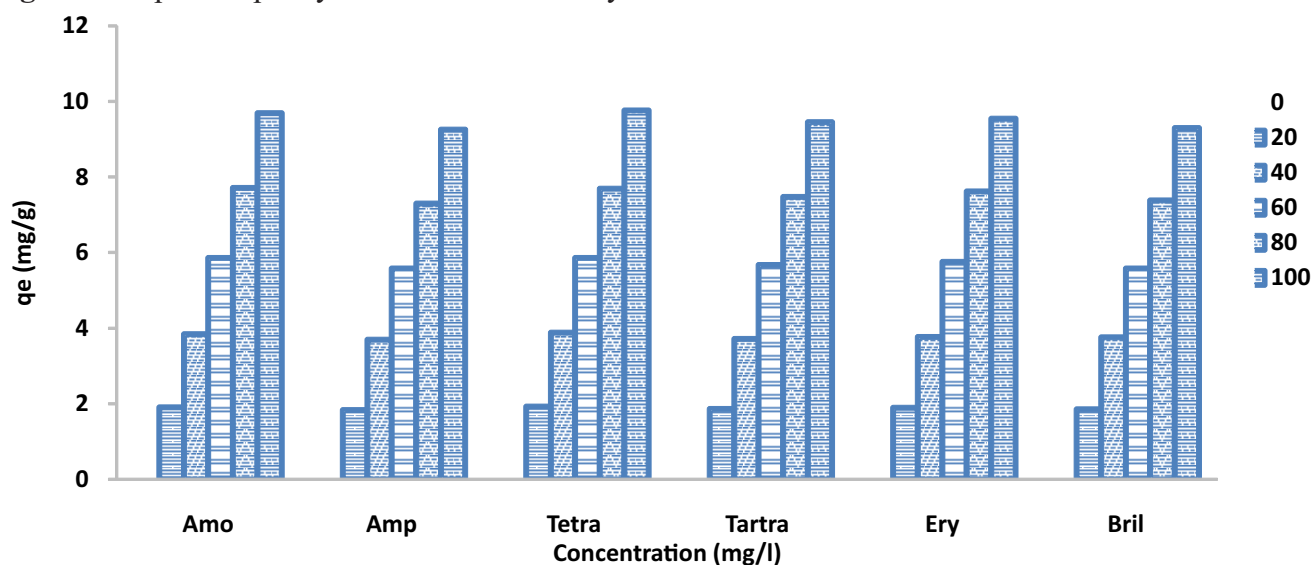


Fig. 3: The plot of adsorption capacity against the initial concentration of DAM onto DRP.

3.3 Diffusion Modelling

The mass transfer diffusion of the dye-antibiotic mixture onto the *Delonix regia* pod copolymeric hydrogel developed in this study was analyzed using the Weber-Morris, Matthew-Weber, Bangham, and McKay film diffusion models.

3.3.1 Weber-Morri's diffusion model

The intraparticle diffusion rate constants (k_{wm}) ranged from 0.1223-0.1301, 0.2441-0.2619, 0.3657-0.3802, 0.4992-0.5054, and 0.2672-0.3918 $\text{mg g}^{-1} \text{min}^{-1/2}$ for amoxicillin, ampicillin, tetracycline, tartrazine, erythrosine, and brilliant blue, respectively, across initial concentrations of 20, 40, 60, 80, and 100 mg/L (Figure 4). These results confirm the occurrence of multiple adsorption stages during the

diffusion process. The intercept values (C) provide insight into the boundary layer thickness. Larger intercepts are associated with stronger boundary layer effects, reflecting the contribution of surface adsorption to the overall rate-determining step. In this study, the boundary layer thickness values (C) ranged from 0.5109 to 6.7520 mg/g, indicating a significant boundary layer influence on the diffusion process (Dharmarathna and Priyantha, 2024).

Furthermore, the determination coefficients (R^2) increased progressively from 0.7636 to 0.8909 as the initial concentration increased from 20 to 100 mg/L (Table 1). This trend suggests improved fitting of the Weber-Morris model at higher concentrations, consistent with enhanced intraparticle diffusion effects under elevated pollutant loads. However, since the plot of q_t versus $t^{0.5}$ did not pass through the origin, intraparticle diffusion was not the sole rate-determining step. However, if a linear graph is obtained and the plot passes through the origin, then intraparticle diffusion is said to be the sole rate-limiting step (Dharmarathna and Priyantha, 2024).

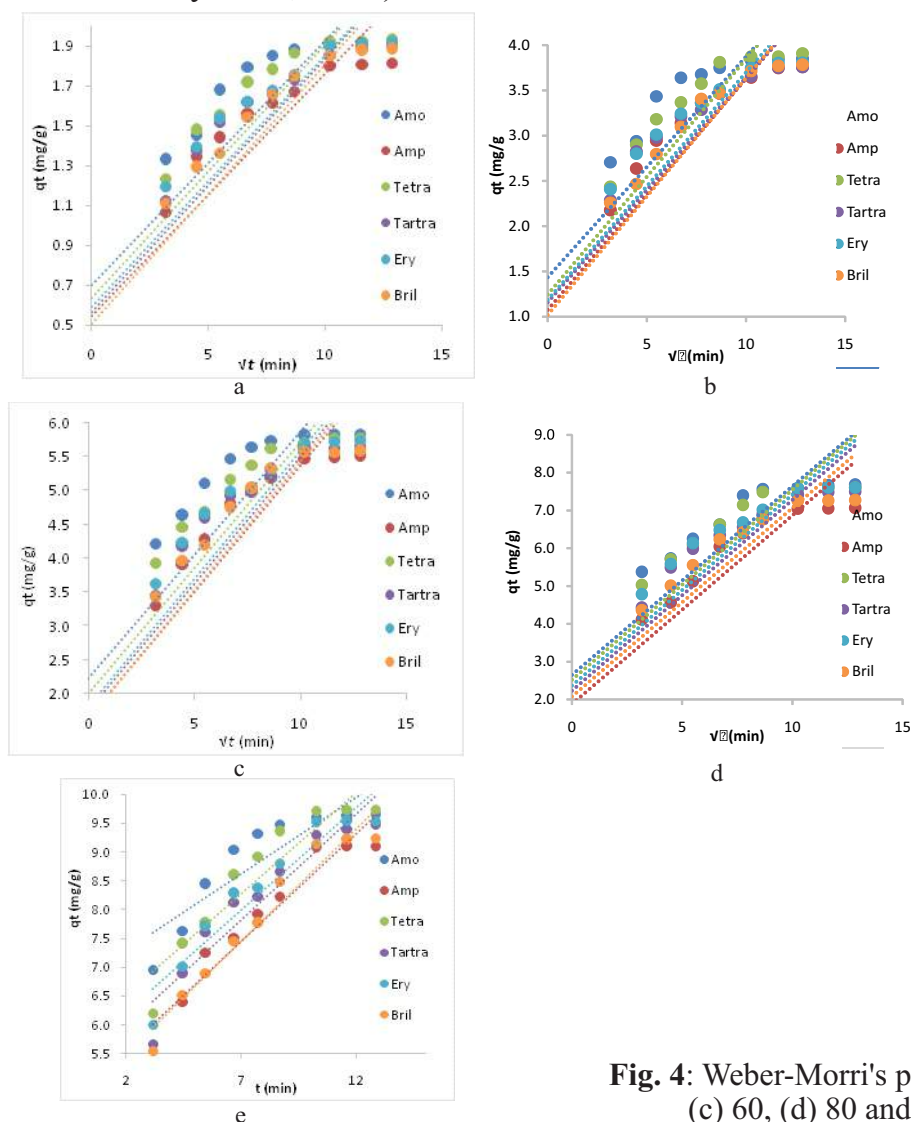


Fig. 4: Weber-Morri's plot for (a) 20, (b) 40, (c) 60, (d) 80 and (e) 100 mg/L.

3.3.2 Matthew-Weber diffusion model

The values of R^2 on average were 0.7094, 0.7132, 0.6930, 0.6960 and 0.7021, as the dye-antibiotic mixture increased from 20-100 mg/L. The highest value of R^2 (0.7068, 0.7561, 0.7369, 0.7384, 0.7725 and 0.8135) were obtained at 80, 100, 20, 40, 40 and 100 mg/L for amoxicillin, ampicillin, tetracycline, tartrazine, erythrosine and brilliant blue, respectively, while the lowest values (0.5893, 0.7005, 0.6818, 0.6803, 0.7426 and 0.7410) were obtained at 40, 20, 40, 20, 60 and 60 mg/L for amoxicillin, ampicillin, tetracycline, tartrazine, erythrosine and brilliant, respectively (Figure 5).

The values of K_{mw} were in the range (0.1612-0.2073), (0.2764-0.3224), (0.2073-0.2764), (0.2303-0.2764), (0.2073-0.2533) and (0.2764-0.3224) mg/g min for amoxicillin, ampicillin, tetracycline, tartrazine, erythrosine and brilliant, respectively, (Table 1), as the initial concentration increased from 20 to 100 mg/L. The trend shows that the Matthew-Weber diffusion model is a function of concentration (Ajani *et al.*, 2022).

Table 1: Weber-Morris' diffusion parameters at different concentrations.

Adsorbate	Weber-Morris' diffusion			Matthew-Weber diffusion		Bangham diffusion		McKay film diffusion			
Cone (mg/L)	K_{mw} (mg/g min ^{0.5})	C (mg/g)	R^2	K_m (mg/g min)	R^2	k_b (min ⁻¹)	θ	R^2	K_m	R^2	Aver R^2
Amoxicillin	0.1232	0.7001	0.6858	0.1842	0.5962	5.1439	0.1438	0.8913	0.0382	0.9906	
Ampicillin	0.1223	0.5446	0.7790	0.2764	0.7005	3.7809	0.1916	0.9525	0.0376	0.9537	
Tetracycline	0.1273	0.6376	0.7388	0.2764	0.7369	4.5687	0.1675	0.9465	0.0497	0.9590	0.9581
Tartrazine	0.1375	0.5634	0.7855	0.2303	0.6803	3.9545	0.1907	0.9670	0.0345	0.9286	
Erythrosine	0.1269	0.5891	0.7721	0.2533	0.7674	4.2403	0.1772	0.9774	0.0385	0.9433	
Brilliant B.	0.1301	0.5109	0.8202	0.3224	0.7748	3.5628	0.2101	0.9769	0.0378	0.9736	
Amoxicillin	0.2441	1.4366	0.6725	0.1842	0.5893	5.3456	0.1360	0.8809	0.0385	0.9840	
Ampicillin	0.2558	1.0744	0.7988	0.2994	0.7256	3.7050	0.2025	0.9677	0.0339	0.9489	
Tetracycline	0.2606	1.2454	0.7541	0.2533	0.6818	4.3984	0.1780	0.9466	0.0330	0.9523	0.9411
Tartrazine	0.2487	1.1598	0.7687	0.2533	0.7384	4.1342	0.1787	0.9656	0.0381	0.8979	
Erythrosine	0.2516	1.1855	0.7680	0.2533	0.7725	4.2854	0.1739	0.9825	0.0446	0.8959	
Brilliant B.	0.2619	1.0199	0.8215	0.3224	0.7718	3.5530	0.2117	0.9702	0.0370	0.9677	
Amoxicillin	0.3657	2.2331	0.6612	0.1612	0.6204	5.6545	0.1262	0.9117	0.0412	0.9985	
Ampicillin	0.3744	1.6368	0.7839	0.2764	0.7065	3.7826	0.1950	0.9592	0.0412	0.9712	
Tetracycline	0.3728	2.0061	0.7158	0.2073	0.7088	4.9487	0.1495	0.9568	0.0440	0.9204	0.9507
Tartrazine	0.3750	1.7591	0.7638	0.2533	0.7114	4.1523	0.1795	0.9560	0.0428	0.9259	
Erythrosine	0.3802	1.6442	0.7896	0.2533	0.7426	4.3681	0.1721	0.9696	0.0378	0.9345	
Brilliant B.	0.3787	1.8186	0.7589	0.2764	0.7410	3.8538	0.1933	0.9655	0.0444	0.9538	
Amoxicillin	0.4992	2.6496	0.7185	0.2073	0.7068	4.9158	0.1507	0.9321	0.0429	0.9594	
Ampicillin	0.4997	1.8763	0.8204	0.3224	0.7137	3.1710	0.2241	0.9461	0.0524	0.9533	
Tetracycline	0.5030	2.5189	0.7390	0.2303	0.6969	4.5509	0.1653	0.9472	0.0521	0.9542	
Tartrazine	0.5048	2.2324	0.7836	0.2764	0.7233	3.9021	0.1913	0.9606	0.0431	0.9285	0.9361
Erythrosine	0.5054	2.3671	0.7682	0.2533	0.7582	4.2579	0.1760	0.9739	0.0563	0.8973	
Brilliant B.	0.4988	2.0769	0.8014	0.2994	0.7428	3.6107	0.2015	0.9702	0.0465	0.9237	
Amoxicillin	0.2672	6.7520	0.7964	0.1842	0.6197	5.5808	0.1270	0.9112	0.0395	0.9968	
Ampicillin	0.3755	4.8182	0.9180	0.2764	0.7561	3.6889	0.1955	0.9705	0.0512	0.8976	
Tetracycline	0.3545	5.8119	0.8741	0.2533	0.6973	4.5341	0.1708	0.9542	0.0526	0.9503	0.9438
Tartrazine	0.3688	5.2475	0.9021	0.2764	0.6255	4.0290	0.1860	0.9610	0.0306	0.9692	
Erythrosine	0.3563	5.4983	0.9085	0.2533	0.7453	4.3102	0.1742	0.9697	0.0495	0.9090	
Brilliant B.	0.3918	4.7156	0.9461	0.2994	0.8135	3.6711	0.1976	0.9824	0.0395	0.9400	

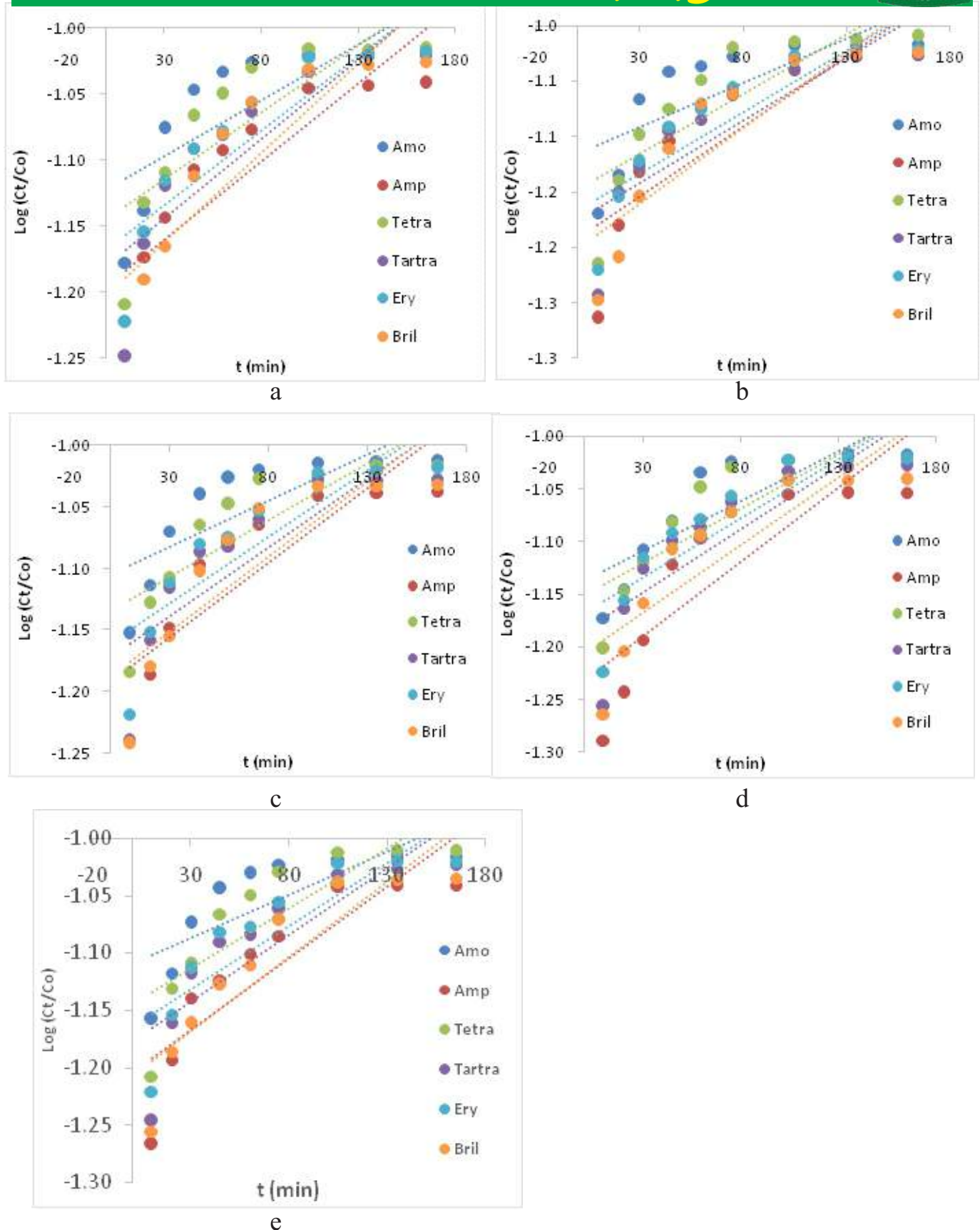


Fig. 5: Matthew-Weber plot for (a) 20, (b) 40, (c) 60, (d) 80 and (e) 100 mg/L.

3.3.3 Bangham diffusion model

The value of k_b increased from 4.9158, 3.1710, 4.3984, 3.9021, 4.2403 and 3.5530 mL/g.L for amoxicillin, ampicillin, tetracycline, tartrazine, erythrosine and brilliant blue, respectively, to 5.5808, 3.7826, 4.9487, 4.1523, 4.3102 and 3.8538, as the concentration increased from 20 to 100 mg/L. The values of θ were in the range of 0.1270-0.1507, 0.1916-0.2241, 0.1495-0.1780, 0.1787-0.1913, 0.1721-0.1772 and 0.1933-0.2117 for amoxicillin, ampicillin, tetracycline, tartrazine, erythrosine and brilliant blue, respectively, when the concentration increased from 20 to 100 mg/L (Figure 6). The change in the parameters showed a trend that could be derived as a function of concentration. The values of θ less than unity show that intraparticle diffusion or pore diffusion is one of the rate-determining steps. The values of R^2 obtained from the Bangham model ranged between 0.9519 and 0.9582 on average, as shown in Table 1, suggesting that pore diffusion was involved in dye-antibiotic mixture uptake onto the DRPCH developed. Bangham's diffusion model showed a good fit to the experimental data, with R^2 values not less than 0.9500 for all concentrations studied. However, the linearity of the Bangham plot suggests that adsorbate pore diffusion is not the only rate-controlling step.

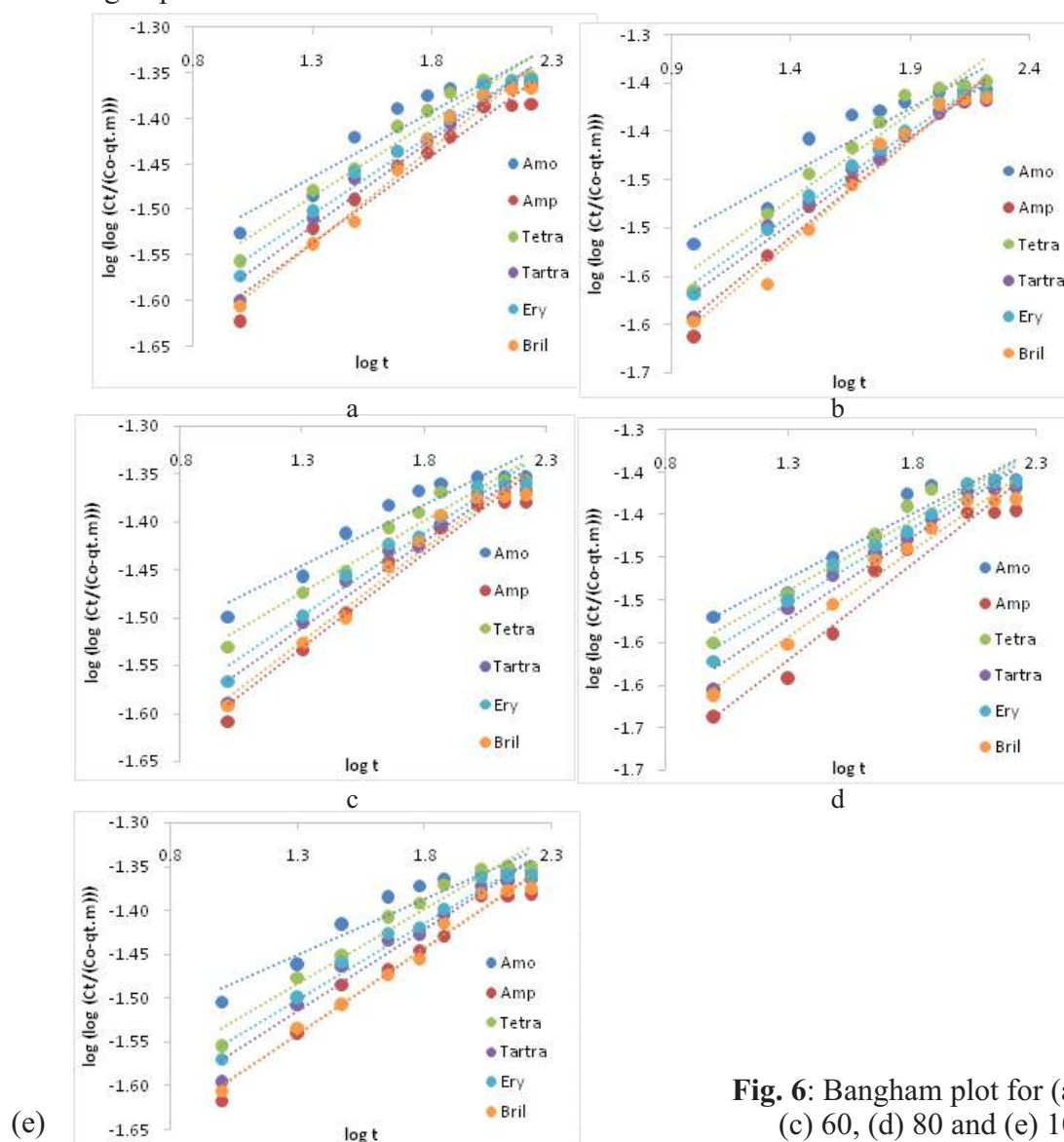
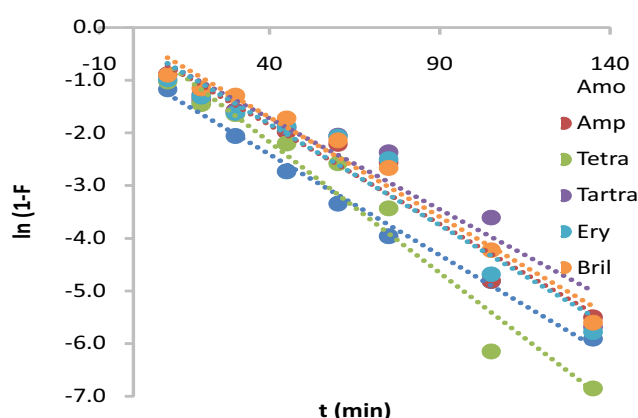


Fig. 6: Bangham plot for (a) 20, (b) 40, (c) 60, (d) 80 and (e) 100 mg/L.

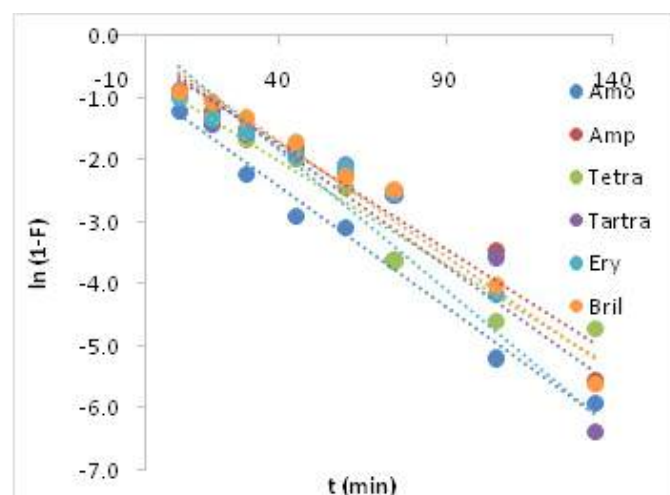
3.3.4 McKay film diffusion model

The McKay mass transfer diffusion model was carried out by plotting $\ln(1-F)$ against time, t , as shown in Figure 7. The intraparticle diffusion constants k_m and R^2 were obtained from the plot, as shown in Table 1.40. The McKay film constant, k_m were in the range of 0.0382-0.0429, 0.0339-0.0524, 0.0330-0.0526, 0.0306-0.0431, 0.0378-0.0563, and 0.0370-0.0465-mL/g/L for amoxicillin, ampicillin, tetracycline, tartrazine, erythrosine and brilliant blue, respectively, as the concentration increases from 20-100 mg/L (Table 1).

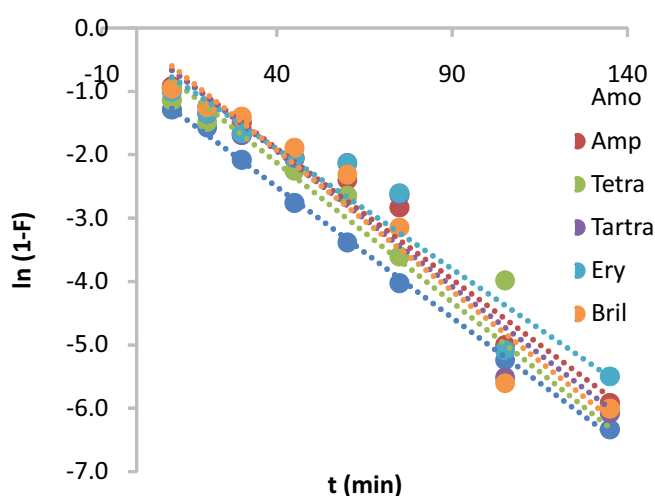
The McKay diffusion model showed a good fit to the experimental data with average (0.9581, 0.9411, 0.9507, 0.9361 and 0.9438) values at 20, 40, 60, 80 and 100 mg/L, respectively, which were close to unity and suggest that the adsorption process was surface diffusion dominant. The McKay model plots showed the second-best fit of all the diffusion models investigated after the Bangham model. The values of K_{mw} and R^2 fluctuated, increased from 20 to 80 mg/L and decreased from 80 to 100 mg/L. The fluctuation of the values of k_m and R^2 as the concentration increased showed a trend that could not be derived as a good function of concentration.



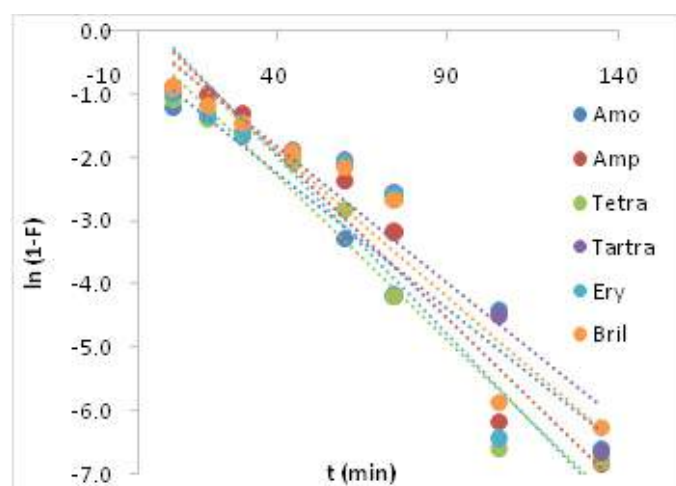
a



b



c



d

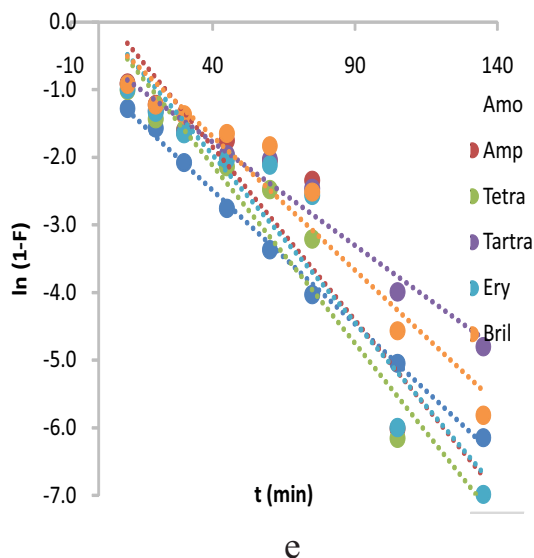


Fig. 7: McKay plot for (a) 20, (b) 40, (c) 60, (d) 80 and (e) 100 mg/L

3.3.5 Selection of the best diffusion model

The Bangham and McKay model plots showed the best fit of all the diffusion models investigated based on the average R^2 at different concentrations of the dye-antibiotic mixture studied (Table 5). Bangham's diffusion model has the highest value (0.9541), followed by the McKay Diffusion Model (0.9460), while Matthew-Weber has the least (0.7027). The sequence of the selection of the mass transfer model based on the average R^2 is Bangham (0.9541) > McKay (0.9460) > Weber-Morris (0.7872) > Matthew-Weber (0.7027). McKay and Bangham's diffusion models showed a good fit to the experimental data, with values not less than 0.9000 for all concentrations studied. And none of the four mass transfer diffusion models is less than 0.7000 on average across different concentrations investigated.

Weber-Morris model plots did not pass through the origin, indicating that intraparticle diffusion was involved but not the sole rate-limiting step. The Matthew-Weber model displayed poor correlation, suggesting a limited influence indicating that surface diffusion from bulk solution to the adsorbent also governed the process. The sequence of model fit was Bangham > McKay > Weber-Morris > Matthew-Weber, underscoring the interplay of pore and surface diffusion mechanisms in controlling adsorption dynamics.

4. Conclusion

This study demonstrated that *Delonix regia* pod-based copolymeric hydrogel (DRPCH) is an efficient, sustainable adsorbent for removing dye-antibiotic mixtures from water, achieving removal efficiencies exceeding 95 %. Mass transfer diffusion modelling revealed that both pore diffusion (Bangham model) and surface diffusion (McKay model) dominated the adsorption process, while intraparticle and external diffusion contributed to lesser extents. These findings provide crucial mechanistic insights for optimizing adsorbent design and scaling up water purification systems. Valorizing agricultural waste for hydrogel production not only addresses pollution control but also supports circular economy strategies and the achievement of SDGs 6, 11, and 12. nce of external mass transfer alone. The Bangham model provided the best fit, demonstrating that pore diffusion played a dominant role in DAM uptake. θ values < 1 confirmed that intraparticle diffusion contributed significantly to rate control. The McKay film diffusion model showed excellent agreement,



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Optimization of Ngbo Synthetic Zeolite Using Response Surface Methodology

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Abstract

In this study, the Central Composite Design (CCD) matrix was used to examine the effect of process variables and the effectiveness of the produced Ngbo synthetic zeolite for adsorption studies. The kaolin clay from Ngbo was treated with different ratios of sodium bicarbonate and sodium hexametaphosphate solution and calcined at three different temperatures. The adsorptive capacity was assessed based on process conditions such as temperature (431.82 – 700 °C), time duration (2 – 6 hr), and chemical ratios (16.48 – 50). This was done to identify the optimal conditions for synthetic zeolite production. The adsorption efficiency of methylene blue dye by Ngbo synthetic zeolite was optimized using RSM models, which indicated an estimated efficiency of over 95%. The predicted and experimental values under the same conditions showed less than 5% difference, demonstrating that the Central Composite Design approach is an efficient, effective, and reliable method for methylene blue dye adsorption. The best-performing synthetic zeolite was further optimized using one-way ANOVA, which revealed a regression correlation coefficient of 0.9590, indicating that 95.90% of the total variation in the adsorption process was due to the experimental variables. The results suggest that this process could be applied to methylene blue dye adsorption to mitigate issues such as corrosion, catalyst loss, and environmental concerns.

Keywords: Optimization, Characterization, Adsorptive Capacity, Synthetic Zeolite, Response Surface Methodology, Central Composite Design

Introduction

In recent decades, developing countries have faced significant challenges in meeting the high demand for catalysts and zeolites for industrial processes (Stojanov et al., 2024). Additionally, the quality of drinking water has continued to decline due to contamination caused by effluents and waste from textile, chemical, mining, and metallurgical industries (Al-Gaashani et al., 2024; Gómez-Álvarez et al., 2011). Various traditional methods, such as precipitation (Liu et al., 2024), ion exchange (Roth et al., 2024; Martins et al., 2010), membrane filtration (Sudalaimuthu et al., 2024), electrochemical processes (Al-Gaashani et al., 2024), and adsorption (Zhou et al., 2025), have been used to remove these pollutants from wastewater. However, these conventional approaches tend to be expensive and sometimes ineffective, especially when contaminant levels exceed 100 mg/l (Yao et al., 2024).

Despite regulations encouraging the replacement of corrosive and unfriendly liquids in the chemical and petrochemical sectors, solid acid catalysts for water contaminant adsorption continue to be crucial (Su et al., 2025). Zeolites are crystalline, hydrated alumina-silicates consisting of groups I and II elements (Sudalaimuthu et al., 2025). Today, synthetic zeolites are preferred over natural ones due to their purity and consistent particle sizes (Orrico et al., 2025). Although manufacturing synthetic zeolites from chemical



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sources like silica and alumina is expensive, costs can be reduced by using geological materials such as clays or industrial waste. To lower costs further, researchers are exploring cheaper raw materials, including clay minerals, natural zeolites, volcanic glasses, diatomite, high-silica bauxite, oil shale, and residues from combustion processes—such as coal ash, municipal solid waste incineration ash, and industrial slags (Xie et al., 2025; Russo et al., 2025). Furthermore, advances in synthesis protocols now allow for the interconversion of zeolite frameworks, enabling the tailored production of specific types for targeted applications. The Ngbo clay deposit represents one such promising, locally sourced raw material for zeolite synthesis. However, the conversion process is complex, governed by multiple interdependent variables including alkalinity, temperature, crystallization time, and solid-to-liquid ratio. Traditional one-variable-at-a-time (OVAT) optimization methods are not only time-consuming and labour-intensive but also fail to capture the complex interactive effects between these parameters. This limitation can lead to suboptimal synthesis conditions and hinder the maximization of the zeolite's adsorptive potential.

To address this critical gap, this study employs Response Surface Methodology (RSM) for the systematic design and optimization of the synthesis process for Ngbo zeolite. RSM is a powerful collection of statistical and mathematical techniques ideal for modelling and analyzing complex processes where a response of interest is influenced by several variables. By constructing a predictive model and generating contour plots, RSM allows for the identification of optimal factor levels that maximize a desired response—in this case, the crystallinity and adsorption capacity of the synthesized zeolite. The primary objective of this work is to leverage RSM to precisely determine the optimal synthesis conditions, thereby producing a high-performance Ngbo zeolite that can serve as a cost-effective and efficient adsorbent for the remediation of industrial wastewater, contributing to both environmental protection and resource sustainability.

2. Materials and Methods

2.1 Source of Raw Materials

The clay sample was collected from Ngbo in Ohaukwu L.G.A., Ebonyi State (N 06°30' 32.8", E 007°58'13.7"). The chemicals used, including methylene blue dye—molecular formula ($C_{16}H_{18}N_3SCl$, molecular weight=319.85, $\lambda_{max} = 663 \text{ nm}$)—as well as silica gel, sodium hydroxide, sodium bicarbonate, sodium hexa-metaphosphate, and deionized water, were all of standard grade and purchased from a chemical shop at Ogbete Main Market, Enugu, Enugu State. The instruments employed consist of common glassware, an electrical furnace, an oven, and a UV spectrophotometer (JASCO UV/Vis-550).

2.2 Physico-Chemical Characterization of Ngbo Clay

The Ngbo clay sample was subjected to some physical analysis to determine its physical properties. The analysis included: bulk density, moisture content, pH, and loss on ignition (LOI).

2.3 Characterization of the Raw Clay and Activated Sample

The Ngbo clay sample was characterized using XRF and XRD.

2.4 Production of Several Synthetic Zeolites from Ngbo Clay

This study used a modified version of the procedure reported by Kovo et al. (2005) [14] to produce several synthetic zeolites.

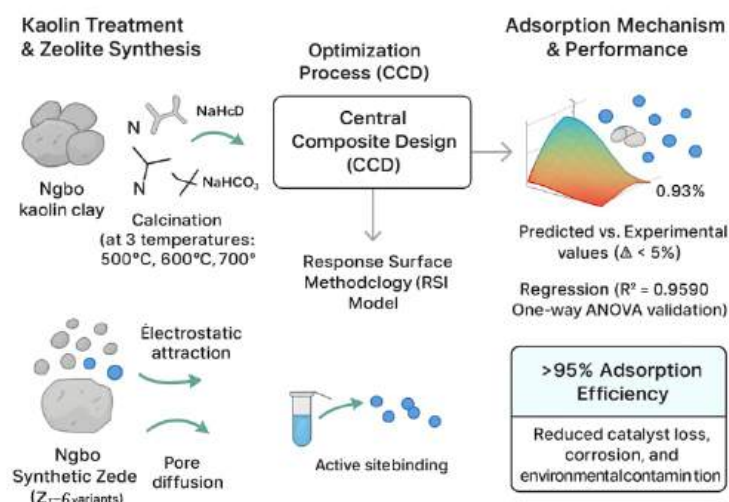


Fig.1: The schematic depicts the synthesis, optimization, and adsorption mechanism of Ngbo synthetic zeolite for removing methylene blue dye.

Ngbo kaolin clay was treated with sodium bicarbonate (NaHCO_3) and sodium hexa-metaphosphate ($\text{Na}_6\text{P}_6\text{O}_{18}$) at various ratios and calcined at 500°C , 600°C , and 700°C to produce different zeolite variants. Parameters like temperature, reaction time, and reagent ratios were optimized using the Central Composite Design (CCD) and Response Surface Methodology (RSM).

Table 1: Central Composite Design Matrix in coded factors

Std	Run	Temperature	Time	Chemical ratio	Yield
5	1	+1	-1	-1	
17	2	0	0	0	
4	3	-1	+1	+1	
13	4	0	0	-1.682	
18	5	0	0	0	
14	6	0	0	+1.682	
10	7	+1.682	0	0	
3	8	-1	+1	-1	
9	9	-1.682	0	0	
16	10	0	0	0	
12	11	0	+1.682	0	
15	12	0	0	0	
1	13	-1	-1	-1	
11	14	0	-1.682	0	
6	15	+1	-1	+1	
2	16	-1	-1	+1	
20	17	0	0	0	
19	18	0	0	0	
8	19	+1	1	1	
7	20	+1	+1	-1	



2.5: Batch Adsorption Studies

Method (Cazetta et al., 2011) was used with some adjustments. Methylene Blue (MB), a cationic dye from B. Herzog, Germany, served as the adsorbate. Its molecular formula is $C_{16}H_{18}N_3SCl$, with a molecular weight of 319.85 g/mol. A stock solution of 1.0 g/L was prepared by dissolving 0.01 g of MB in 100 mL, then diluting to 1000 mL with distilled water. Batch adsorption tests involved 20 Viju bottles, each containing 10 mL of MB solution. To each, 0.25 g of synthetic zeolite was added, and the bottles were kept at 25°C in a water bath shaker. For equilibrium testing, each run lasted 50 minutes. Samples were filtered through 0.45 μm membranes to remove small zeolite particles before analysis. MB concentrations in the supernatants before and after adsorption were measured with a UV–Vis spectrophotometer (Varian Cary 50 UV/Vis) at 664 nm, and concentrations were calculated using a calibration curve. The amount of MB adsorbed (q_e , mg/g) was calculated by: $q_e = (C_o - C_e)V/W$

where C_o and C_e (mg/l) are the initial and equilibrium liquid phase concentrations of MB, respectively, V (l) is the volume of the solution, and W (g) is the mass of dry adsorbent used.

The clay-catalyzed adsorption was modelled using Box-Behnken Response Surface Methodology. For three factors inputs of x_1 , x_2 , and x_3 , the equation of the quadratic response is given as;

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2$$

3. Results and Discussion

3.1 Physical Properties of the Raw Clay

The physical properties of raw Ngbo clay are outlined in Table 2. Results show it has a moisture content of 3.3% and a bulk density of 1.25 g/ml. These findings are consistent with previous studies by (Cazetta et al., 2011; Russo et al., 2025; Xie et al., 2025), which reported kaolinite clay moisture levels between 3.0% and 4.0%, and bulk densities from 1.2 to 1.4 g/ml.

Table 2: Results of Bulk density, Moisture content, pH, and LOI

Clay type	Bulk density (g/ml)	% moisture content	pH	LOI (%)
Ngbo clay	1.25	3.33	7.5	10.52



3.2 Characterization of Raw Clay and Activated Clay

The chemical properties of the raw Ngbo clay were analysed using XRF and XRD. Table 3 presents the XRF composition analysis results of raw Ngbo clay and activated Ngbo clays. Both types contain oxides and impurities, but their clay mineral compositions are largely unaffected by treatments, even at temperatures below 500°C, as supported by previous studies (Stojanov et al., 2024; Liu et al., 2025; Kovo et al., 2005). This indicates that enhancing clay properties chemically below 500°C is difficult due to its low reactivity. The data also show that the optimal synthetic zeolite is rich in silicon, aluminium, calcium, sulphur, and chloride oxides, with major components being SiO₂, Al₂O₃, SO₃, CaO, and Cl.

Table 3: Results of XRF analysis of raw Ngbo Clay and activated Ngbo clay

Chemical constituent	Raw clay (Wt. %)	Activated Ngbo Clay (Wt. %)
SiO ₂	62.70	5.575
TiO ₂	1.52	0.088
Al ₂ O ₃	19.70	1.467
Fe ₂ O ₃	2.06	0.501
P ₂ O ₃	—	1.165
CaO	0.789	68.354
MgO	0.026	0.863
Na ₂ O	0.20	0.443
K ₂ O	0.85	0.193
Mn ₂ O ₃	—	0.033
V ₂ O ₅	0.071	—
Cr ₂ O ₃	0.035	0.004
CuO	0.044	—
BaO	0.19	—
L.O.I	11.82	—
SO ₃	—	1.712
Cl	—	19.286
ZnO	—	0.004
SrO	—	0.028

Figure 2 shows the XRD pattern analysis results of raw Ngbo clay. The pattern reveals several characteristic peaks resulting from its mineral content. A prominent peak at $2\theta = 22.64^\circ$ indicates a high quartz presence. Minor impurities such as illite, muscovite, halloysite, hydrated mica, non-crystalline hydroxide iron, and halloysite are also detected. To utilize Ngbo clay for industrial purposes, particularly in zeolite development—consistent with findings from [22 and 23]—these impurities and quartz content should be minimized. The XRD results support the data obtained from the XRF analysis.

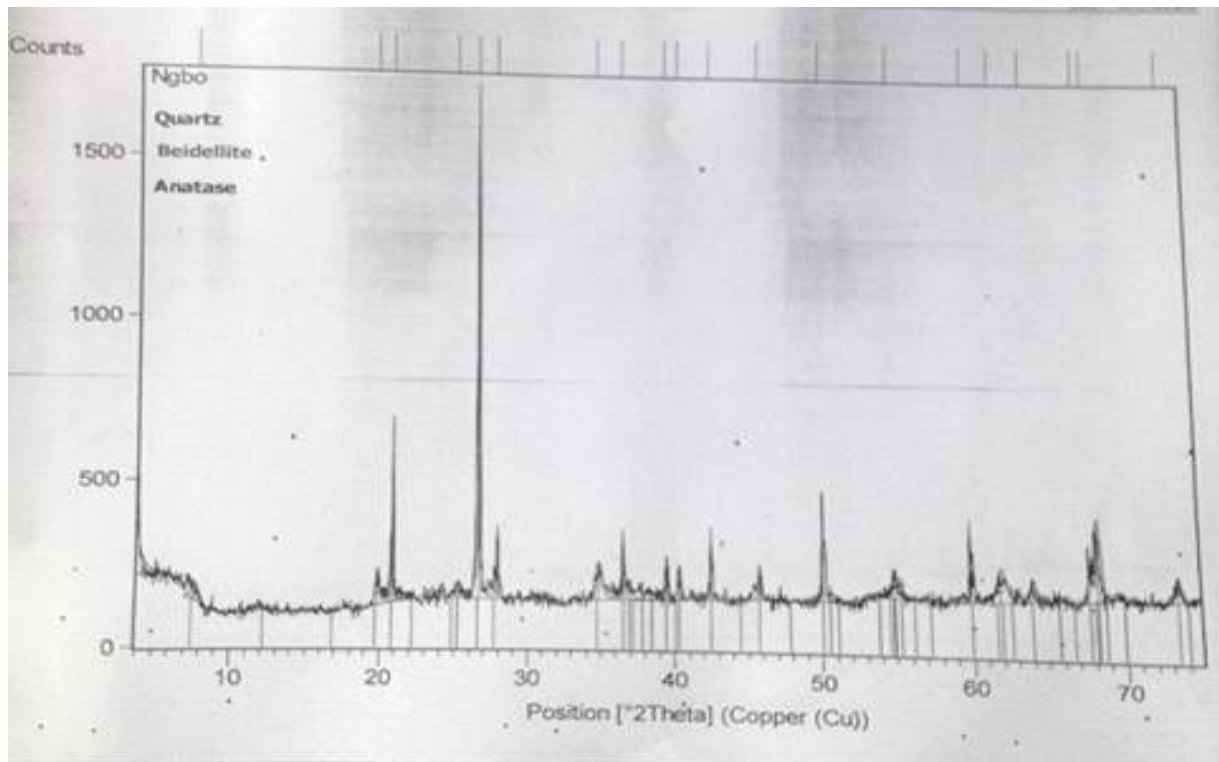


Fig. 2 : Results of XRD analysis of Ngbo raw clay

The chemical properties of the optimal synthetic zeolite were analysed using XRD. Figure 3 presents the XRD pattern of the optimized synthetic zeolite. The pattern shows several characteristic peaks, reflecting the mineral compositions present. Notably, a peak at $2\theta = 27^\circ$ indicates a significant amount of kaolinite.

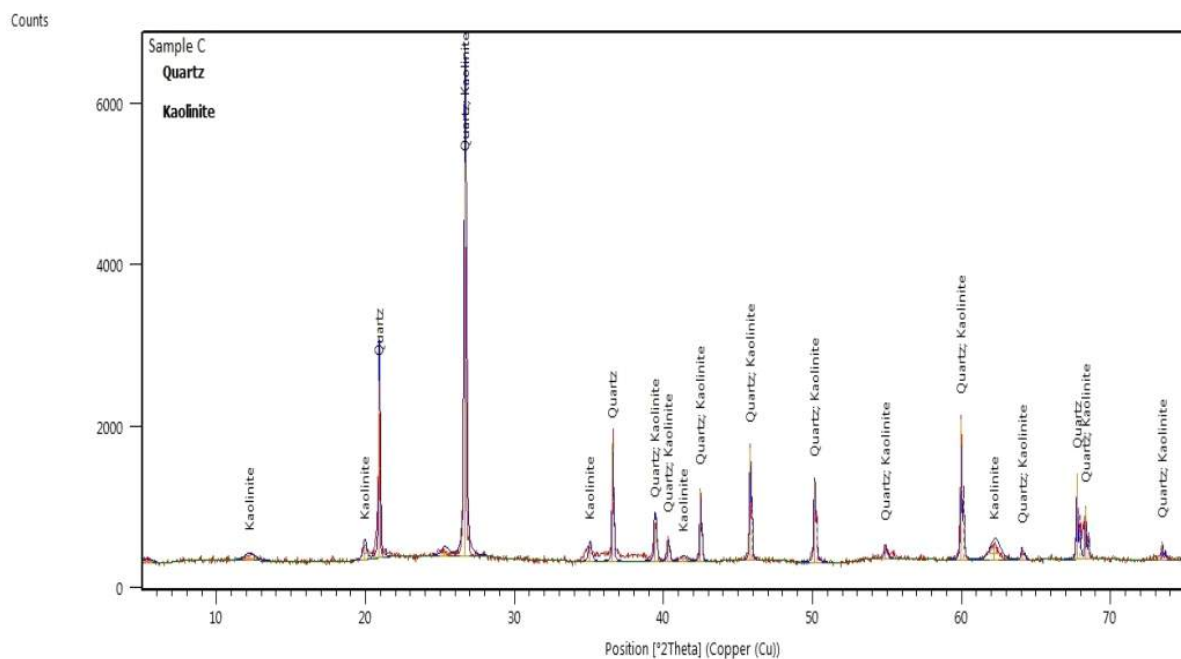


Fig. 3: Results of XRD pattern of optimal synthetic zeolite



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3.3 Adsorption Process Results

Batch adsorption studies were conducted to determine the responses and yields of various synthetic zeolites, as shown in Table 4.

Table 4: Results of the Adsorptive capacity of several synthetic zeolites produced

Std	Run	Temperature (C)	Time (hr)	Chemical ratio (g)	Adsorptive capacity (mg/g)
5	1	500.00	2.00	50.00	0.202
17	2	600.00	4.00	37.50	0.257
4	3	700.00	6.00	25.00	0.224
13	4	600.00	4.00	16.48	0.254
18	5	600.00	4.00	37.50	0.271
14	6	600.00	4.00	58.52	0.239
10	7	768.18	4.00	37.50	0.219
3	8	500.00	6.00	25.00	0.256
9	9	431.82	4.00	37.50	0.220
16	10	600.00	4.00	37.50	0.259
12	11	600.00	7.36	37.50	0.264
15	12	600.00	4.00	37.50	0.259
1	13	500.00	2.00	25.00	1.970
11	14	600.00	0.64	37.50	0.174
6	15	700.00	2.00	50.00	0.208
2	16	700.00	2.00	25.00	0.204
20	17	600.00	4.00	37.50	0.271
19	18	600.00	4.00	37.50	0.260
8	19	700.00	6.00	50.00	0.264
7	20	500.00	6.00	50.00	0.234

3.4 Analysis of Variance (ANOVA) for Synthetic Zeolite

The ANOVA results for the regression model in Table 5 demonstrate that the model is highly significant, with a calculated F-value of 26.02 and a very low p-value ($P = 0.0001$). The lack of fit F-value of 36.31 indicates a significant lack of fit, with only a 0.06% likelihood of this being due to noise. Model terms with "Prob > F" less than 0.0500 are considered significant; in Table 6, B, C, AC, BC, and C2 are significant. This signifies that the linear effects of time and chemical ratio, the effects of temperature and chemical ratio, their combined effects, and the quadratic effect of chemical ratio are important factors. Other included effects support hierarchy in the model. The model's effectiveness was assessed using the correlation coefficient, yielding an R^2 of 0.9590, meaning 95.90% of the variability in final concentration is explained by the variables. The "Pred R-Squared" of 0.6962 is lower than the "Adj R-Squared" of 0.9222, indicating possible block effects or issues with the model or data. The "Adeq Precision" metric, which measures the signal-to-noise ratio, is 19.072, exceeding the desirable threshold of 4 and indicating sufficient signal strength. This model is suitable for exploring the design space. The standard deviation of the model was 0.013.

The Final Equation in Terms of Coded Factors:

$$\text{Adsorptive capacity} = +0.33 - 0.13 * A - 0.11 * B - 0.13 * C + 0.22 * A*B + 0.23 * A*C + 0.22 * B*C$$

Table 5: ANOVA for Response Surface Quadratic Model for Adsorptive capacity

Source	Sum of squares	df	Mean Square	F Value	p-value Prob > F
Model	0.040	9	4.465E-003	26.02	<0.0001 significant
A-Temperature	7.045E-004	1	7.045E-004	4.10	0.0703
B-Time	0.010	1	0.010	59.30	< 0.0001
C-Chemical ratio	0.017	1	0.017	96.30	< 0.0001
AB	6.301E-004	1	6.301E-004	3.67	0.0844
AC	2.415E-003	1	2.415E-003	14.07	0.0038
BC	1.953E-003	1	1.953E-003	11.38	0.0071
A ²	6.376E-004	1	6.376E-004	3.72	0.0828
B ²	5.093E-004	1	5.093E-004	2.97	0.1157
C ²	7.336E-003	1	7.336E-003	42.74	< 0.0001
Residual	1.716E-003	10	1.716E-004		
Lack of Fit	1.670E-003	5	3.341E-004	36.31	0.0006 significant
Pure Error	4.600E-005	5	9.200E-006		
Cor Total	0.042	19			

The optimal conditions yielded an adsorption efficiency above 95%, with predicted and experimental results differing by less than 5% ($R^2 = 0.9590$, validated by ANOVA). The adsorption mechanism involves electrostatic attraction and pore diffusion, leading to the binding of methylene blue molecules on active sites of the zeolite, which helps reduce catalyst loss, corrosion, and environmental contamination.

3.4.1: Residual plot for synthetic zeolite

The regression model was also evaluated with residual plots, shown in Figures 4 - 6. A residual represents the difference between the experimental value and the model's predicted value. This analysis checks the assumption of constant variance in the data.

Figures 4 to 6 display the predicted versus actual response plots. These plots emphasize the values that the model struggles to predict. The residuals versus run chart examines potential lurking variables that might have affected the response during testing. The normal probability plot of residuals assesses whether the residuals are normally distributed, while the predicted versus actual response plot aids in identifying specific values or groups that are difficult for the model to predict (Ejikeme et al., 2013).

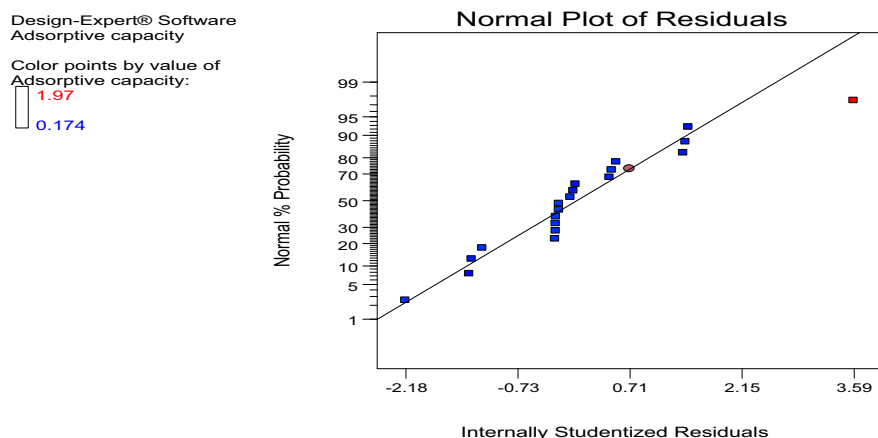


Fig. 4: Normal plot vs residual of Adsorptive capacity for Optimal synthetic zeolite

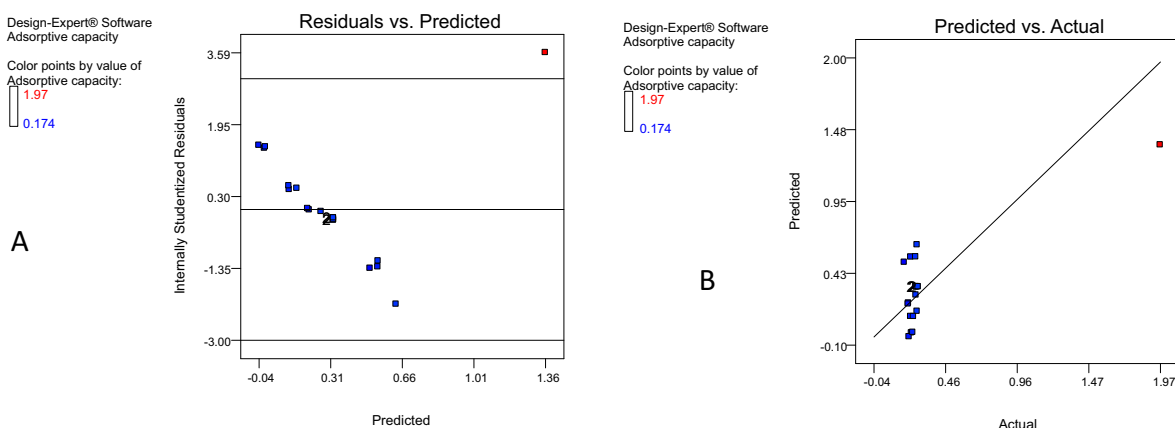


Fig. 5A: Residual vs predicted plot of adsorptive capacity for synthetic zeolite; **5b** Predicted vs actual plot of adsorptive capacity for synthetic zeolite

3.4.2: Contour plots for synthetic zeolite

Figure 7 displays the contour plot results for the optimal synthetic zeolite. The circular contour plots suggest that interactions between the variables are not significant, complicating the identification of optimal test process variable values (Anupam et al., 2011; Ejikeme et al., 2011). In contrast, the non-circular contour plots indicate interactions among the process variables, making it easier to determine their optimal values.

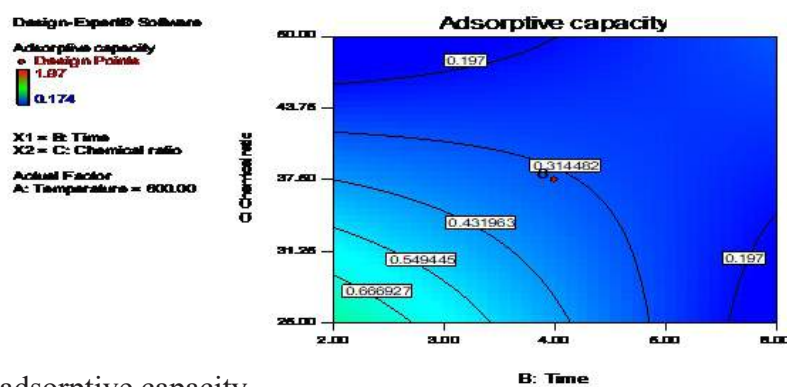


Fig. 6. Contour plot of adsorptive capacity, chemical ratio and time for synthetic zeolite

3.4.3: The 3D plot for synthetic zeolite

Figures 7 to 9 display the 3D plots of the response surface model. The findings show that the optimal conversion value is 49 for the studied process variables, consistent with results from (Sudalaimuthu et al., 2024; Yao et al., 2024). As the process duration increases, both excess reactants and yield increase. The response surface plots reveal distinct peaks, indicating that the maximum response is affected by the influencing factors within the design space. These 3D surfaces offer key insights into how the system behaves within the experimental design, facilitating the analysis of the impact of factors on responses and the interpretation of contour plots between variables (Anupam et al., 2011; Ejikeme et al., 2011). The 3D plots were created by varying two variables at a time while maintaining all other input variables at their baseline levels. The resulting elliptical shapes of the curves suggest that the quadratic model is appropriate and that a significant correlation exists between the two variables (Russo et al., 2025; Yao et al., 2024).

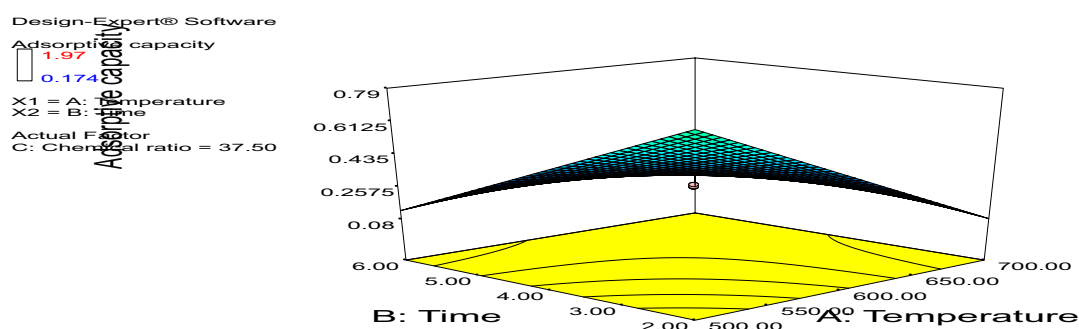


Fig. 7: 3-D plot of Adsorptive capacity, time and temperature for synthetic zeolite

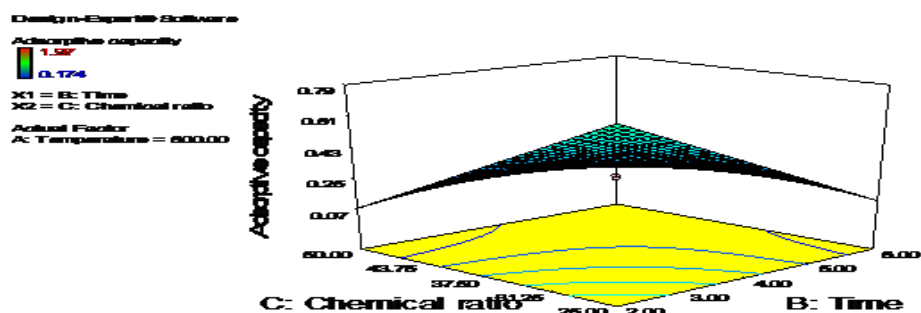


Fig. 8:3-D plot of Adsorptive capacity, chemical ratio and temperature for synthetic zeolite

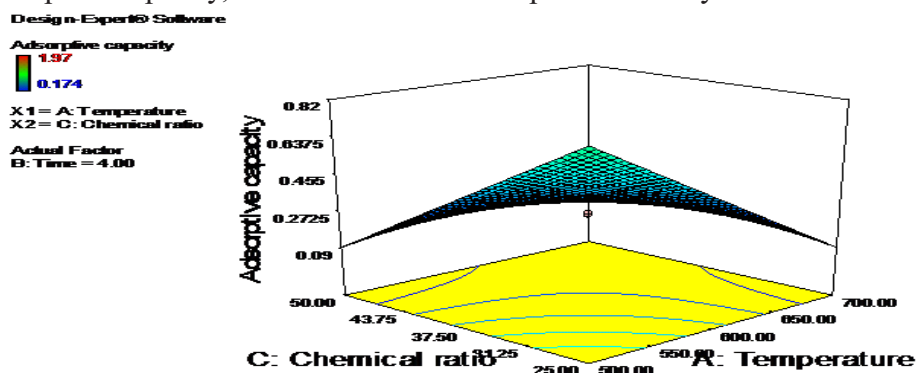


Fig. 9: 3-D plot of Adsorptive capacity, chemical ratio and time for synthetic zeolite



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3.4.4: Process optimization for synthetic zeolite

In optimizing the production process of the ideal synthetic zeolite, a desirability function was employed to identify the best parameters. The optimal conditions for the variables studied were 5.636 hours for time, 676°C for temperature, and 25.00g for the chemical ratio. The desirability score was 49.00, with a predicted conversion yield of 37.5361. These conditions were validated experimentally, achieving an actual conversion yield of 45.65.

4. Conclusions

The study identified the optimal conditions for using Ngbo synthetic zeolite catalyst. Response Surface Methodology (RSM) was employed to determine ideal parameters for adsorption, considering factors like temperature, time, and chemical ratio. The optimal settings are approximately 5.636 hours, 676°C, and 25.00 g for time, temperature, and chemical ratio, respectively. The maximum predicted adsorptive capacity was 37.5361.

XRF analysis showed the clay mainly contains SiO₂ and aluminium, while XRD revealed quartz as the primary component, suggesting Ngbo clay is kaolinite. The difference between predicted and experimental values was less than 5%, confirming that the Central Composite design matrix is an efficient and reliable method for using Ngbo synthetic zeolite clay catalyst to absorb Methylene Blue dye.

COMPETING INTERESTS

The authors have declared that no competing interests exist



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Iron (III) Oxide-Reduced Graphene Oxide (Fe₃O₄-rGO): A Novel Electrocatalyst for Room Temperature Electrochemical Oxidation of Formic Acid

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Abstract

The urgent need for sustainable and low-cost alternatives to noble metal catalysts applications in fuel cells has driven interest in transition metal–carbon composites. This work presented the development of a novel Fe₃O₄-rGO composite anode electrocatalyst for formic acid oxidation, synthesized by chemical co-precipitation and characterized by Fourier Transform-Infrared Spectroscopy (FT-IR), Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray (EDX), X-Ray Diffraction (XRD), and Thermogravimetric Analysis (TGA). Structural analyses confirmed well-dispersed Fe₃O₄ nanoparticles embedded within the reduced graphene oxide (rGO) framework, enabling strong interfacial contact and enhanced conductivity. Electrochemical characterization using cyclic voltammetry (CV), chronoamperometry (CA), and electrochemical impedance spectroscopy (EIS) demonstrated promising activity. CV revealed a peak current of 0.58 mA at 0.73 V with mixed reversible and quasi-reversible kinetics, while stability was retained across 50 cycles. CA results indicated fast oxidation of formic acid with an initial current of 0.87 mA stabilizing at 0.005 mA, suggesting strong catalytic reactivity, though limited by mass transport. EIS confirmed a large Warburg resistance consistent with restricted ion diffusion, underscoring the need for electrode engineering and optimized catalyst loading. These findings establish Fe₃O₄-rGO as a viable, cost-effective alternative to noble metals for liquid biomass redox flow fuel cells. With proper optimization of synthesis and electrode architecture, this catalyst holds strong potential for advancing affordable, sustainable power generation technologies.

Keywords: Fe₃O₄-rGO Electrocatalyst, Formic Acid Oxidation, Room Temperature, Formic Fuel Cell Application

1 Introduction

Fuel cells are increasingly recognized as vital energy conversion systems with wide-ranging applications in portable electronic devices, such as mobile phones, laptops, and other consumer electronics (Wang et al., 2016). More importantly, they offer a clean alternative to internal combustion engines in vehicles, industrial power systems, and as independent energy sources in commercial power plants (Al-Akraa et al., 2018). significantly reducing greenhouse gas emissions and supporting global efforts to achieve Net-Zero 2050 goal.

Direct and indirect formic acid fuel cells (FAFCs) are proton exchange membrane fuel cells (PEMFCs) that stand out due to their high theoretical cell potential, low operating temperature, minimal environmental impact, and enhanced safety profile. These attributes make FAFCs not only efficient and sustainable, but also long-lasting and quiet during operation



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However, despite these advantages, FAFCs currently rely heavily on costly noble metal catalysts, particularly platinum (Pt) and palladium (Pd), that are expensive and susceptible to performance degradation. Notably, Pd is less expensive than Pt, but suffers from poisoning by carbon monoxide (CO), an intermediate product of formic acid oxidation. Its catalytic efficiency depends on particle size, morphology, and surface structure, which can be tuned by an electrochemical process (Hu et al., 2012). Moreover, cyclic voltammetry (CV), chronoamperometry (CA), and electrochemical impedance spectroscopy (EIS) characterizations have shown that an improved performance of Pd catalyst can be achieved using Pd-based alloys, such as Pd-Cu (Yang et al., 2021) and Pd-Bi (Yang et al., 2017). To further reduce cost, nanostructured carbon materials have been used as support for noble metal catalysts. These supports provide high surface areas and excellent electrical conductivity, improving catalyst dispersion and utilization ——— (Al-Akraa et al., 2018; Ji et al., 2010). For instance, Pd supported on sulfonated carbon materials or helical carbon nanofibers functionalized with benzyl mercaptan exhibited notable improvements in formic acid oxidation efficiency (Hu et al., 2012). Similarly, PdCo alloys supported on graphitic carbon nitride (g-C₃N₄) demonstrated superior performance due to the synergistic effect of the bimetallic system and the textural properties of the support (Navlani-García et al., 2019).

Building on these innovations, reduced graphene oxide (rGO) has emerged as a promising catalyst support due to its exceptionally large surface area, tunable surface chemistry, and outstanding electron transport properties. These materials have been widely applied in sensors and electrochemical devices — (Peik-see et al., 2014). Recent studies have demonstrated the effectiveness of metal oxide-rGO composites, such as ZnO-Fe₂O₃-rGO, for glucose oxidation, yielding current densities far higher than those of the individual metal oxides — (Nur et al., 2024).

Iron oxide (Fe₂O₃) is a low-cost, environmentally friendly, and redox-active material that has been widely studied for batteries, capacitors, catalysis, and adsorption applications (Munasir et al., 2020). However, its poor conductivity limits its standalone catalytic performance. Integrating Fe₂O₃ into conductive rGO provides a synergistic platform that enhances electron mobility, dispersed active sites, and may offer anti-CO poisoning capability due to rGO's high surface area and functional edge groups. However, its poor conductivity limits its standalone catalytic performance. Integrating Fe₂O₃ into conductive rGO provides a synergistic platform that enhances electron mobility, disperses active sites, and may offer anti-CO poisoning capability due to rGO's high surface area and functional edge groups. Despite these advances, there remains a significant gap in the application of Fe₂O₃-rGO composites for formic acid oxidation in FAFCs.

This study addressed the gap by developing a novel Fe₂O₃-rGO nanocomposite as a co-catalyst for formic acid oxidation at room temperature. In this study, the electrochemical performance of this catalyst was evaluated using standard techniques, and its activity was compared with other catalysts reported in the literature. The results demonstrated that Fe₂O₃-rGO exhibited impressive catalytic behaviour, with the potential to revolutionize FAFC technology by offering a low-cost, stable, and efficient alternative to noble metal-based systems. This work contributes to the advancement of sustainable energy technologies and provides insight into the design of next-generation fuel cell catalysts.



2 Materials and Methods

2.1 Materials

Graphene oxide (GO), Ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), Ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), 80% hydrazine hydrate, 30% ammonium hydroxide (NH_4OH), and Formic acid were purchased from Sigma Aldrich.

2.2 Synthesis of Fe_3O_4 -rGO Nanocomposite

The Fe_3O_4 -rGO nanocomposite was synthesized via a modified chemical co-precipitation method, as described by Yang et al. (2015). Initially, 1.0 g of graphene oxide (GO) was dispersed in 200 mL of deionized (DI) water in a 500 mL round-bottom flask and sonicated for 2 hours using an ACMESONIC ultrasonic homogenizer at room temperature to ensure complete exfoliation. Separately, 1.35 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.5 g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ were dissolved in 100 mL of DI water in a 250 mL conical flask, maintaining a molar ratio of 2:1.

The iron precursor solution was then added dropwise into the GO suspension under vigorous stirring using a thermostatic magnetic stirrer and allowed to react for 1 hour. To induce co-precipitation, 30% ammonia solution was gradually added to the mixture until the pH reached 9–10, ensuring continuous stirring throughout. The reaction mixture was then transferred to a 500 mL three-neck flask placed in an oil bath and heated to 80 °C under constant stirring.

Subsequently, 1 mL of 80% hydrazine hydrate was introduced slowly into the heated mixture to facilitate the simultaneous reduction of GO and the formation of Fe_3O_4 nanoparticles. The system was maintained at 80 °C with continuous stirring for an additional 6 hours. Upon completion, the reaction mixture was allowed to cool to room temperature.

The resulting Fe_3O_4 -rGO composite was separated by centrifugation at 4000 rpm for 15 minutes and washed repeatedly with deionized water until the pH of the supernatant reached 6.8–7.2. The washed product was then freeze-dried for 12 hours to yield a dry, powdery Fe_3O_4 -rGO nanocomposite catalyst.

2.2 Fe_3O_4 -rGO Characterization

The physicochemical properties of the synthesized Fe_3O_4 -rGO nanocomposite were systematically investigated using High-Resolution Scanning Electron Microscopy (HR-SEM), Energy Dispersive X-ray Spectroscopy (EDX), Fourier Transform Infrared Spectroscopy (FT-IR), X-ray Diffraction (XRD), and Thermogravimetric Analysis (TGA). These techniques provided insights into the morphology, elemental composition, functional groups, crystallinity, and thermal stability of the composite material.



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The surface morphology of the nanocomposite was examined using a JEOL-JSM 7600F HR-SEM equipped with a backscatter electron (BSE) detector. Elemental composition was concurrently analyzed using the integrated energy-dispersive X-ray (EDX) spectrometer. Functional group identification was performed using FT-IR spectroscopy (Nicolet Nexus 470) at a resolution of 4 cm^{-1} , with 64 scans recorded in the wavenumber range of $400\text{--}4000\text{ cm}^{-1}$.

Crystallographic structure and phase identification were determined using X-ray diffraction (Rigaku D/Max-IIIIC, PW 1800 model) with $\text{Cu K}\alpha$ radiation as the X-ray source. The sample was scanned continuously, and diffraction peaks were recorded at a maximum intensity of 3000 cps to assess the crystallinity of the nanocomposite.

Thermal stability was evaluated via thermogravimetric analysis (TGA) using a PerkinElmer Thermal Analyzer. The measurement was performed under a nitrogen atmosphere at a heating rate of $20\text{ }^{\circ}\text{C}/\text{min}$ to provide insight into the decomposition behaviour of the $\text{Fe}_3\text{O}_4\text{-rGO}$ nanocatalyst across varying temperature ranges.

2.2.1 Electrochemical characterization.

The electrochemical oxidation of formic acid (FA) was investigated using a Biologic SP-200 potentiostat coupled with EC-Lab software for data acquisition and control. A standard three-electrode electrochemical cell was connected to the potentiostat, consisting of a glassy carbon electrode (GCE) modified with the $\text{Fe}_3\text{O}_4\text{-rGO}$ nanocomposite as the working electrode, a platinum wire as the counter electrode, and an Ag/AgCl reference electrode.

The experiments were conducted in an electrolyte solution containing 0.1 M formic acid as the fuel and 0.1 M sulfuric acid as the supporting electrolyte. Electrochemical measurements were carried out at a controlled temperature of $28\text{ }^{\circ}\text{C}$, with scan rates ranging from 10 mV/s to 100 mV/s to evaluate the catalytic activity of the $\text{Fe}_3\text{O}_4\text{-rGO}$ toward FA oxidation.

Chronoamperometry was also performed at 0.64 V , while the Electrochemical Impedance Spectroscopy (EIS) within the frequency range of 0.01 Hz to $100,000\text{ Hz}$ using the same setup to monitor the current response over time, providing insight into the catalyst's long-term electrocatalytic behaviour. Additionally, the stability of the $\text{Fe}_3\text{O}_4\text{-rGO}$ -modified electrode was assessed by subjecting it to 50 consecutive cyclic voltammetry scans at a fixed scan rate of 50 mV/s , demonstrating its electrochemical durability under repeated operation.

3 Results and Discussion

3.1 Formic Acid Oxidation

The electrochemical characterization of Fe₃O₄-rGO was performed by using it to modify a glassy carbon electrode (MGCE) and assessing its performance in the oxidation of 0.1M FA in 0.1M H₂SO₄ supporting electrolyte, as presented in Figure 1.

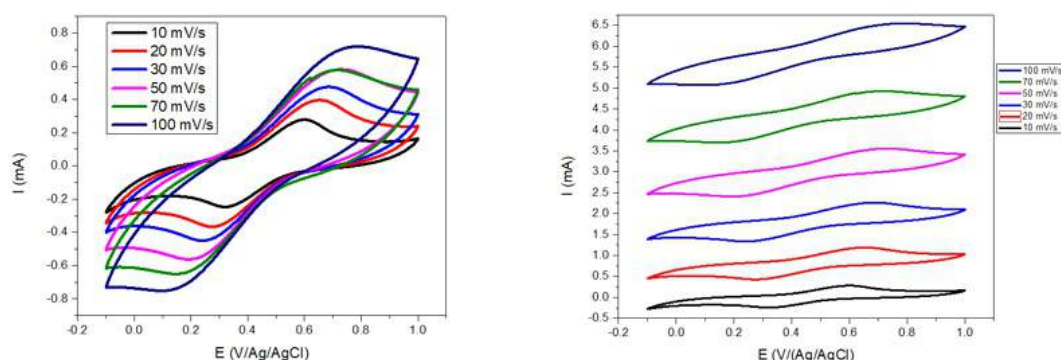


Fig. 1: 0.1M FA oxidation using MGCE with Fe₃O₄-rGO catalyst within 10-100mV/s at room temperature. The CV voltammograms for 10-100mV/s possess anodic and cathodic peak currents within 0.4-0.8V potential window for the FA anodic oxidation, and 0.1-0.35V for the cathodic reduction, indicating current generation from the oxidation of FA. The patterns of the voltammograms show that the peak currents increase as the potentials were swept from 10mV/s to 100mV/s. It is also evident that the oxidation potentials shift in the direction of increasing potential for the anodic FA oxidation, but in the negative potential direction for the cathodic FA reduction, a trend that characterizes a quasi-reversible process. Within the potential windows for oxidation and reduction of FA, only one peak is exhibited in each case. This behaviour can be attributed to the complete oxidation of FA to CO₂ (Wang et al., 2016) as a result of the anti-poisoning property of Fe₃O₄ of the catalyst, which supplied the O₂ to complete the oxidation of the CO intermediate product during FA oxidation. However, there is yet no literature to support this behaviour. The evidence for quasi-reversible features displayed by the catalyst for FA oxidation is further supported by the catalyst performance characteristics based on the ratios of peak oxidation current (I_{pa}) to that of peak reduction current (I_{pc}), as presented in Table 1

Table1: Performance of Fe₃O₄-rGO-Modified Glassy Carbon Electrode on 0.1M FA Oxidation at RT

S	Scan	Oxidation	Reduction	Peak	Peak	$E_{pa} - E_p$	I_{pa} / I_{pc}	$(E_{pa} + E_p)/2$	Sqrt of
/	Rate	Potential	Potential	Anodic	Cathodic	(V)		(V)	Scan
N	(mV/s)	(V)	E_{pc} (V)	Current	Current				Rate(mV/S)
				I_{pa} (mA)	I_{pc} (mA)				
1	10.0	0.6014	0.3198	0.2784	0.2466	0.2816	1.1290	0.4606	3.1623
2	20.0	0.6548	0.2746	0.3965	0.3661	0.3802	1.0830	0.4647	4.4721
3	30.0	0.686	0.2404	0.4755	0.4497	0.4456	1.0574	0.4632	5.4772
4	50.0	0.7315	0.1927	0.5812	0.5623	0.5388	1.0336	0.4621	7.0711
5	70.0	0.719	0.1481	0.5772	0.6499	0.5679	0.8881	0.4336	8.3666
6	100.0	0.7892	0.0928	0.7189	0.7522	0.6964	0.9557	0.4410	10.0000



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From the ratios values of the peak currents in Table 1, it is evident that all the values for the scan rates from 10-50mV/s are approximately 1.0, a feature which characterizes a reversible process. This result has rarely been reported in the literature for FA oxidation. For 70mV/s and 100mV/s, there is a shift in the FA oxidation in terms of the average of the peak potentials and the ratio of peak currents, exhibiting a quasi-reversible feature. It implies that FA oxidation on MGCE with Fe₃O₄-rGO displays are likely to exhibit both reversible and quasi-reversible mechanisms.

In comparing the performance of FA oxidation on MGCE with Fe₃O₄-rGO, there is little literature on the electrochemical oxidation of FA on MGCE with Fe₃O₄-rGO. However, it was reported that hydrogen was liberated from FA over an iron pincer complex catalyst (Zell et al., 2013) at 40 °C. Though by thermochemical means, the Iron pincer complex catalyst was able to convert FA into CO₂ and H₂, indicating the tendency of materials with the presence of Iron to oxidize FA. Quite a good number of metal catalysts supported on carbon materials for FA in alkali solutions have been published with good performances (Wang et al., 2016). Jia et al. (2017) investigated the activities of Palladium supported on different activated carbons developed from polyaniline and modified lignosulfonate composite (PAn-MLS) under different temperatures as electrodes for FA oxidation. The result from the Cyclic Voltammetry with 0.5 mol/L H₂SO₄ solution indicated that the Pd dispersed on activated carbons produced at 800 °C and 900 °C performed well with peak current density of 0.5-1.0mAcm⁻² at a potential range of 0.4-0.8V. The scan rates at which the oxidation peak currents were observed were not stated, a condition that made the comparison of the results and this work difficult. Electrochemical oxidation of FA was studied with a modified glassy carbon electrode with electrodeposited Pt and Pd (e.g., Pt and PtPd) catalysts on titanium dioxide (TiO₂) modified reduced graphene oxide (rGO) support using Cyclic Voltammetry and Chronoamperometry –(Promsawan et al., 2018). They recorded the best performance for FA oxidation on 4Pt2Pd/rGO-TiO₂ composite with an oxidation peak current density of 4.2mAcm⁻² using N₂ saturated 0.5M HCOOH + 0.5M H₂SO₄ at 50mV/s and a potential window of 0.0 to 1.0 V.

However, the basis, such as the geometrical surface area or the electrochemical surface area, ECSA, upon which the highest current density was obtained was not stated. It was also observed that the FA oxidation process is irreversible, with the ratio of peak current being 0.45, which is far less than 1.0 for a reversible system, as it is with FA (Table 1). At the same scan rate of 50mV/s, the ratio of peak currents exhibited in FA oxidation on Fe₃O₄-rGO catalyst is approximately 1.03, indicating a very high tendency of FA reversible oxidation. Under, these conditions, the current density obtained from this work is about 8.22mAcm⁻², based on the geometrical electrode surface area of 0.07cm², which is almost double the peak current density of FA oxidation on 4Pt2Pd/rGO-TiO₂ composite. Promsawan et al. (2018) used a FA concentration of 0.5M in 0.5M H₂SO₄, which should have given a higher current density than the 0.1M FA in 0.1M H₂SO₄ that was used in this work. Moreover, Kim et al. (2015) reported on a triple-junction AuPt/Fe₃O₄-rGO nanocomposite catalyst structure with high catalytic performance, in terms of activity and durability for FA oxidation.

The mechanism of FA oxidation on $\text{Fe}_3\text{O}_4\text{-rGO}$ was further investigated by plotting the peak anodic current against the square root of the scan rates for the mechanism, and running CV at 50mV/s for 50 cycles, as shown in Figure 2

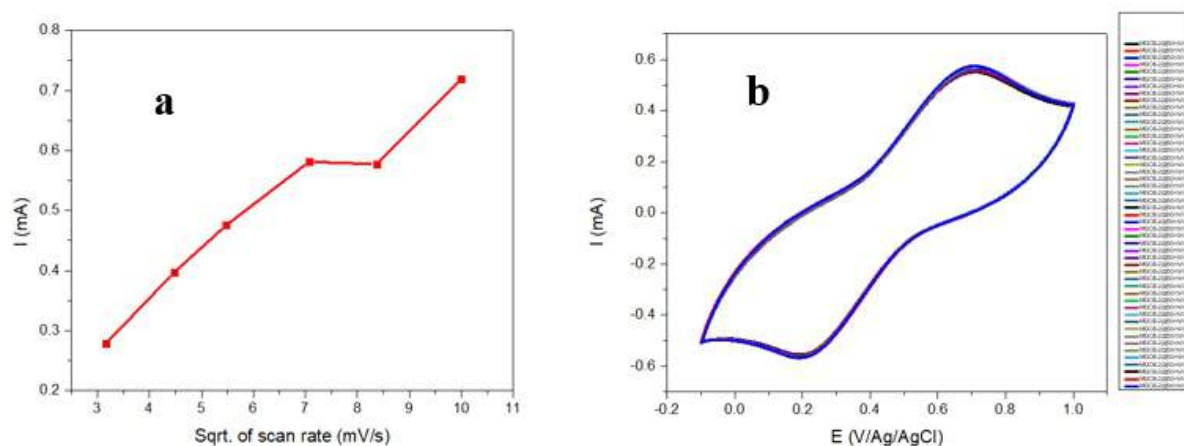


Fig. 2: a) FA oxidation mechanism and b) oxidation stability of $\text{Fe}_3\text{O}_4\text{-rGO}$

3.2 Chronoamperometry and EIS of FA Oxidation on $\text{Fe}_3\text{O}_4\text{-rGO}$

Chronoamperometric and Electrochemical Impedance Spectroscopy methods were further used to probe FA oxidation and provide insight into the performance of the catalyst, as presented in Figure 3. The efficiency of the $\text{Fe}_3\text{O}_4\text{-rGO}$ catalyst for FA oxidation was assessed using a three-electrode electrochemical cell in which a glassy carbon electrode modified with the catalyst is the working electrode. Chronoamperometric result (Figure 3a) at 0.64V for 1000s reveals a sudden drop in current from 0.87mA, in a few seconds and attained a steady-state current of 0.005mA for over 1000 s. The observed behaviour may be attributed to the slow charging of the double layer and the establishment of steady-state equilibrium (Maturost et al., 2021).

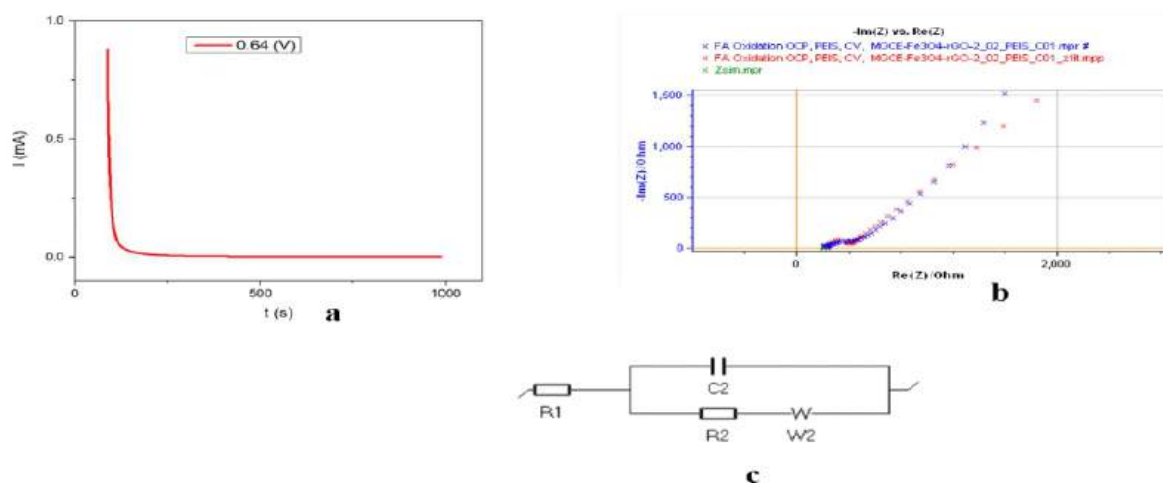


Fig. 3: Chronoamperometry (a) Electrochemical Impedance Spectroscopy (b), and Randle's Circuit (c) of FA oxidation mechanism on $\text{Fe}_3\text{O}_4\text{-rGO}$ catalyst



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The CA result indicates that the Fe_3O_4 -rGO catalyst has both a high catalytic activity, which is evident from the high initial current of 0.87mA, while the sudden drop to a stable low value of about 0.005mA is an indication that there was a very fast consumption of formic acid at the electrode interface or poisoning of the active sites of the Fe_3O_4 -rGO. The stability test on the catalyst presented in Figure 2b contradicts the probable sudden decline in current due to the catalyst poisoning as stated. There is yet no literature to explain the phenomenon exhibited by the I vs t curve, but the one reported on formic acid oxidation using xPtyPd – CeO_2 /CNT catalysts exhibited the same trend as that of the Fe_3O_4 -rGO (Maturrost et al., 2021). Moreover, the rGO component of the catalyst provides an effective conductivity and dispersion, such that Fe redox couples can assist in the fast oxidation of FA. This trend highlights both the strong intrinsic activity of Fe_3O_4 -rGO and the importance of diffusion and adsorption dynamics in dictating chronoamperometric profiles. An interaction between Fe_3O_4 and rGO can promote charge transportation together with concentrating the formic acid around Fe_3O_4 as a result of the large surface area, an exceptional electron conductivity and hydrophobicity of rGO, respectively (Qi et al., 2013).

The electrochemical impedance spectroscopy (EIS) is a useful technique for the evaluation of the kinetic and mechanistic information of electrode materials. The electrochemical impedance spectroscopy (EIS) properties of the synthesized Fe_3O_4 -rGO nanocomposite catalyst for formic acid oxidation were evaluated within 100,000 kHz–0.01 kHz frequency using the Nyquist plot (Figure 3b). The plot is made up of two parts: the semicircle and linear parts. The semicircle in the high-frequency range corresponds to the charge-transfer resistance (R_{ct}), which is caused by the charge transfer reaction at the interface of the electrolyte and electrode. The semicircular loop at high frequency is too small to identify, indicating the small interfacial charge-transfer resistance and good electrical conductivity of the Fe_3O_4 -rGO nanocomposite-modified glassy carbon. As can be seen in Figure 3b, at very high frequencies, the intercept at the real part (Z') represents the ionic resistance of the electrolyte (R_i). The straight part of the curves with a slope of the 45° portion is Warburg resistance (Z_w), resulting from the frequency dependence of ion diffusion/transport in the electrolyte (Hernández et al., 2020).

The 45° slope of the impedance plot at low frequency increases and tends to become purely capacitive, which implies that the charge transfer between the Fe_3O_4 and the conductive rGO sheets is a fast process. The large Warburg region of both curves indicates the great variations in ion diffusion path lengths and increased obstruction of ion movement. Randle's equivalent circuit for redox reaction was obtained by curve-fitting the Nyquist plot (Figure 3c) with blue and red curves representing the real and the curve-fitted data, respectively. The circuit is made up of formic acid solution resistance, R_1 (236.6 Ω), double-layer capacitance, C_2 (4.095 μF), charge-transfer resistance, R_2 (156.4 Ω), and finite-length Warburg resistance, R_{d2} (6253 Ω) as expressed in Equation (1). From these values, finite-length

$$Z' = R_1 + C_2 / (C_2 + W_{d2}) \quad (1)$$

Warburg resistance is the highest, which accounts for the slow diffusion of charges to the solution-electrode interphase. This also resulted in charges being depleted at a very fast rate at the electrode- electrolyte interphase, which led to the fast decline in current as presented in Figure 3a. It can then be inferred that since $R_{d2} > R_1$, mass transport dominates the very low-frequency response in the oxidation of FA on Fe_3O_4 -rGO catalyst, and may account for the fast current drop in the CA curve.

3.3 Physico-Chemical Characterization of Fe_3O_4 -rGO

A sample of Fe_3O_4 -rGO nanocomposite catalyst designated as Fe_3O_4 -rGO, with 2.7g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ loading, was synthesized and characterized using FT-IR, SEM, EDX, XRD, and TGA.

3.3.1 FT-IR characterization

Fourier Transform-Infrared spectroscopy (FT-IR) is a physicochemical analysis that reveals the surface functional groups, chemical bonding, and modifications in a material sample under investigation.

The FT-IR result of the Fe_3O_4 -rGO is shown in Figure 4

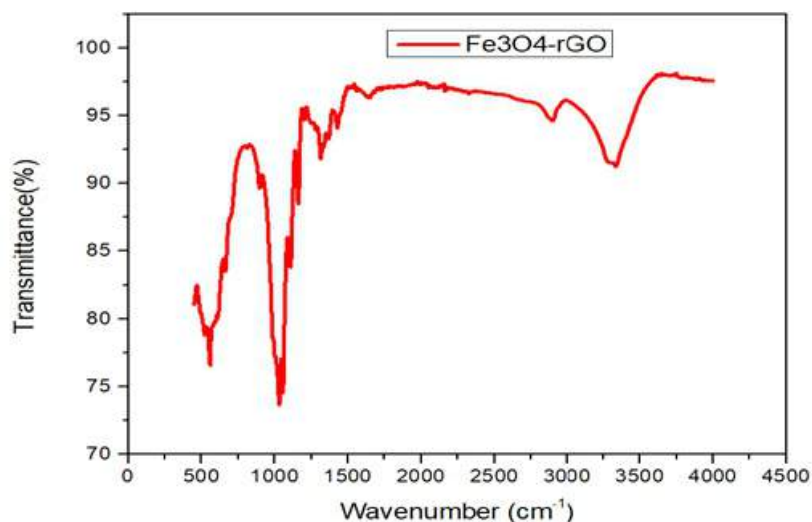


Fig. 4:FT-IR of Nanocomposites Fe_3O_4 -rGO

The FT-IR result indicates that during the synthesis of the nanocomposite catalyst, the Fe_3O_4 nanoparticle was dispersed in rGO, which is reflected by the spectra peak of the Fe=O stretching between 570-580 wavenumbers, indicating the strong interaction of F-O and presence of Fe_3O_4 in the Fe_3O_4 -rGO nanocomposites (Zhao et al., 2018). In the FT-IR spectra of the synthesized nanocomposite catalyst, there is also a broad band between 3400 and 3500 cm^{-1} , which is very pronounced, with the -OH group stretching vibrations, indicating the presence of adsorbed moisture or hydroxyl groups on the surface (Liang & Lu, 2020). There are also noticeable signals in the FT-IR spectra of the sample between 800 and 1000 cm^{-1} , 1200 and 1400, and 1500 to 1750 cm^{-1} . The signal between 1500 to 1750 may be attributed to the C=O

stretching vibrations of the carboxylic functional group (COOH) at the edges of the rGO sheets —(Nur et al., 2024), while the 1200 and 1400 cm^{-1} may be as a result of the C-O stretching vibration of the epoxy (C-O-C) and alkoxy functional groups (Liang & Lu, 2020). The observed spectra between 800 and 1000 cm^{-1} may be the effect of C-H stretching vibration due to the reduction of the GO, resulting in the Fe_3O_4 -rGO nanocomposites. Significantly, the results revealed the incorporation of Fe_3O_4 and other functional groups. The Fe_3O_4 nanoparticles are properly dispersed on the reduced graphene oxide (rGO) (Kim et al., 2015), and their presence in the Fe_3O_4 -rGO bequeaths the catalyst with magnetic properties for easy separation from the electrolyte with a magnet after the electrochemical process.

3.3.2 SEM characterization

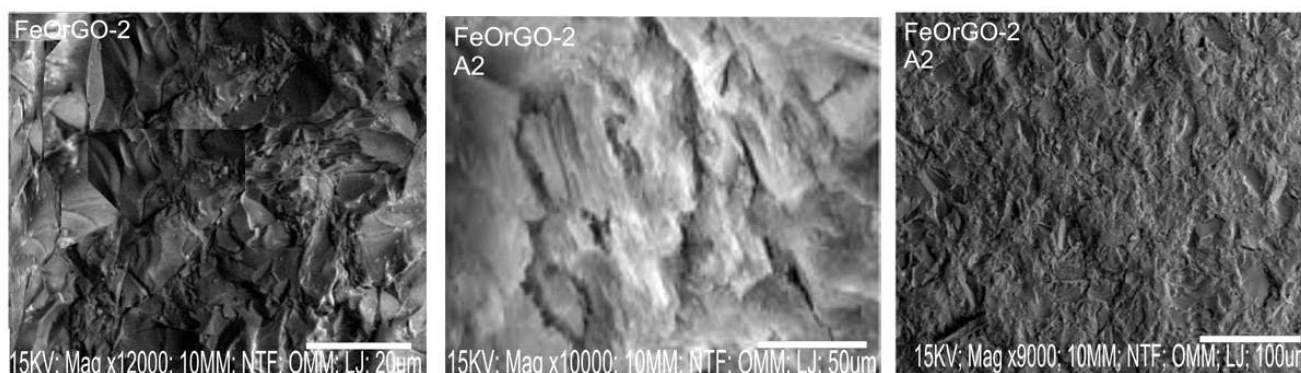


Fig. 5: SEM images of Fe_3O_4 -rGO

Scanning electron microscopy of materials provides an insight into the morphology, surface area and particle dispersion with the materials, revealing their unique characteristics and performances. In Figure 5, the synthesized Fe_3O_4 -rGO with three different magnifications of 100 μm , 50 μm , and 20 μm of SEM images were used to present the characterized surfaces of the nanocomposite, revealing distinct morphologies. In all three SEM images, the sample with 20 μm magnification has a flower-like morphology (Hidayah et al., 2017), which is an indication of the greater presence of rGO —(With & Ag, 2022). The SEM image of the Fe_3O_4 -rGO shares the features of Fe_3O_4 and rGO, indicating a good dispersibility of the Fe_3O_4 on rGO. The flower-like surface area of the samples due to the rGO also indicates that the nanocatalysts possess a large surface area suitable for catalytic activities.

3.3.3 EDX analysis

Energy-dispersive X-ray spectroscopy (EDX) is a material analytical technique that provides elemental composition data, which is critical for confirming the presence of functional groups and elements introduced during material synthesis. Energy dispersive X-ray spectroscopy of the nano catalyst sample result is presented in Figure 6.

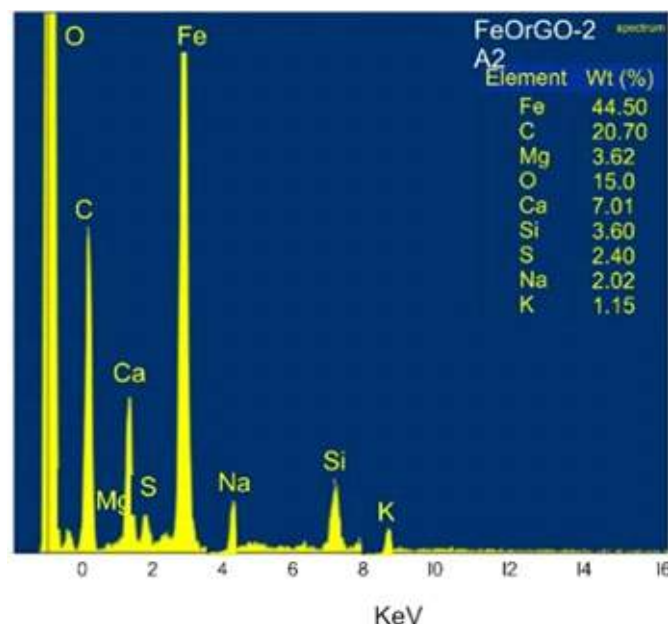


Fig. 6: EDX results for $\text{Fe}_3\text{O}_4\text{-rGO}$.

The EDX result shows that the major elements in the $\text{Fe}_3\text{O}_4\text{-rGO}$ sample (Figure 6) are carbon, C, oxygen, O, Iron Fe, and traces of the other elements, such as sulphur, S, silicon, Si, and Calcium, Ca., which may have been inherited from the synthesized parent graphene oxide due to the chemical reagents that may have been used during the synthesis, or from the source of the parent graphite material used (Dreyer et al., 2014). Significantly, the high contents of Fe and C indicate the presence of Fe_3O_4 and rGO in the sample. Fe has the highest value (44.70%) of all the elements, followed by carbon value of 20.70 wt% and oxygen, 15.0%. This result agrees with the sample's synthesis protocol, reflecting the compositions of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ that were used. The FT-IR result of the sample (Figure 1) lends support to the EDX data (Figure 6), indicating the active elements in the sample that may be responsible for its catalytic FA oxidation and electron conduction. It is also important to perform SEM and EDX characterization on the $\text{Fe}_3\text{O}_4\text{-rGO}$ sample after FA oxidation to determine the surface physicochemical changes that may have occurred for a better insight into FA oxidation on the $\text{Fe}_3\text{O}_4\text{-rGO}$ catalyst.

3.3.4 XRD analysis

XRD analysis provides great information about the crystal structure, phase purity, crystallite size, and degree of functionalization of the materials. The crystallographic structure of the sample is presented in Figure 7.

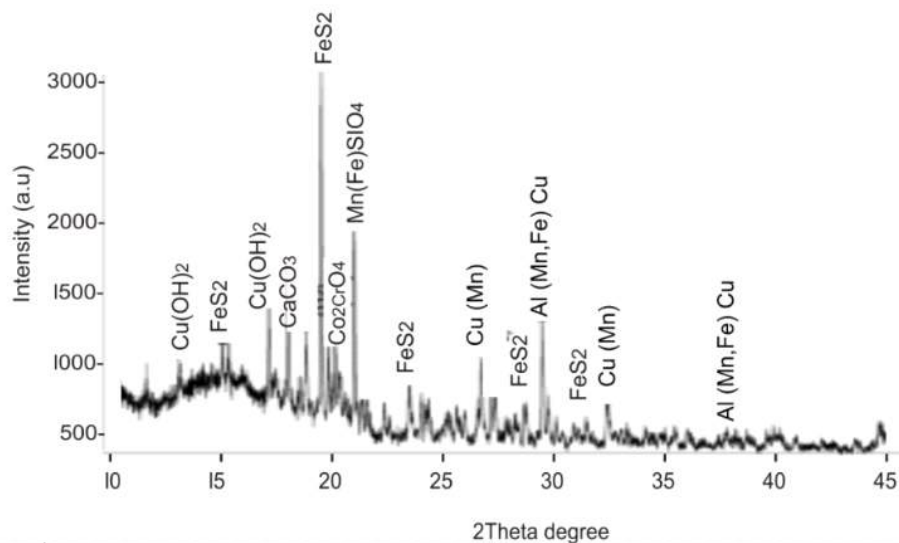


Fig. 7: XRD results of $\text{Fe}_3\text{O}_4\text{-rGO}$

A prominent peak that is pronounced in the XRD result of the sample is the FeS_2 peak, which is identified as Iron disulphide or pyrite. The sulphur that formed FeS_2 may have been inherited from the graphene oxide synthesis process, most likely from the chemical reagents used, otherwise, there would not have been a justification for it. FeS_2 has a well-defined crystal structure and crystallizes in the isometric system. It has also been reported that FeS_2 has rich redox chemistry and physicochemical properties that enhance the catalytic activity of the material. This goes to support the co-precipitation of Fe_3O_4 during the preparation of the samples. Moreover, $\text{Fe}_3\text{O}_4\text{-rGO}$ has a very high peak of FeS_2 , as can be seen from the XRD result, indicating the utilization of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ during its synthesis. The pyrite has crystallographic planes of (100) and (111), and these planes influence the material's surface properties for catalytic applications —.

3.3.5 TGA characterization

Thermogravimetric Analysis (TGA) is used to gain insight into the thermal stability and decomposition of material samples when subjected to different degrees of temperature. This analysis is important in order to assess the suitability of the $\text{Fe}_3\text{O}_4\text{-rGO}$ for application in processes with different operating temperatures.

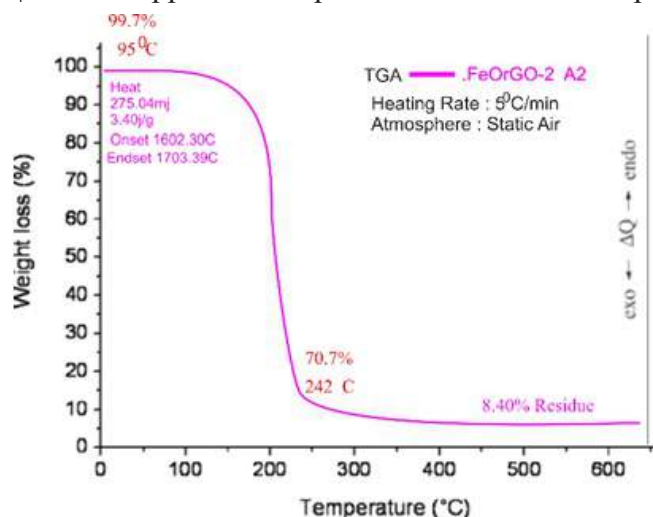


Fig. 8: Thermogravimetric analysis of $\text{Fe}_3\text{O}_4\text{-rGO}$



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The TGA analysis result of the sample is shown in Figure 8, which revealed that the thermal stability of the sample increases with an increase in Fe content, as supported by the EDX and XRD results. This means that Fe_3O_4 -rGO with the Fe content of 44.50 wt% is very stable, probably due to the high melting point of Fe. At the heating rate of 5 °C/min, these volatile matters, such as adsorbed water molecules, began to detach themselves from the nano composite material sample between 100-150 °C. Beyond 150 °C and up to 250 °C, the major weight losses were observed for the sample. Above 200 °C, the material remains stable, leaving behind 8.4% of the residues, resulting from the complete decomposition of the Fe_3O_4 -rGO materials into ashes. Within the range of this temperature, rGO and the FeS_2 components of the nanocomposites may have decomposed into CO_3 , SO_2 and Fe_3O_4 and the oxides of the other trace metals in the samples. The TGA analysis results imply that these samples can be deployed in a direct biomass redox flow fuel cell (DBRFFC), without any noticeable degradation, since it operates within the temperature range of 70 to 110 °C.

4 Conclusion

The study successfully synthesized Fe_3O_4 -rGO electrocatalyst by the chemical co-precipitation method and characterized it using physicochemical and electrochemical techniques. The physicochemical characterization using FT-IR, SEM, EDX, XRD, and TGA techniques revealed a well-dispersed Fe_3O_4 on rGO, which enhanced the overall performance of the catalyst. Similarly, CV, CA, and EIS analyses gave insight into the FA oxidation on the Fe_3O_4 -rGO with promising performances, as has been clearly discussed in the text. With the progress that has been achieved, the catalyst can be further optimized by using varying loading of Fe_3O_4 on rGO, concentrations of FA and supporting electrolyte, and temperatures. The optimized Fe_3O_4 -rGO can then be tested on a bench-scale formic acid fuel cell for further development.



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B. Sustainable National Energy Supply: A Panacea to Stable Industrial Development and Growth

Assessment of Barriers to Fiscal and Reward Models for Promoting Universal Green Energy Resilience

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Abstract

The global transition to a low-carbon economy depends significantly on the deployment of renewable energy (RE) managed by the effectiveness of strategic financing mechanisms. This paper evaluates both public and private RE financing instruments, incentive structures, and policy frameworks shaping the global expansion of RE. A systematic review of 178 scholarly articles published between 2013 and 2024, sourced from Science Direct, IEEE Xplore, and Google Scholar, identifies key trends in RE deployment, including leading countries, regional dynamics, and core technologies such as solar, wind, hydro, biomass, and geothermal. China, the United States, and Germany emerge as global RE investment frontrunners, driven by policies such as Feed-in Tariffs (FiTs), Power Purchase Agreements (PPAs), and Investment Tax Credits (ITCs). Conversely, regions like Africa and the Caribbean continue to lag due to policy instability, inadequate funding, and political risk. The study underscores emerging financing innovations such as green bonds, ecological securities, energy transition funds, and public-private partnerships as pivotal tools for bridging investment gaps. Policy recommendations emphasised the need for regulatory coherence, long-term incentive schemes, and stronger institutional frameworks. Future research should focus on adaptive financing models for vulnerable economies, performance-based finance, and regional pathways to scalable RE investment. Diversified, resilient financing remains critical to achieving Paris Agreement goals and sustainable energy futures.

Keywords: Renewable energy, green finance, sustainable energy, investment models, energy transition

1 Introduction

Among the main drivers of climate change are the increasing (Imran et al., 2024) dependence on fossil fuels and the widespread release of carbon dioxide (CO₂) from industrial operations. Achieving carbon neutrality by 2060 will require strategic resource management and a firm commitment to energy transition. According to the International Energy Agency (IEA), energy-related CO₂ emissions increased by 1.1% in 2023, reaching 37.4 billion tonnes (Liu et al., 2024). The largest emitters include China (27.8%) and the United States (15.2%) (Oreoluwa, 2025). Moreover, fossil fuel depletion threatens the sustainability of the global energy market (Guzović et al., 2022).



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A low-carbon economy can be advanced through two key strategies: optimising resource efficiency and expanding the use of renewable energy (RE). Clean energy from solar, wind, hydro, biomass, ocean, and geothermal sources offers viable RE technologies to help bridge the energy gap (Veronese et al., 2024). However, the deployment, production, and installation of RE technologies demand significant capital investment. Institutions such as the International Monetary Fund, corporate and local banks, governments, and private investors—including insurance providers and security consultants—have financed solar, wind, and hydro projects in some countries (Xiang et al., 2023). Despite these efforts, many schemes have become unviable due to inadequate funding, lack of clear policies, and weak targets (Xie et al., 2023).

Meanwhile, global energy demand continues to rise due to population growth and industrial expansion. Regions like Africa and the Caribbean face limited RE access due to unclear targets, unsustainable incentives, weak policy structures, insufficient funding, and political instability (Reynolds et al., 2022). Even in developed nations, progress is hindered by outdated incentives, a lack of innovative financing models, and slow policy revisions. High start-up costs, perceived financial risks, and uncertainties remain major barriers. Other challenges include inadequate incentive schemes, weak legislative and regulatory frameworks, market limitations, technical gaps, and competing economic priorities (Chen et al., 2023a). To overcome these barriers, there is a pressing need to develop resilient and specialised funding models while strengthening incentive frameworks.

This article aims to appraise existing public and private RE financing instruments, as well as the policies and targets guiding RE deployment. It reviews scholarly publications on RE investment by technology, country, and region and proposes innovative financing and incentive structures. These efforts are crucial to scaling sustainable RE, cutting greenhouse gas emissions, and enhancing global energy security in line with the 2015 Paris Agreement.

2 Methodology

The study analysed academic publications on policies, financing, and incentive schemes for RE. The sources were drawn from reputable databases, including Springer Publishers, Web of Science, Google Scholar, ScienceDirect, IEEE Xplore, and ResearchGate. The study examined reviews on RE funding, journal articles, and conference proceedings. First, the search focused on the structure of financing various forms of RE installations. Secondly, it identified countries and regions with notable RE growth as well as those with limited progress. Lastly, all the retrieved articles were subsequently filtered by Distiller SR using keywords related to the funding models, incentive structures, targets and policies used to promote RE production. Only English-language papers published between 2013 and 2024 were included in the analysis.

3 Results

In the first stage, three hundred and eighty-nine (389) publications were identified. The second stage produced two hundred and sixty-eight (268) papers. The final stage found one hundred and seventy-eight (178) suitable publications for the analysis. As shown in Figure 1, the distribution of articles shows a



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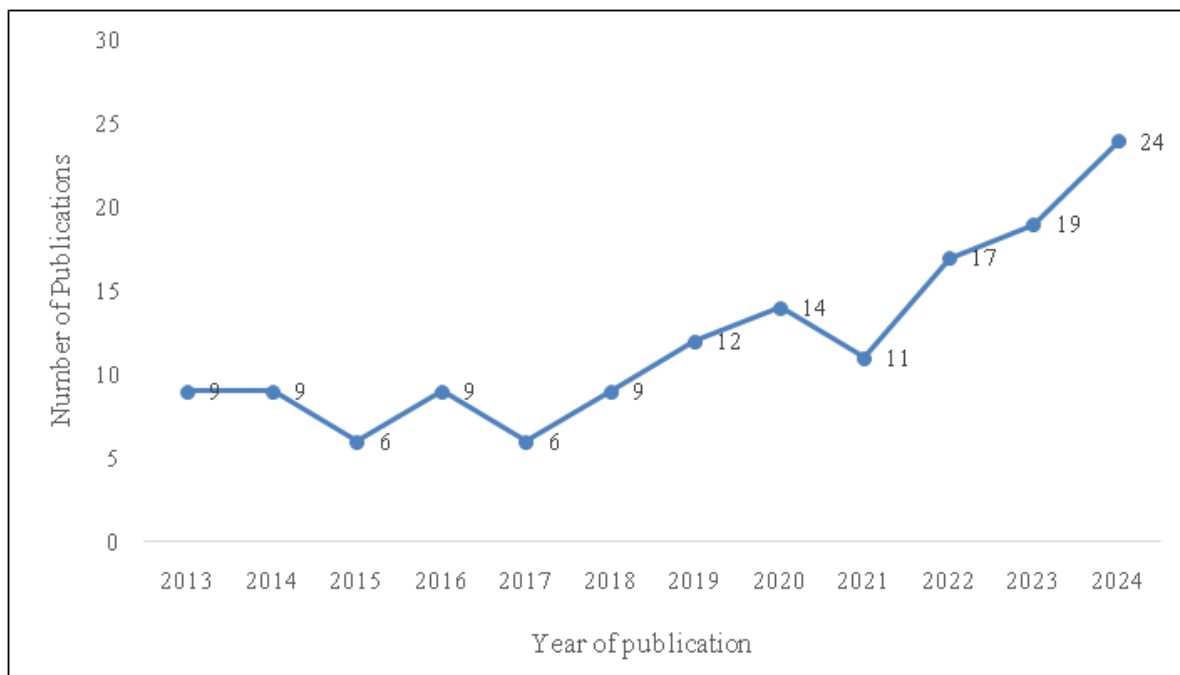


Fig. 1 Number of Publications from 2013 – 2024

3.1 Renewable Energy Installed by Countries

As shown in Figure 2, by 2024, the commissioned output of RE in twenty-nine nations totalled 3,001GW (Bai & Lin, 2024). China dominates the world with a cumulative of 1,700GW from 2013 to 2024, of which 120GW was installed in 2024 from hydroelectricity, wind, solar, and bioenergy. Profitable FiT for photovoltaic (PV) and wind producers regulated the cost of energy for a good period (Chen et al., 2023b), and played a significant role in cutting the price of energy at homes and businesses (Briera & Lefèvre, 2024). Legal requirements created an international solar panel production, distribution, and export boom that solidified China's leadership status in the world's solar energy industry (Chen et al., 2023c).

In the United States of America (USA), power purchase agreements (PPA) in Texas and Investment Tax Credits (ITC) in the state of California are two examples of local tariffs that have helped to finance a 25GW solar project in 2024, having a cumulative of 300GW in 2012–2024 (Pan et al., 2024). Germany's solar capacity increased significantly in 2024 to 150GW with an addition of 10GW in 2024 (Lee et al., 2024), and it is expected to increase by 5% before 2030 (Behera et al., 2024). The Renewable Energy Sources Act (RESA) and the periodic FiT modifications guaranteed the long-term viability of financing for Germany's solar market (Lu et al., 2024).

India installed 17GW of renewable power in 2024, having a total of 130GW from 2013–2024 (Chen et al., 2023c). The National Solar Energy Mission (NSEM) policies declared in 2010 spurred green bonds and viability gap funding (VGF), made this easier by covering solar cost differences and biofuel subsidy (Dai et al., 2025). By 2030, 500GW of power is targeted to be installed, with 280GW and 140GW coming from solar and wind power (Omri & Ben-Jabeur, 2024)

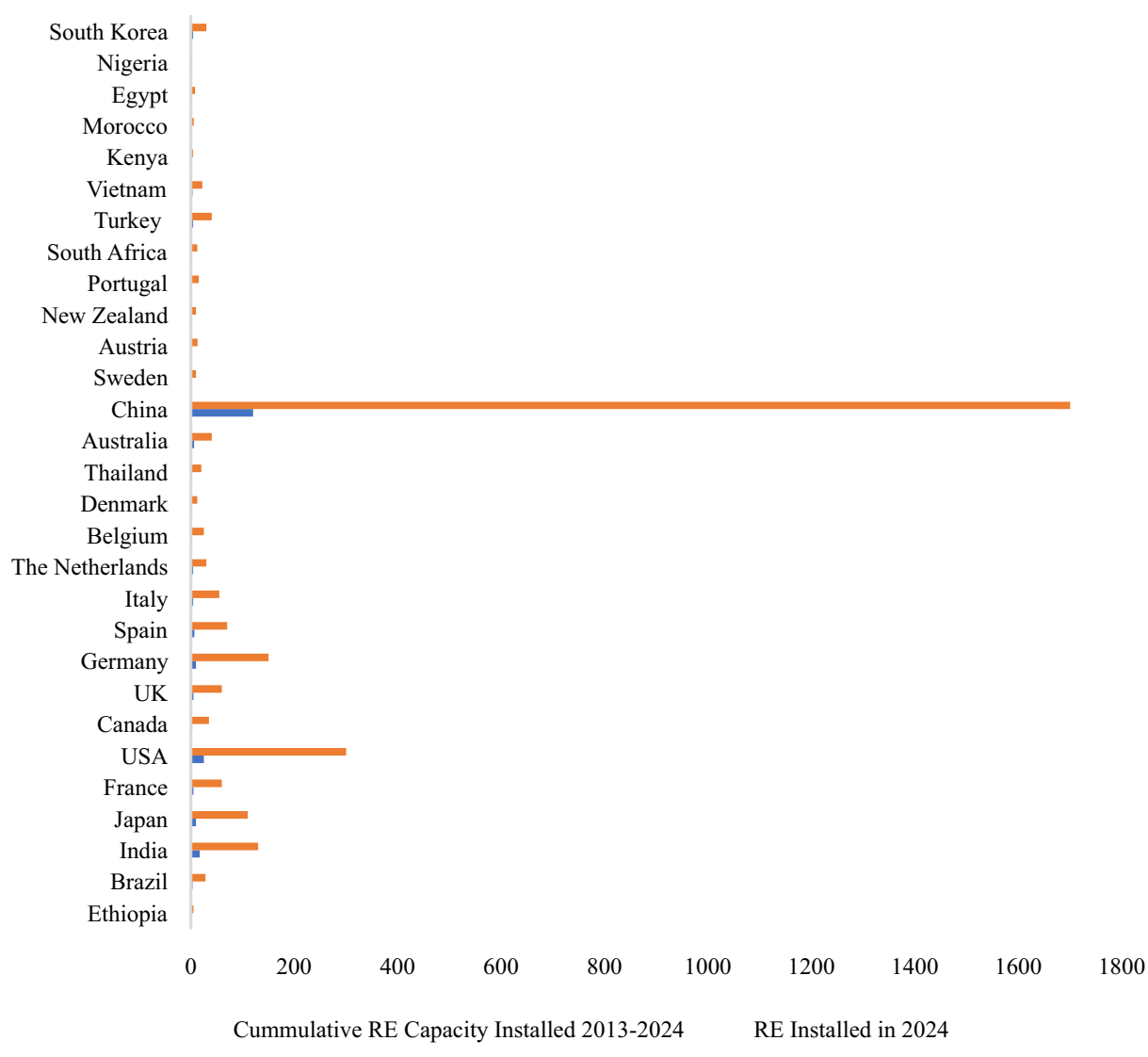


Fig. 2 Renewable Energy Installed by Twenty-Nine Nations in 2024 (Omri & Ben-Jabeur, 2024)

Through the implementation of various policies and incentives to encourage the spread of RE, the Feed-in Tariff (FIT) system was enhanced in 2020 to the Fit-in-Premium (FIP) system, stimulating Japan's RE installation to 10GW in 2024 (Khalique et al., 2025) and a cumulative of 110GW between 2013 and 2024, including RE (Rahman & Raeisi-Sarkandiz, 2023b). Japan has made growing offshore wind power and the development of hydrogen as a key energy source a priority (Pan et al., 2024). Japan encourages public-private cooperation on the adoption of RE technology, the enormous-scale execution of projects, technology innovation, and knowledge exchange through these partnerships. In the UK, the use of sustainable obligations for coastal windmills and solar power facilities generated 5GW of RE in 2024 (Imran et al., 2024), making a total of 60GW (Veronese et al., 2024). This was aided by tax breaks, subsidies, and the decarbonisation of the power sector. They set a target to increase the percentage to 70% (Yahyazadeh, 2023) with the goal of net zero emissions by 2050 for electric vehicles (EVs), energy efficiency, hydrogen economy, Carbon Capture Utilisation and Storage (CCUS), and the development of energy storage systems.



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In 2024, Australia's installed capacity for RE reached 40GW, marking an increase of 6GW from 2021–2022 (Pang et al., 2024). This growth was mostly attributed to rooftop solar installations, with 337,498 homes and businesses installing 3.1GW (Safi et al., 2024) of new capacity. Approximately 40% of Australia's electricity supply comes from renewable sources (Veronese et al., 2024), with solar energy through FiTs and rebates for rooftop solar. Canada's hydroelectric, wind, and solar power production is slow, with the installation of 2.5GW (Sibt-e-Ali et al., 2024) in 2024 and a cumulative of 35GW (Chen et al., 2023d). This is due to the PPA duration of 10 to 25 years, which elapsed without renewal (Chen et al., 2023e). The pan-Canadian framework on clean growth and climate change – carbon pricing and net metering programs aims to be used as tax-cutting incentives to cut coal and greenhouse gas emissions by 2030 (Xiang et al., 2023).

The National Energy Plan (PNE), which enforced net metering legislation over three years, boosted the installation of Brazilian RE (Mohseni et al., 2022). Tax exemptions, FiT, and energy auctions were the incentives used to propel Brazil's 3.2GW of RE in 2021–2023 (Jiang et al., 2024), totalling 28GW in 2024 (Pan et al., 2024). Brazil's RE sector is growing faster due to financing methods like international finance, development bank loans, and green bonds (He et al., 2025). Legislative security and tax concessions (TC) enabled France to construct 60GW of solar and wind technologies from 2020 to 2023 (Muazu et al., 2023), facilitated by FiTs, sales, and rebates (Sadiq et al., 2024). The Kingdom of Spain and the Republic of Turkey developed 7GW and 4GW in 2023 (Guo & Tan, 2024) and 70GW and 40GW from 2013 to 2024, respectively (Bilal & Shaheen, 2024). Nigeria, Egypt, Morocco, Kenya, Ethiopia, and South Africa remained stagnant at 1.5, 8, 5.5, 4, 5, and 12GW combined from hydroelectricity, solar, and wind energy (Guo et al., 2025). These countries seem to face inadequate local financial resources, economic instability, unreliable policies, bureaucratic inefficiencies, limited incentive arrangements, ambitious targets, and implementation.

3.2 Installation of Renewable Energy by Regions

Figure 3 presents the distribution of RE output by region in 2024. The Asian region is clearly at the forefront of the installation, production, deployment, and use of RE. The rapid adoption of funding, ambitious laws and targets, and subsidies (Bashir et al., 2024) in nations like China, Japan, and India has encouraged a large number of RE ventures in the Asian continent. The shift in North America's RE adoption levels from PPA to ITC has assisted both the USA and Canada in moderately raising the boost of electricity (Wu et al., 2024). Adjustments of FiT to FiP, and the recurrence of sales in countries such as the UK and Germany have favoured RE projects across the European Union (Wang et al., 2024). Expanded tax-free considerations have also led to significant savings in biofuels by South American nations, for example, Brazil (Li et al., 2024).

The African continent, Central America, the Caribbean, and Oceania show the least amount of growth in RE.

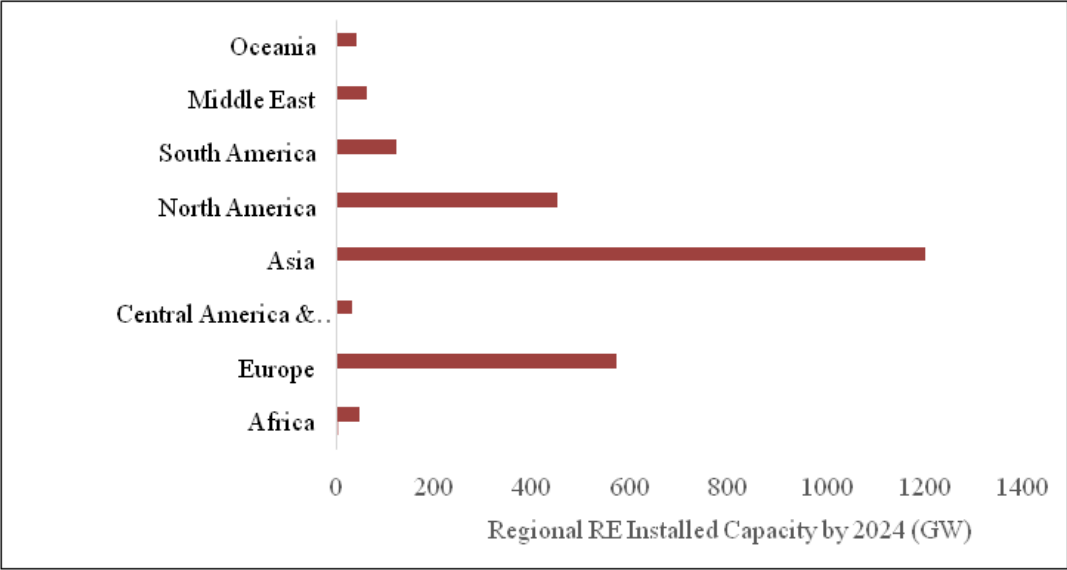


Fig. 3 Installation of Renewable Energy by Region (Li et al., 2024)

3.3 Renewable Energy Installed and Generated by Technology Globally

The distribution of power generated and installed globally in 2024 by various energy sources is shown in Figure 4. Hydropower takes the lead in both installation and generation with 4,560GW and 1,450GW, representing 58% and 44%, in that order (Zheng et al., 2024). This is followed by solar energy with 2,500GW installed and 1,200GW generated. This represents approximately 14% installed and 7.5 % generated (Hashemizadeh et al., 2024; Wang et al., 2024). Wind energy had a global installed capacity of 1,710GW and generated 900GW, corresponding to about 12% and 5.5%, respectively (Yiming et al., 2024). In comparison to other RE forms like hydroelectric and geothermal energy, solar and wind energy frequently have lower capacity factors. This is due to solar irradiance and wind speed fluctuations, which decrease generation, transmission, and distribution. Bioenergy ranked fourth with installed and generated capacities of 570GW and 150GW, accounting for 8% and 4% (Mirza et al., 2024), respectively. Geothermal energy takes the farthest position with the installation and generation at 114GW and 16GW, corresponding to 1.1% and 0.5%, respectively (Sampene et al., 2024).

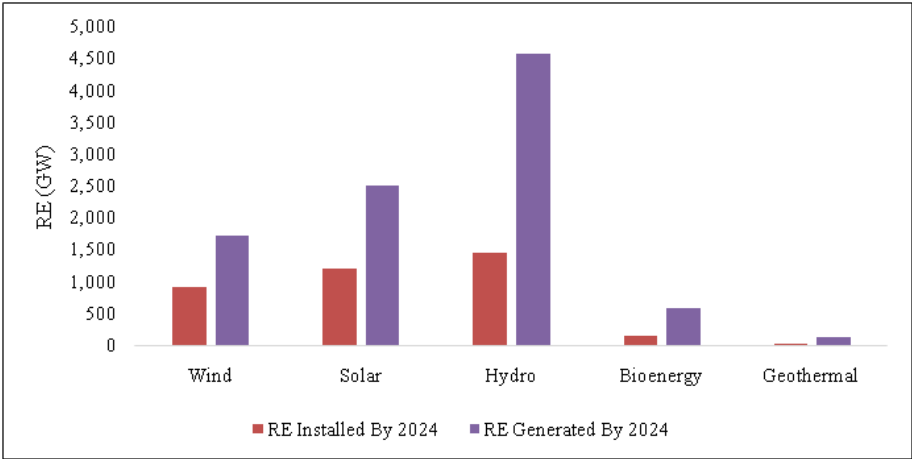


Fig. 4 Global Capacity Generated and Installed Renewables in 2024 (Mirza et al., 2024)

3.4 Renewable Energy Funding

The global RE funding by 2024 is depicted in Figure 5. Solar attracted the most investment, totaling more than USD1.75 trillion (Veronese et al., 2024). Wind power followed with an investment of USD1.15 trillion, and hydroelectricity engulfed USD0.80 trillion (Zhao et al., 2024). Bioenergy and geothermal energy recorded the least funding. The lower investment or funding in bioenergy was due to feedstock supply and cost (Saeed & Siraj, 2024), competition with other renewables such as solar and wind energy (Qing et al., 2024), environmental concerns such as land use and deforestation, and regulatory uncertainty (Nepal et al., 2024). Other challenges include high initial costs and risks, long development time, geographical limitations, technological barriers such as enhanced geothermal systems, which are still in experimental stages, and policy support (Chen et al., 2024). Solar and wind energy emerged as the leading recipients of global investments due to their rapidly declining costs and technological maturity, which make them highly competitive and low-risk. The modular nature, shorter development timelines, quicker returns and widespread availability of solar and wind resources across regions enhance their scalability compared to more location-bound options like geothermal or biomass, allowing for further appeal to investors. Strong policy support, incentives, auctions, and regulatory frameworks have also played a critical role in driving investment momentum in these sectors.

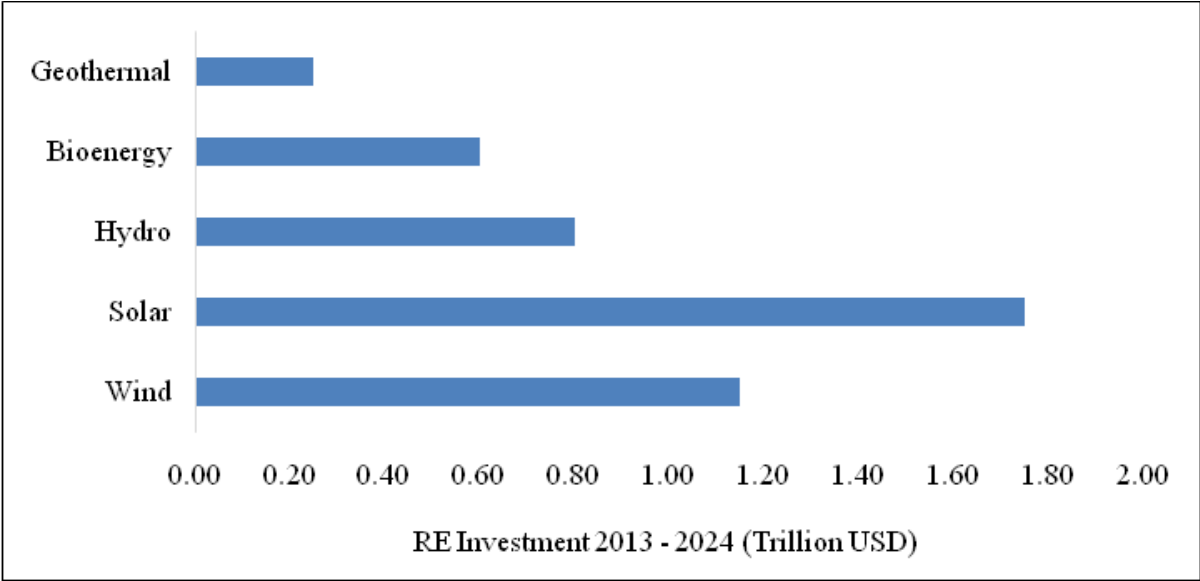


Fig. 5 Global Renewable Energy Investment in 2024 (Chen et al., 2024)

3.5 Renewable Energy Policies and Rewards

Figure 6 presents a comparative overview of key incentive mechanisms, revealing both growth patterns and shifts in strategic emphasis over the years. Feed-in Tariffs (FiTs) and premium payments were among the most widely used instruments at the start of the period, beginning with a value of 71 in 2013. Their popularity grew steadily, peaking at 125 in 2019. However, the years following saw a notable decline, with a sharp drop to 78 in 2020, likely due to global disruptions such as the COVID-19 pandemic and the transition toward more market-driven mechanisms. Although there was a modest recovery afterwards, FiTs reached only 90 by 2024, indicating a gradual shift away from this approach as other incentive models gained prominence.

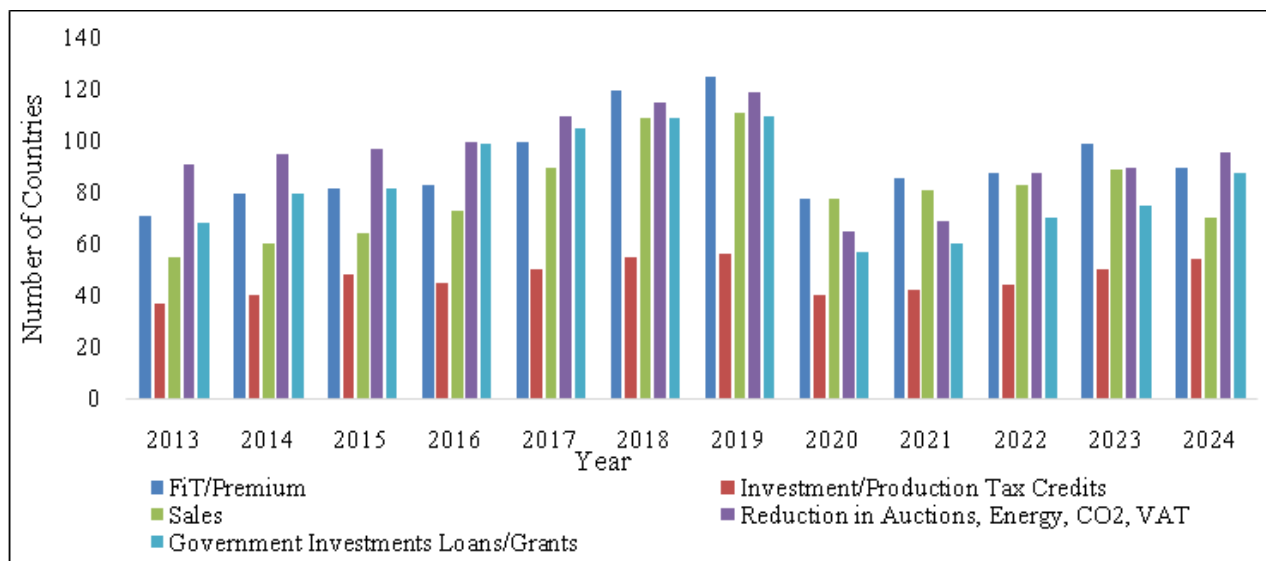


Fig. 6 Incentives Used for Global RE Expansion (Pan et al., 2024)

Investment and production tax credits showed a steady and reliable upward trend, rising from 37 in 2013 to 54 in 2024. This growth suggests consistent governmental support for private sector participation in RE development, positioning tax credits as a long-term, investor-friendly mechanism. Sales incentives experienced rapid growth during the mid-to-late 2010s, increasing from 55 in 2013 to a peak of 111 in 2019. However, like FiTs, these incentives saw a significant decline in subsequent years, dropping to 70 in 2024. This trend may reflect a global policy shift from broad-based subsidies to more targeted and results-oriented strategies.

Reductions in auctions, energy tariffs, CO₂ taxes, and value-added taxes (VAT) also played a vital role in promoting RE. These mechanisms rose consistently from 91 in 2013 to 119 in 2019, before experiencing a dramatic dip in 2020. Despite this setback, there was a strong rebound in the following years, with figures reaching 96 in 2024. Their resurgence underlines the continued relevance of fiscal and regulatory adjustments in shaping market behaviour. Government investments, including loans and grants, followed a similar cyclical pattern. From 68 in 2013, they increased steadily to 110 in 2019 before dipping during the early 2020s. By 2024, government financial support had climbed again to 88, highlighting its importance in sustaining momentum, particularly in times of economic uncertainty or in less-developed markets.

4 Discussion

Despite significant progress in renewable energy (RE) adoption, both developed and developing nations continue to face major challenges in financing, policy consistency, and market volatility. Emerging economies, particularly in Africa and Central America/Caribbean, struggle with inadequate infrastructure, political instability, and limited financing options. South Sudan, for instance, had only 8% electricity access in 2021, reflecting the severity of these challenges. Political uncertainty and weak regulatory frameworks further discourage investment, hindering RE expansion. High upfront costs, lack of technical expertise, and insufficient incentives exacerbate the financing gap. Subsidised fossil fuels and hydropower often appear



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more cost-effective, reducing the competitiveness of RE. Limited grid infrastructure and planning capacity also impede the integration of RE into national power systems. To overcome these barriers, governments and international institutions must provide support through grants, subsidies, tax breaks, and fiscal incentives to de-risk investments and stimulate development.

Many financing mechanisms like Power Purchase Agreements (PPAs), Feed-in Tariffs (FiT), tax incentives (ITCs/PTCs), and Renewable Portfolio Standards (RPS) have been implemented globally. However, short durations of FiTs in countries like the UK and Denmark limit their long-term impact. Extending such policies from 1–2 years to 5–10 years or more would provide stability and attract investment. Alternative models like YieldCos and public-private partnerships (PPP) offer potential, though they come with drawbacks such as complex tax structures and limited reinvestment capacity.

Crowdfunding and impact investing present flexible, community-driven financing solutions. These methods increase access to capital but face challenges, including regulatory barriers and limited investor confidence. Long-term instruments like green bonds, ecological securities, and green loans offer lower-cost financing and stable returns. Securitising RE assets can also enhance market liquidity and reduce the cost of capital. Tax equity financing and performance-based incentives, rewarding actual energy output rather than installed capacity, further enhance investment viability. Carbon pricing, through direct taxes or cap-and-trade systems, creates financial incentives for low-carbon technologies. The Green Climate Fund (GCF) can bridge funding gaps for large-scale RE projects in high-risk regions. On-bill financing enables consumers to repay installation costs through utility bills, reducing upfront barriers.

Internationally, countries have employed varied strategies. Germany and China leveraged FiTs, VAT exemptions, and customs relief to promote solar and wind energy. The U.S. replaced FiTs with favourable tax rates, while the UK shifted to generation-based rewards. In contrast, South Africa failed to implement PPAs effectively, and countries like Sweden halted incentives due to fiscal constraints. Brazil's biofuel success stems from long-standing policies, and India's revised housing standards have boosted solar deployment. Key barriers to RE development include land rights issues, inadequate data transparency, and a shortage of technical skills. Addressing these through education, R&D investment, and policy reforms is critical. While some countries have advanced due to strong frameworks and incentives, many in Africa and Central America/Caribbean lag due to financial, legal, and infrastructural limitations.

Effective RE expansion requires international cooperation, innovative financing, consistent policy frameworks, and targeted incentives. This multi-split approach can help nations overcome existing challenges, promote sustainable development, and ensure a global transition to clean energy.



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5 Conclusion

In conclusion, this study affirms that effective RE deployment is heavily reliant on financing strategies, consistent policies, and supportive institutional frameworks. Despite remarkable progress in global RE adoption, especially in countries like China, the United States, and Germany, numerous challenges persist, particularly in developing regions. Financial constraints, weak regulatory environments, and political instability continue to hinder growth in Africa, the Caribbean, and parts of Asia. Without objective support, these regions risk falling further behind in the global energy transition. The analysis confirms that while mechanisms such as FiTs, PPAs, and ITCs have accelerated RE adoption, short policy durations and inconsistent implementation weaken long-term effectiveness. Countries that extended these policies and introduced innovations like green bonds, public-private partnerships, and tax equity financing achieved greater RE penetration. Moreover, performance-based incentives, securitisation of RE assets, and carbon pricing frameworks emerged as viable tools for enhancing investment stability and reducing perceived risks.

To close the financing gap and meet the 2060 net-zero targets, global collaboration is essential. National governments must ensure policy clarity, extend incentive durations, and de-risk private sector investments. Multilateral institutions and development banks should increase access to concessional financing and technical assistance for vulnerable regions. Additionally, community-driven models such as crowdfunding and on-bill financing offer promise for decentralised RE systems, particularly in off-grid rural communities. Ultimately, achieving a resilient, low-carbon energy future requires a multi-dimensional approach. Combining robust financing models, clear regulatory signals, and inclusive policy planning will be critical in fostering sustainable RE development. Governments, investors, and civil society must work collaboratively to increase RE financing to unlock the full potential of clean energy and secure energy equity for future generations.

Declaration of interest
None.

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Biodiesel Production from Linseed Oil Catalyzed by Clay Doped Ionic Liquid – A soft computing approach

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Abstract

A novel clay-doped ionic liquid (CD-IL) heterogeneous catalyst was synthesized via calcination at 600 °C for four hours and applied in the transesterification of linseed oil to biodiesel. The catalyst was characterized using Scanning Electron Micrograph (SEM), X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET), Fourier Transform Infrared Spectroscopy (FT-IR), and X-ray Fluorescence (XRF), while linseed oil suitability was confirmed by FT-IR and Gas Chromatography Mass Spectrometry (GC-MS) analyses. Process optimization using Response Surface Methodology (RSM) produced a quadratic polynomial model with $R^2 = 0.9843$, adjusted $R^2 = 0.9557$, and predicted $R^2 = 0.8389$. Optimal conditions for a maximum biodiesel yield of 92.24% were obtained at 2.188 wt.% catalyst loading, 6.064:1 methanol-to-oil molar ratio, 1.74 h reaction time, 64.3 °C temperature, and 396.83 rpm agitation speed. To validate RSM predictions, Artificial Neural Network (ANN) and Adaptive Neuro-Fuzzy Inference System (ANFIS) models were developed. The ANN achieved $R^2 = 0.999$ with an MSE of 0.0210, while ANFIS provided $R^2 = 0.99$ with a lower MSE of 0.00070, confirming superior predictive accuracy. The biodiesel produced satisfied ASTM D6751 standards, demonstrating the efficiency of the CD-IL catalyst and the robustness of the hybrid optimization and modelling approach.

Keywords: Response Surface Methodology, Artificial Neural Network, Linseed oil, Transesterification, Biodiesel

1. Introduction

Environmental pollution, rising energy demand, and the finite nature of fossil fuels have driven the search for alternative, sustainable energy sources such as bio-fuels. Bio-diesel, produced from renewable plant and animal oils, is an eco-friendly and cost-effective substitute for petroleum diesel. Various vegetable oils have been explored as feed-stocks: Deka and Basumatary (2011) optimized yellow oleander oil and achieved high yields; Basumatary et al. (2021) reported 92.84% from jatropha oil; Brahma et al. (2023) obtained 95.82% from a mixed oil system at mild conditions; and Saikia et al. (2023) reported 96.7% with soybean oil. Linseed oil, derived from mature flax seeds (*Linaceae* family), is commonly extracted by solvent methods. It contains high levels of polyunsaturated triglycerides and exhibits physicochemical

properties comparable to petrodiesel, meeting ASTM biodiesel standards (Dixit et al., 2012; Ogunkunle et al., 2022). These attributes make it a strong candidate for bio-diesel production.

Catalysts play a central role in transesterification. Homogeneous catalysts often yield fast conversions but complicate product separation and promote soap formation in high-FFA systems (Basumatary et al., 2023). Heterogeneous catalysts, in contrast, can be prepared from low-cost renewable materials, reused multiple times, and simplify purification (Nadeem et al., 2021). Several promising solid catalysts have been reported: biomass-based (plantain peel, cocoa pod, Musa champa peduncle), metal–organic frameworks (MOFs), and nanostructured oxides (Basumatary et al., 2024; Nath et al., 2023; Ruatpvia et al., 2023). Clay minerals are particularly attractive because of their abundance, thermal stability, porosity, and ion-exchange capacity. They have shown strong catalytic activity in the transesterification of various oils, including Gmelina (Ude & Onukwuli, 2019), sunflower (Salmasi et al., 2020), and waste frying oils (Inayat et al., 2019).

Ionic liquids (ILs) are salts with melting points below 100 °C and tunable properties. They have been applied as phase-transfer and esterification catalysts (Liu et al., 2012; Lin et al., 2021). Heterogenized ILs, such as heteropolyanion-based systems, combine the advantages of ILs with easier recovery (Dadhania et al., 2021). To date, no work has benchmarked the modelling of linseed oil transesterification using a clay-doped ionic liquid (CD-IL) catalyst. This study fills that gap by evaluating response surface methodology (RSM), artificial neural networks (ANN), and adaptive neuro-fuzzy inference systems (ANFIS) for bio-diesel optimization.

Optimization tools have been widely used in bio-diesel research. RSM establishes polynomial models to capture interactions between variables (Balajii & Niju, 2020), but its predictive scope is limited. ANN and ANFIS, as soft-computing methods, excel at handling nonlinearities. ANN has been applied to waste sunflower oil and algae-derived oils, often outperforming RSM (Okpalaeke et al., 2020; Kolakoti, 2020). ANFIS has shown high accuracy in microalgae and *Thevetia peruviana* bio-diesel studies (Nassef et al., 2021; Ogaga et al., 2017). Comparative analyses across feedstocks such as palm kernel oil and waste vegetable oil often indicate ANFIS superiority (Hariram et al., 2019; Betiku et al., 2021; Ameghanawon et al., 2021).

2. Materials and Methods

2.1 Materials

Linseed oil was obtained from the National Research Institute, Umudike. Clay was chosen as the catalyst base material for modification due to its availability and favourable physicochemical properties. Imidazolium salt (98%), bromoethane (98%), and methanol (99%) were purchased from Sigma-Aldrich, Poole, England.



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2.1.1 Apparatus

Key equipment included: 250 mL three-necked and 500 mL round-bottom flasks, thermometers, stirrers, a hot plate magnetic stirrer, storage containers, condensation and distillation units, burettes, conical flasks, beakers, measuring cylinders, a stopwatch, and 1 L separating funnels for phase separation. A vacuum rotary evaporator and muffle furnace were also used.

2.2 Experimental Procedure

2.2.1 Catalyst synthesis

Alkyl imidazolium ionic liquid was synthesized by reacting imidazolium salt with bromoethane in a 1:3 molar ratio. The reaction was carried out in a round-bottom flask at 40–50 °C for 8 hours under stirring (100 rpm). The ionic liquid was collected and stored at room temperature (Dadhania et al., 2021; Lin et al., 2021). For catalyst preparation, the synthesized IL was blended with clay in a 2:1 weight ratio and aged for 12 hours.

The mixture was oven-dried at 105 °C and calcinated at 300 °C for 4 hours in a muffle furnace. The resulting clay-doped ionic liquid (CD-IL) was stored in airtight containers (Karmakar et al., 2020).

2.2.2 Characterization of clay

Raw and modified clays were characterized according to ASTM D4067 (1986). FTIR was used to identify functional groups, SEM for surface morphology, and XRD for mineralogical composition.

2.2.3 Transesterification process

For each reaction run, 30 g of linseed oil was placed in a flat-bottom flask mounted on a magnetic stirrer. Methanol and the CD-IL catalyst were premixed and introduced into the flask. The mixture was stirred at 300 rpm under the selected conditions. After completion, the mixture was cooled and transferred to a separating funnel for overnight settling. Two layers formed: biodiesel (upper) and glycerol (lower). The bio-diesel layer was washed with petroleum ether, shaken vigorously, and allowed to separate. Washing was repeated two to three times to ensure purity. The bio-diesel was then filtered and dried at 60 °C using a vacuum rotary evaporator to remove residual solvents. Reaction conditions were varied based on preliminary studies (Ude & Onukwuli, 2019). Independent variables included catalyst concentration (1–5 wt.%), methanol-to-oil molar ratio (4:1 – 12:1), temperature (40–80 °C), time (1–3 h), and agitation speed (150–350 rpm).

Bio-diesel yield was calculated using Equation (1).

$$\text{Yield (\%)} = \frac{\text{weight of methyl ester}}{\text{weight of oil used}} \times 100 \quad (1)$$

2.3 Experimental Factors Coding for the Transesterification Process

Table 1: Experimental design for the transesterification process

Factor	Units	Low level	Mid-low level	Mid-level	Mid-high level	High level
Methanol/oil ratio	Mol/mol	4:1(-2)	6:1(-1)	8:1(0)	10:1(+1)	12:1(+2)
Time	Hour	1(-2)	1.5(-1)	2(0)	2.5(+1)	3(+2)
Agitation speed	rpm	150(-2)	200(-1)	250(0)	300(+1)	350(+2)
Temperature	°C	40(-2)	50(-1)	60(0)	70(+1)	80(+2)
Catalyst concentration	Wt%	1(-2)	2(-1)	3(0)	4(+1)	5(+2)

The influence of five independent variables on bio-diesel yield was investigated: methanol-to-oil molar ratio (4:1, 6:1, 8:1, 10:1, and 12:1 mol/mol), catalyst concentration (1–5 wt.%), reaction temperature (40–80 °C), reaction time (1–3 hours), and agitation speed (150–350 rpm), as summarized in Table 1. Bio-diesel yield (%) was used as the response variable.

2.4 ANN Model Development

An artificial neural network (ANN) model was constructed to simulate the bio-diesel production process, drawing inspiration from the functionality of biological neural systems. The model incorporated three stages: training, validation, and testing. A multi-layer perceptron (MLP) with a feed-forward architecture and back-propagation learning algorithm was used. The network consisted of an input layer with five neurons corresponding to the input parameters (catalyst concentration, methanol/oil ratio, reaction time, temperature, and agitation speed), one hidden layer containing ten neurons, and an output layer representing the bio-diesel yield (%). The experimental data-set was randomly divided into training (70%), validation (15%), and testing (15%) subsets, following the procedure outlined by Foroutan et al. (2021).

2.5 ANFIS Model Development

A fuzzy inference model was utilized to predict the transesterification process, as demonstrated in previous studies (e.g., Betiku et al., 2016). The model incorporated five input variables: catalyst concentration (wt.%), methanol-to-oil molar ratio (mol/mol), reaction time (hours), temperature (°C), and agitation speed (rpm) to predict a single output: biodiesel yield (%). This approach was designed to capture and analyze the non-linear behaviour of the system. The modelling was carried out using MATLAB R2015b with its fuzzy logic toolbox.



3. Results and Discussion

3.1 Physicochemical properties of Linseed oil

Table 2: Linseed oil's characterization

Physicochemical properties	Linseed oil
Specific gravity	0.8815
Acid value (mg/OH)	8.976
Peroxide value	4.78
Saponification value (mgKOH/g)	253.49
Iodine value (gI ₂ /100g)	81.6
Kinematic viscosity at 40 °C (mm ² /s)	52.685
Flash point	59
Cloud point	-2.89
Pour point	-3.17
Moisture content (%)	0.17
Oxidation stability @110°C	4.2
Refractive index	1.4638
Free fatty acid (FFA) (%)	4.4488
Molecular weight	688.30

The physicochemical properties of linseed oil (Table 2) show a high acid value (8.976 mg KOH/g) and free fatty acid (FFA) content (4.488%), which are unsuitable for direct single-step transesterification due to the risk of soap formation and poor glycerol separation. Pre-treatment is therefore required. The saponification value (253.49 mg KOH/g) and peroxide value (4.78 meq/kg) suggest that the oil is not highly prone to rancidity. Its iodine value (81.6 g I₂/100 g) indicates a moderate level of unsaturation, implying the presence of unsaturated triglycerides. The specific gravity (0.8815) confirms the need for processing before direct use as bio-diesel (Bai et al., 2021). The oxidation stability of 4.2 hours exceeds the ASTM D6751 minimum (3 hours), likely due to the extraction method. The viscosity (52.685 mm²/s), though high, is comparable to Thevetia peruviana oil (57.34 mm²/s) reported by Ighose et al. (2017), showing its potential as a quality feed-stock. The cetane number further highlights its suitability for bio-diesel production.

3.2 FTIR Spectral Analysis of Linseed Oil

FTIR analysis in Fig. 1 revealed absorption bands at 749.2 cm⁻¹ (=C–H bending), 995.2 cm⁻¹ (C–O/C–O–C stretching), 1114.5 cm⁻¹ (C=C bending), 1640.0 cm⁻¹ (aromatic compounds), 2776.9 cm⁻¹ (O–H

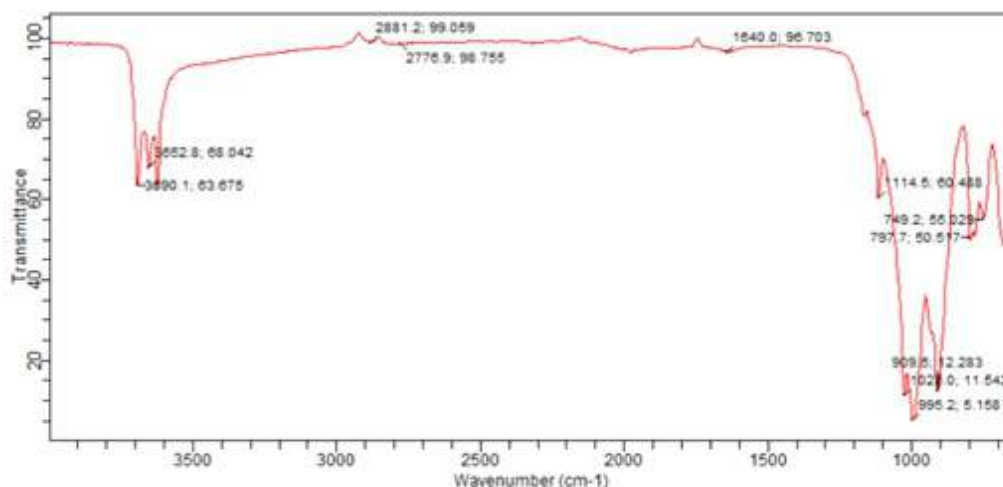


Fig. 1. FTIR of raw Linseed oil

3.3 Fatty Acid Profile of Linseed Oil

The fatty acid composition of linseed oil was analyzed using gas chromatography–mass spectrometry (GC-MS). Results showed that 13.55% of the fatty acids are saturated, while 86.5% are unsaturated. According to Qasemi et al. (2021), linseed oil is classified in the oleic acid group, with linolenic acid (56.5%) and linoleic acid (14%) identified as the dominant unsaturated fatty acids. Nikos et al. (2019) reported that this composition indicates a high proportion of unsaturated triglycerides, which is favourable for transesterification. Furthermore, the fatty acid profile was found to be comparable to those of other common biodiesel feedstocks (Wang et al., 2021). These findings are consistent with the study of Nwosu-Obieogu et al. (2024), who modelled and optimized shea butter transesterification using a clay-doped barium ionic liquid catalyst.

3.4 Characterization of the Synthesized Catalyst

3.4.1 FTIR of the clay synthesized catalyst

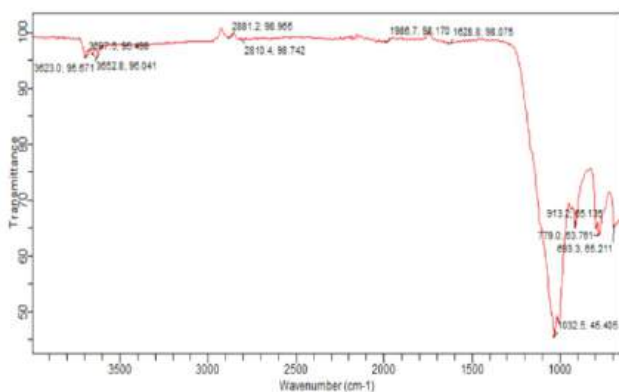


Fig. 2a. FTIR analysis of raw clay

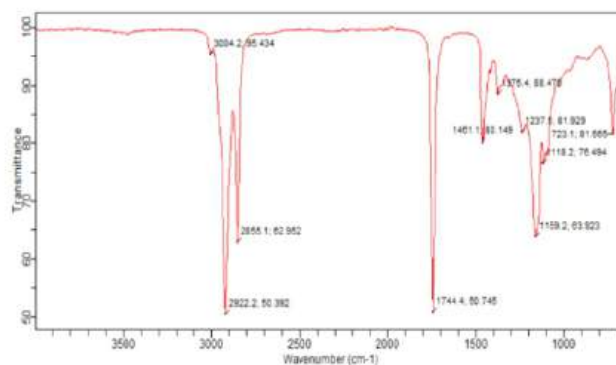


Fig.2b. FTIR of CD-IL

FTIR spectroscopy in Figs. 2a and b identified functional groups in the raw clay and CD-IL (clay doped with ionic liquid). Major bands included Si–O–Si linkages, C–Cl (aliphatic chloro compounds), C–H stretches (aromatic/vinyl), Si–O–C (organosilicone), Si–O stretching, C=C, –OH (primary alcohols), and Al–OH–Al vibrations. The Si–O–Si deformation band at 693.3 cm^{-1} persisted in both raw and modified samples with little intensity loss, suggesting minor structural changes. The Al–OH–Al band at 913.2 cm^{-1} decreased in the modified catalyst, likely due to partial dissolution of Al^{3+} octahedral cations, consistent with Rezanian et al. (2021). Si–O stretching at 1032.5 cm^{-1} in raw clay shifted to 1159.2 cm^{-1} (CD-IL), indicating increased silica content or altered bonding. A new band at 1744 cm^{-1} in CD-IL corresponded to C=O stretching, confirming ionic liquid functionalization. The absence of cyanide-related bands further suggested improved catalytic suitability.

3.4.2 SEM of the catalysts

SEM micrographs (Figs. 3a and b) showed that CD-IL had more pores and larger pore sizes than raw clay, reflecting structural reorganization and increased surface area after modification. These textural changes suggest enhanced catalytic activity. Similar observations have been reported for $\text{K}_2\text{CO}_3/\text{Talc}$ catalysts (Salmasi et al., 2020), alkaline-activated clay for gmelina seed oil (Ude & Onukwuli, 2019), ionic liquid-modified clay for shea butter transesterification (Nwosu-Obieogu et al., 2024), and barium-doped clay for linseed oil bio-diesel (Onukwuli et al., 2023).

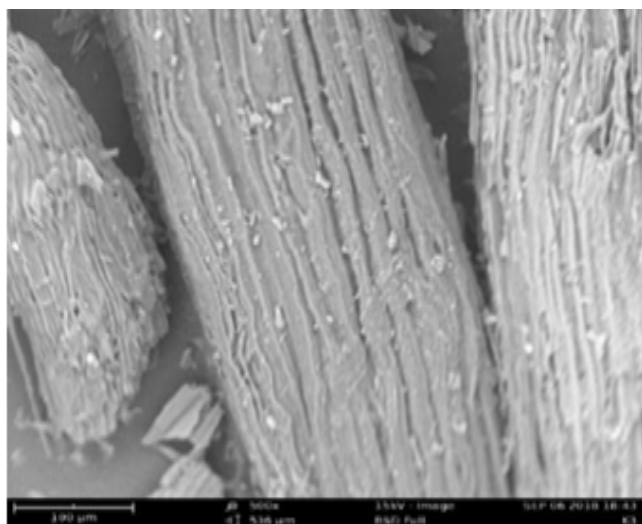


Fig. 3a. SEM of the raw clay

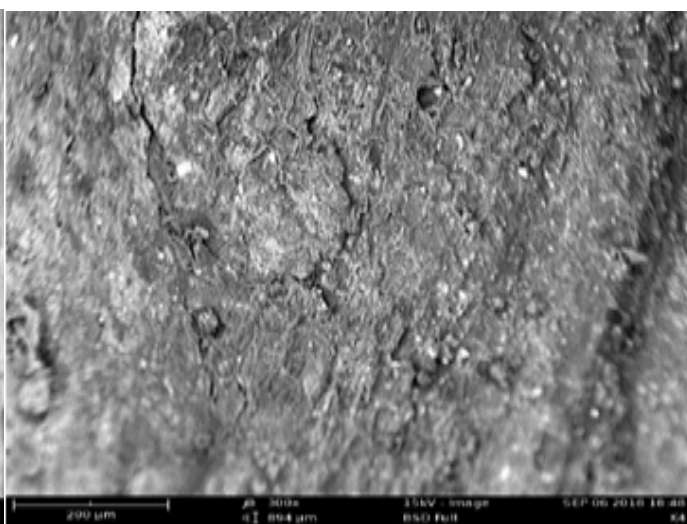


Fig. 3b. SEM of the catalyst

3.4.3 XRF of the catalyst

Table 3. XRF evaluation

Elements	RC	CD-IL	Recycled CD-IL
SiO ₂	62.051	61.790	60.323
V ₂ O ₅	0.189	0.192	0.190
Fe ₂ O ₃	3.971	4.072	4.001
SO ₃	0.341	0.232	0.325
CaO	0.331	0.366	0.321
K ₂ O	0.228	-	-
BaO	0.130	-	-
Al ₂ O ₃	27.323	27.449	27.412
TiO ₂	4.354	4.306	4.231
Cl	0.561	0.684	0.593
ZrO ₂	0.265	0.261	0.253
HNO ₃		0.131	0.128
Na ₂ CO ₃	-	0.265	0.255
Concentration (wt %)			

XRF analysis (Table 3) showed clay contained Si, Al, Ti, Fe, and oxides typical of heterogeneous catalysts. After alkyl halide modification, Cl increased, confirming ionic liquid incorporation. Reduced SiO₂, increased Al₂O₃, and enhanced acidity supported improved catalytic performance, consistent with Pavlović et al. (2020) and Nwosu-Obieogu et al. (2023).

3.4.4 XRD analysis

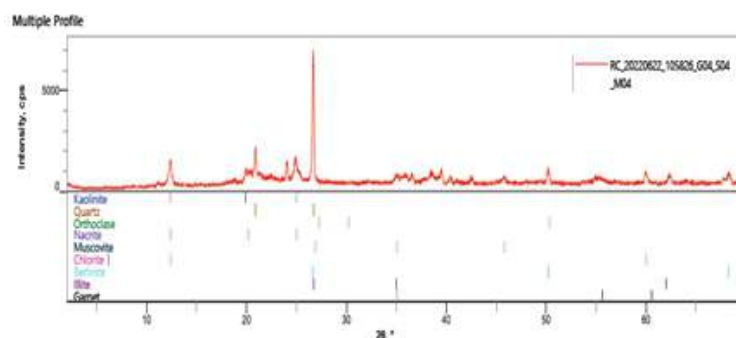


Fig. 4b. XRD evaluation of catalyst

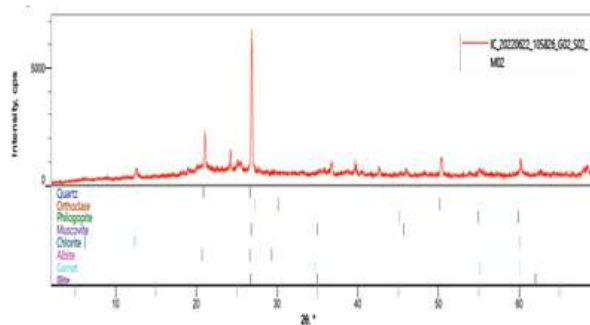


Fig. 4a. XRD evaluation of the clay

The raw clay diffractogram (Fig. 4a) showed a major peak at $2\theta = 27^\circ$, characteristic of kaolinite, along with peaks of quartz, alumina, and silica. In the CD-IL catalyst (Fig. 4b), this peak shifted slightly to $2\theta = 27.4^\circ$, indicating structural changes from ionic liquid incorporation. New peaks corresponding to illite, muscovite, and nacrite further confirmed mineralogical modification. These results align with findings by Bargole et al. (2021) on clay-based catalysts for biodiesel production.

Table 4 Experimental runs for linseed oil transesterification

Run	Catalyst con.	methanol/oil ratio	time	temperature	Agitation speed	Biodiesel yield	RSM predicted yield	ANN predicted yield	ANFIS predicted yield
	wt %	mol/mol	hour	°C	rpm	%			
1	2	6	2.5	70	400	89.5	92.66	90.99	92.65
2	4	6	2.5	50	400	79.38	79.38	79.1	79.37
3	3	8	2	60	500	91.15	91.15	90.85	91.14
4	3	4	2	60	300	85.26	85.26	85.26	84.40
5	3	8	3	60	300	81.66	81.66	81.87	81.65
6	4	6	2.5	70	200	79.93	79.93	79.66	79.92
7	4	10	1.5	70	200	75.73	75.73	76.91	75.72
8	2	10	2.5	70	200	83.42	83.42	83.65	83.41
9	2	6	1.5	50	400	90.5	90.5	90.49	90.49
10	1	8	2	60	300	82.94	82.94	83.1	84.40
11	3	8	2	60	300	85.37	85.37	85.39	84.40
12	3	8	2	60	300	85.37	85.37	85.39	84.40
13	4	10	2.5	70	400	89.84	89.84	89.85	89.83
14	2	10	1.5	50	200	83.2	90.66	90.62	90.65
15	3	8	2	60	300	85.37	85.37	85.39	84.40
16	4	10	1.5	50	400	82.76	82.76	82.85	82.75
17	2	6	2.5	50	200	72.2	71.71	71.51	71.70
18	3	8	2	60	300	85.37	85.37	85.39	84.40
19	3	8	2	40	300	73.44	73.44	73.58	73.43
20	5	8	2	60	300	80.01	80.01	79.78	80.00
21	2	10	2.5	50	400	71.23	69.98	68.58	69.97
22	2	10	1.5	70	400	86.84	86.84	86.48	86.83
23	4	6	1.5	50	200	79.29	79.29	79.05	79.28
24	4	6	1.5	70	400	79.83	79.83	79.52	79.82
25	3	12	2	60	300	89.2	88.1	88.65	88.09
26	3	8	2	60	300	85.37	85.37	85.39	84.40
27	3	8	2	60	300	85.37	85.37	85.39	84.40
28	3	8	1	60	300	84.98	84.98	84.91	84.40
29	4	10	2.5	50	200	85.82	85.82	85.8	85.81
30	3	8	2	80	300	78.61	78.61	78.83	84.40
31	3	8	2	60	100	83.95	83.95	84.01	81.95
32	2	6	1.5	70	200	81.09	79.97	79.72	81.95

$$\text{Yield of LSO FAME by CD-IL} = 84.9802 - 0.539167A + 0.695B - 0.536667C + 1.40917D + 1.74667E + 1.415 AB + 2.56 AC - 1.7075 AD - 0.34AE - 0.8225BC - 0.345 BD - 1.6175 BE + 3CD - 0.8575 CE + 1.3 DE - 0.967727 A^2 + 0.471023B^2 - 0.506477 C^2 - 2.33023 D^2 + 0.551023 E^2 \quad (2)$$

Table 4 shows the experimental matrix for linseed oil bio-diesel yield, highlighting the significant influence of process variables on production. A quadratic polynomial model was developed to describe the relationship between catalyst concentration (A), methanol/oil molar ratio (B), reaction temperature (C), reaction time (D), and agitation speed (E). Response Surface Methodology (RSM) was employed to optimize these parameters in the transesterification process. Using a Central Composite Design (CCD), 32 experimental runs were generated to evaluate the effect of each factor. The regression coefficients of the quadratic model (Equation 2) were estimated through multiple regression analysis. The first-order terms captured the individual effects of variables, while interaction and quadratic terms described combined and nonlinear influences. Comparison of experimental results with predictions from RSM, Artificial Neural Network (ANN), and Adaptive Neuro-Fuzzy Inference System (ANFIS) demonstrated close agreement, confirming the models' accuracy and reliability for process optimization (Betiku et al., 2016; Nwosu-Obieogu et al., 2024b; Onukwuli et al., 2023).

Table 5. ANOVA for the model of bio-diesel yield by CD-IL for linseed oil



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Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	782.41	20	39.12	34.42	< 0.0001	Significant
A-catalyst con.	6.98	1	6.98	6.14	0.0307	
B-methanol/oil ratio	11.59	1	11.59	10.20	0.0086	
C-time	6.91	1	6.91	6.08	0.0313	
D-temperature	47.66	1	47.66	41.93	< 0.0001	
E-agitation speed	73.22	1	73.22	64.42	< 0.0001	
AB	32.04	1	32.04	28.18	0.0002	
AC	104.86	1	104.86	92.25	< 0.0001	
AD	46.65	1	46.65	41.04	< 0.0001	
AE	1.85	1	1.85	1.63	0.2284	
BC	10.82	1	10.82	9.52	0.0104	
BD	1.90	1	1.90	1.68	0.2220	
BE	41.86	1	41.86	36.83	< 0.0001	
CD	144.00	1	144.00	126.69	< 0.0001	
CE	11.76	1	11.76	10.35	0.0082	
DE	27.04	1	27.04	23.79	0.0005	
A ²	27.47	1	27.47	24.17	0.0005	
B ²	6.51	1	6.51	5.73	0.0357	
C ²	7.52	1	7.52	6.62	0.0259	
D ²	159.28	1	159.28	140.13	< 0.0001	
E ²	8.91	1	8.91	7.84	0.0173	
Residual	12.50	11	1.14			not significant
Lack of Fit	4.65	6	0.7748	0.4933	0.7926	

Pure Error		7.85	5	1.57
Cor Total		794.92	31	
Std. Dev.	1.07	R ²	0.9843	
Mean	82.89	Adjusted R ²	0.9557	
C.V. %	1.29	Predicted R ²	0.8389	
PRESS	128.03	Adeq	22.3157	
		Precision		

Table 5 presents the ANOVA results for the quadratic model. The coefficients of determination ($R^2 = 0.9843$, adjusted $R^2 = 0.9557$, and predicted $R^2 = 0.8389$) demonstrate a strong correlation between experimental and predicted biodiesel yields. The model was statistically significant ($p < 0.05$), with most linear, interaction, and quadratic terms contributing significantly, except for reaction time, which showed no notable effect. The standard deviation (1.07) and mean response (82.89) yielded a coefficient of variation (C.V. = 1.29%), reflecting high precision and minimal variability. An adequate precision value of 128.03 confirmed the model's robustness and strong signal-to-noise ratio. Moreover, the nonsignificant lack of fit ($p = 0.7926$) validated the suitability of the model for describing the transesterification process. These outcomes align with previous studies on biodiesel optimization, including Olatunji et al. (2021) for shea butter oil, Ajala et al. (2017) for two-stage biodiesel synthesis, Roberto Cardoso Bastos et al. (2020) for sulfonated agro-waste catalysts, and Nwosu-Obieogu et al. (2024c) for neem seed oil epoxidation using melon seed peel catalyst.

3.5 ANN simulation

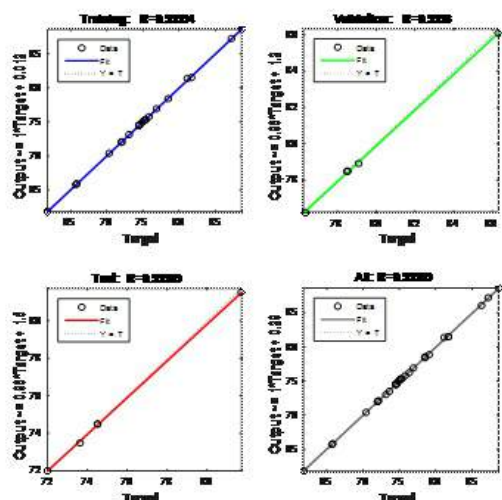


Fig. 5: ANN regression graph

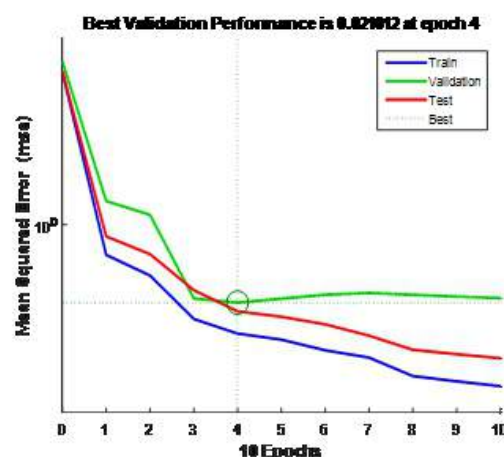


Fig. 6: MSE graph

An artificial neural network (ANN) with a multiple-input–single-output configuration was developed to predict bio-diesel yield from LSO. Experimental data were split into training (70%), testing (15%), and validation (15%) sets. The network employed a five-layer structure with one hidden layer of ten neurons, trained using the Levenberg–Marquardt (trainlm) algorithm. A tangent sigmoid (tansig) function was used in the hidden layer, while a linear (purelin) function was applied in the output layer. The number of hidden neurons (2–15) was varied through trial-and-error to minimize prediction error. Increasing the number improved model accuracy by reducing training errors. Model evaluation for linseed bio-diesel catalyzed by CD-IL showed excellent predictive power ($R^2 = 0.99$; $MSE = 0.021012$), confirming a strong correlation between experimental and predicted values as shown in Figs. 5 and 6. These findings are consistent with reports by Sai et al. (2019), Betiku et al. (2016), Suresh et al. (2021), and Nwosu-Obieogu et al. (2023b) on ANN-based bio-diesel prediction models.

3.6 ANFIS simulation

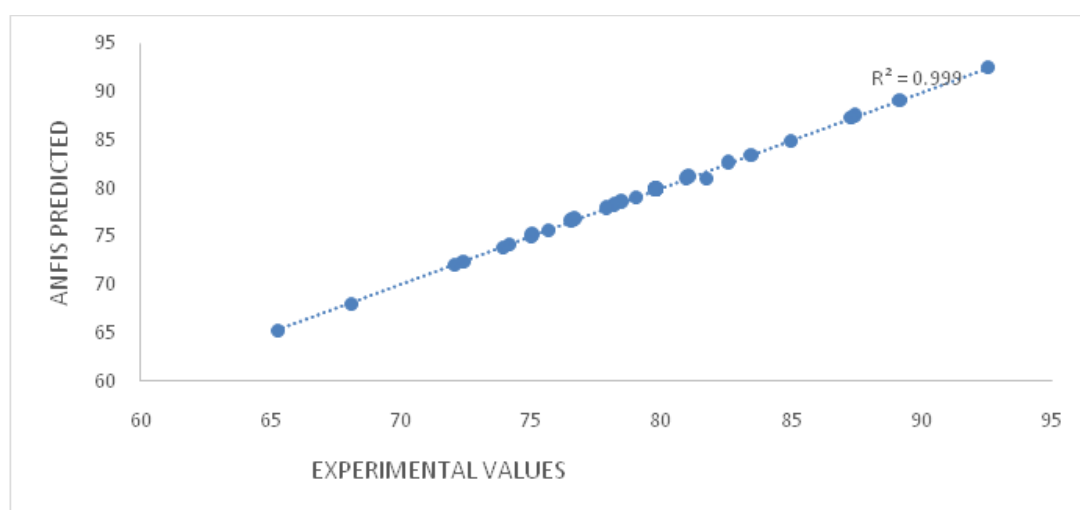


Fig. 7: R^2 ANFIS model for yield of linseed bio-diesel (yield) catalyzed with CD-IL

The developed Adaptive Neuro-Fuzzy Inference System (ANFIS) model was employed to predict bio-diesel production using the CD-IL catalyst, as shown in Fig. 7. The trapezoidal membership function (trap mf) was selected, as it produced the lowest mean square error (MSE) with a fixed epoch value of 1000. To evaluate the model's accuracy, the coefficient of determination (R^2) and MSE were used. The results for the ANFIS model in predicting linseed bio-diesel production catalyzed by CD-IL were as follows: yield ($R^2 = 0.99$), as shown in Fig. 9. The R^2 value of 0.99, which is close to 1, indicates strong predictive reliability of the model. These findings are consistent with similar studies on predictive modelling of bio-diesel production (Abdelkareem & Olabi, 2019; Betiku et al., 2016; Allen et al., 2024).

3.7 Optimization studies

From the optimization study, the maximum bio-diesel yield was achieved at 2.188 wt.% catalyst concentration, methanol/oil ratio of 6.064 mol/mol, reaction time of 1.74 h, temperature of 64.3 °C, and agitation speed of 396.83 rpm. These conditions gave a predicted yield of 92.24% with a desirability of 1, closely matching the experimental yield of 91.15% (error = 1.09%). The result is consistent with previous reports: 96.72% yield with clay-doped BaCl₂-IL (Nwosu-Obieogu et al., 2024), 89.54% with clay-doped BaCl₂ (Onukwuli et al., 2023), and 98.4% using triethylammonium amino acid IL (Wang et al., 2022). While ionic liquids exhibit high selectivity in transesterification, their cost limits industrial application; hence, clay, a cheap and abundant material, is doped with IL to improve economic viability. These findings also align with Nwosu-Obieogu et al. (2024a) on the shea butter bio-diesel, which was obtained under optimized conditions.

3.8 Biodiesel characterization

Table 6. Characterisation of the biodiesel from linseed oil

Physicochemical properties	Linseed biodiesel	ASTM D6751
Free fatty acid value (mgKOH/g)	0.16	
Aniline point (°F)	188.00	
Diesel index	57.39	
API gravity	30.53	
Iodine value (gI ₂ /100g)	3.12	
Cetane number	49.9	min- 47
Gross calorific value (J/g)	7855.32	
Kinematic viscosity @ 40 °C (mm ² s ⁻¹)	5.5	1.9-60
Specific gravity	0.854	
Flashpoint (°C)	172	min- 130
Moisture (%)	0.015	
Cloud point (°C)	9.50	-15 to 15
Acid value (mg KOH/g)	0.32	Max 0.5



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The physicochemical properties of linseed bio-diesel (Table 6) were compared with those of conventional diesel. The fuel showed a specific gravity of 0.854 and a moisture content of 0.015%, both within limits, though still susceptible to spoilage. Its iodine value (3.12) confirms the transesterification of unsaturated triglycerides. Acid value (0.32) and FFA (0.16) met ASTM standards, reducing corrosion and deposits. A high cetane number (49.9) indicates good combustibility, short ignition delay, and cleaner burning, surpassing the ASTM minimum of 47. Other properties, such as aniline point, diesel index, flash point, cloud point, calorific value, and viscosity (5.5 mm²/s within 1.9–6.0 ASTM range), also complied with standards, confirming fuel quality.

Conclusion

The CD-IL catalyst effectively enhanced linseed oil transesterification, producing bio-diesel with a 92.24% yield under optimized conditions. Characterization confirmed successful catalyst modification, while modelling (RSM, ANN, ANFIS) validated process predictability. The bio-diesel met ASTM standards, demonstrating high fuel quality. Incorporating clay with ionic liquid reduced catalyst cost while maintaining performance. Future work should include techno-economic and life-cycle assessments for large-scale bio-diesel production from diverse feed-stocks.



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Sustainable Energy Supply for Industrial Growth: Effective Lubricating oil Contamination Management Strategies for Gas Turbines

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Abstract

Lube oil contamination management is crucial for maintaining equipment reliability, reducing maintenance costs and extending machinery lifespan. Particle and water ingress are primary contaminants that compromise oil integrity, leading to premature wear, corrosion and equipment failure. This article provides ways to identify and mitigate particle and water ingress in lube oil systems of gas turbine generators. Effective contamination control begins with regular oil sampling and analysis, utilizing techniques such as spectroscopy and particle counting. Advanced filtration technologies, including membrane filters and centrifugation, are discussed as efficient analysis procedures. One sample Particle count reveals particulate contaminant ingress more than the allowable particulate concentration at 25/23/18, the limit was 17/15/12. The Spectrometer analysis reveals wear metals above the acceptable range (Copper at 65.87 ppm as against 50 ppm, Aluminium at 41.7 ppm as against 30 ppm, Silicon at 35.80 ppm as against 30 ppm and Chromium at 42.39 ppm as against 30 ppm). Oil purification systems, such as vacuum distillation and chemical treatment, were also explored. Contaminants were reduced in the managed sample thus: Copper (99.42%), Aluminium (97.07%), Silicon (98.28%), Chromium (100%) and dissolved water content (100%). Best practices for maintaining clean oil storage, handling and dispensing procedures are outlined, the paper emphasized the role of operator training and awareness in preventing lube oil contamination. Case studies demonstrate the efficacy of these strategies in real-world applications, showcasing significant reductions in contamination levels and associated maintenance costs. By implementing effective identification and mitigation strategies, organizations can minimize the risks associated with maintenance (bearing/shaft replacement) cost, particle and water ingress, ensuring optimal equipment performance and sustainable energy supplies for industrial growth.

Keywords: Contamination control, Equipment reliability, Oil condition monitoring, Particle mitigation, Water ingress.

1. Introduction

Lube oil is an essential element in the functioning of gas turbine generators (GTGs), contributing significantly to reducing friction, dissipating heat and ensuring optimal mechanical performance (Khan et al., 2020). The GTG is an internal combustion engine that uses a combination of air, fuel and heat to generate power. Key components of the GTG are the compressor, combustion chamber, turbine and generator. Air is drawn into the compressor, where it is compressed and heated. Fuel is added to the compressed air in the combustion chamber, and the mixture is ignited. The hot gas expands through the turbine, generating mechanical energy. The mechanical energy is converted into electrical energy by the generator. Gas turbines are widely used in power plants to generate electricity, drive compressors, pumps and other equipment in industrial applications. They are also used in aircraft engines to provide propulsion (Khan et al., 2020).



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Lube oil contamination control methods include the use of high-efficiency filters that remove particles and contaminants from the oil, preventing damage to turbine components. Regular inspection and replacement of filters are essential to maintain their effectiveness. Proper installation of seals, breathers, and vapour extractors is vital to remove water and gases from the oil, reducing the risk of corrosion and degradation. Operators and the Maintenance team are to use clean, dedicated containers for transferring oil to prevent cross-contamination. Oil should be stored away from potential sources of contamination, such as dust or moisture. Another approach is to clearly label all containers to prevent mix-ups with other lubricants. The efficiency and lifespan of these systems depend largely on the quality of the lubricant used (Smith & Patel, 2019). However, contamination can severely hinder performance and may lead to catastrophic equipment failures, resulting in costly repairs and extended operational downtime (Smith & Patel, 2019). The two primary contaminants that pose significant risks are particulate matter and water, both of which can infiltrate the lube oil system through various routes, compromising lubrication integrity (Johnson, 2021).

Contaminants can enter lube oil through multiple channels, including environmental exposure, wear and tear of components and inadequate maintenance practices. Particulate contamination often stems from the deterioration of mechanical parts, dust ingress or the introduction of foreign substances during maintenance activities (Williams et al., 2022). In contrast, water contamination can arise from condensation, leaks in cooling systems or poor sealing (Nguyen & Garcia, 2020). Both forms of contamination create an adverse environment for gas turbines, potentially leading to increased wear rates, diminished efficiency and eventual system failure (O'Brien, 2023).

Effectively managing lube oil contamination is crucial for the dependable operation of gas turbine generators. Various strategies for identifying and mitigating contamination exist, typically including regular quality monitoring, advanced filtration systems, and moisture control techniques. Studies have shown that particle contamination is the root cause of 82% of wear-related failures, highlighting the importance of effective contamination control. (Lee et al., 2021). Implementing these proactive measures helps preserve the integrity of the lubrication system and enhances the operational lifespan of gas turbine generators.

Regular monitoring serves as a fundamental step in contamination management. Techniques such as spectrometric analysis, particle counting and water detection methods offer valuable insights into lube oil condition and contamination levels (Thompson & Blake, 2018). These methods enable operators to track contamination trends and initiate corrective measures before contaminant levels become critical. Incorporating real-time monitoring systems can further improve the ability to respond quickly to contamination events, thus minimizing potential damage (Kumar & Singh, 2022).

Filtration systems are also pivotal in controlling lube oil contamination. Advanced filtration technologies, such as microfiltration and nanofiltration, effectively remove both particles and water, thereby enhancing

the quality of the lubricant (Miller & Johnson, 2020). The design and maintenance of these filtration systems are crucial; operators must ensure filters are appropriately sized, routinely replaced and strategically positioned to capture contaminants before they circulate through the system (Fisher & Taylor, 2021).

Moisture control is another vital aspect of managing contamination. Water in lube oil can lead to emulsion formation, which adversely affects lubrication properties and increases the risk of rust and corrosion (Gonzalez et al., 2019). Effective moisture control strategies may include using water-absorbing materials, ensuring proper sealing within the system and maintaining optimal operating temperatures to reduce condensation (Brown & Green, 2022).

Beyond technical approaches, training and awareness among operators are crucial for effective contamination management. Personnel involved in the operation and maintenance of gas turbine generators must understand the sources and implications of lube oil contamination and the importance of following best practices for oil handling (Sullivan, 2023). Fostering a culture of proactive contamination management can significantly lower the risk of failures associated with lube oil quality.

Despite advancements in technologies and strategies for managing contamination, several challenges persist. The complexity of gas turbine systems and variations in operational environments can complicate the identification and mitigation of contaminants (Harrison & Lee, 2020). Additionally, economic constraints may lead to reduced maintenance budgets, potentially compromising lube oil quality. Organizations must recognize the long-term advantages of investing in contamination management practices, as the costs linked to equipment failures/replacement of bearings/shaft (running into 100,000/350,000 United States dollars respectively) and repairs can far exceed those associated with proper maintenance (Martinez et al., 2021).

Lube oil plays a vital role in maintaining the optimal performance and reliability of gas turbine generators. However, contamination can compromise equipment integrity, leading to catastrophic failures. Particle and water ingress are primary contaminants that can enter the lube oil system through various means. Water contamination arises from humidity, ingress through the lid of the oil console, condensation and coolant leakage.

2 Materials and Method

The methodology deployed was sampling the lube oil (DTE oil light C2340064) at four different times at equal intervals in two samples (before and after lube oil replacement) to identify and quantify particle contamination and water ingress, focusing on both laboratory and field sampling techniques.



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2.1 Sampling Techniques

a. Field sampling

Field sampling involved collecting lube oil directly from the operating GTG oil filter under normal working conditions at 80% load and 3,000 rpm. The lube oil temperature was 65°C. Sample 1 (before oil replacement/management) was taken four different times, and Sample 2 (after oil replacement) was taken one time. The following steps outline the procedure:

- **Equipment:** Clean, dry and sealed sampling containers (four in number) labelled #6366, #6346, #6337 and #001, (high-density polyethene bottles, to prevent contamination) were used (Miller, 2020).
- **Timing:** Fifty hourly samples were taken (during routine maintenance of the gas turbine) at regular intervals to ensure consistency (Jones & Smith, 2019).
- **Location:** Samples were taken from the lube oil filter of the GTG lube oil circulatory system.

2.2. Laboratory Sampling

In the laboratory, controlled conditions allow for more precise analysis of the lube oil. The methodology included:

- **Sample preparation:** Prior to testing, samples obtained from the GTG lube oil filter were stored at room temperature and analyzed within 48 hours to minimize changes in composition (Johnson, 2021).
- **Filtration:** A Filtration apparatus was used to separate particulate matter from the oil (Thompson, 2022). A filter with a pore size of 0.45 micrometre was used to capture significant particle sizes. The study focused on this mesh size because it is the same as that of the GTG lube oil filter.
- **Water content analysis:** We employed the Karl Fischer titration to accurately measure water content in the samples, providing a quantitative assessment of water ingress (Martinez et al., 2020).

2.3 Analytical Techniques

a. Particle identification

To identify and quantify particulate contamination, the following techniques were utilized:

- **Microscopy:** SpectroQ153 Minilab electron microscopy was used to provide detailed images of particles, allowing for size and morphology analysis as recommended by Lee (2021).

- **Laser particle size analyzer:** This method quantifies particle sizes and distributions, essential for understanding contamination levels (Khan et al., 2019).

b. Water analysis

Water contamination can be detrimental to lubricant performance. The methodology includes:

- **Spectroscopic techniques:** The standard for spectrometer analysis used was ASTM (American Society for Testing and Materials) standards-ASTM D6595. This standard test method covers the determination of wear metals and contaminants in used lubricating oils or hydraulic fluids using rotating disc electrode atomic emission spectrometry (RDE-AES). Fourier-transform infrared (FTIR) spectroscopy can detect water presence and other contaminants, offering rapid and non-destructive analysis (Davis, 2020).
- **Gravimetric methods:** Weighing the sample before and after drying provided a simple measure of water content as recommended by Parker (2019).

2.4 Data Analysis

Data collected from particle and water analyses were tabulated in Tables 1 (sample 1) and 2 (sample 2) and analyzed using the SpectroQ153 Minilab. Descriptive statistics summarized the data, to show contamination levels and operational parameters (Smith & Johnson, 2023).

Table 1: Wear, contaminant and chemistry result for oil analysis before management (Sample 1)

Sample #	6356	6345	6337	001
Unit Usage - mo				
Oil Usage - mo				
Oil Added - l				
Wear	85	85	85	30
Ferrous Idx - idx				
Chromium - ppm	42.39	27.81	35.63	.09
Copper - ppm	65.87	59.04	80.79	.44
LCont Ferrous - idx				
Iron - ppm	61.7	51.3	54.4	0.0
Lead - ppm	42.55	34.86	43.33	.34
Aluminum - ppm	41.70	34.17	44.13	0.00
Nickel - ppm	12.82	36.69	47.01	0.00
Tin - ppm	10.30	32.97	43.92	0.00
Titanium - ppm	12.77	27.14	40.84	.22
Contamination	85	85	85	85
Boron - ppm	2.97	13.01	18.94	.05
LCont NonFe - idx				
Cnts >4 - pmi	247.887	580.890	511.456	3.106
Cnts >6 - pmi	55.531	138.432	133.591	.740
Cnts >14 - pmi	1,915	2,406	10,645	.23
Cnts >22 - pmi	576	560	2,995	.2
Cnts >38 - pmi	67	102	64	.2
Cnts >56 - pmi	18.6	33.3	3.9	2.0
Cnts >70 - pmi	7.7	16.7	.7	2.0
ISO >4 - n/a	25	26	26	.19
ISO >6 - n/a	23	24	24	.17
ISO >14 - n/a	18	18	21	.12
Silicon - ppm	35.80	33.17	41.38	.56
Sodium - ppm	11.40	29.33	37.37	0.00
Water K.Fish - ppm	460.00	478.00	492.00	68.00
Contam Idx - idx				
NAS 1638 - idx	12	12	12	10
Chemistry	0	0	0	0
Barium - ppm	5.93	14.16	15.89	0.00
IR Oxidation - au	3.00	3.10	3.30	2.20
IR Nitration - au				
Visc 40C - cSt	29.9	30.9	30.5	29.0
Calcium - ppm	119.76	205.74	36.68	0.00
Total Acid - koh	0.00	0.00	.45	1.69
Magnesium - ppm	22.43	44.84	43.03	0.00
Molybdenum - ppm	17.14	49.07	60.61	.02
Phosphorus - ppm	192.43	401.60	227.02	.58
Zinc - ppm	119.60	78.82	95.16	.30
Water K.Fish - ppm	460.00	478.00	492.00	68.00
Visc 100C - cSt				

Table 2: Wear, contaminant and chemistry result for oil analysis after management (Sample 2)



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Unit Usage - hrs					
Oil Usage - hrs					
Oil Added - gus					
Wear	0				
Ferrous Idx - Idx					
Chromium - ppm	0.00				
Copper - ppm	.38				
LCont Ferrous - Idx					
Iron - ppm	1.5				
Lead - ppm	.76				
Aluminum - ppm	1.22				
Nickel - ppm	.01				
Tin - ppm	2.16				
Titanium - ppm	0.00				
Contamination	0				
Boron - ppm	0.00				
LCont NonFe - Idx					
Cnts >4 - pml					
Cnts >6 - pml					
Cnts >14 - pml					
Cnts >22 - pml					
Cnts >38 - pml					
Cnts >56 - pml					
Cnts >70 - pml					
ISO >4 - n/a					
ISO >6 - n/a					
ISO >14 - n/a					
Silicon - ppm	.62				
Sodium - ppm	0.00				
Water K.Fish - ppm	0.00				
Contam Idx - Idx					
NAS 1638 - Idx					
Chemistry	0				
Barium - ppm	0.00				
IR Oxidation - au					
IR Nitration - au					
Visc 40C - cSt	26.7				
Calcium - ppm	1.94				
Total Acid - koh					
Magnesium - ppm	5.51				

3 Results And Discussion

The Wear, contaminant and chemistry results for oil analysis before management (Table 1) revealed excessive particulate contaminant ingress, surpassing the allowable limits of 17/15/12, at 25/23/18. The standard for particulate contamination ingress limit 17/15/12 refers to the ISO 4406:1999 standard, which defines the cleanliness code for fluids used in hydraulic systems, including lubricating oils. The ISO 4406:1999 standard uses a code consisting of three numbers to classify the particulate contamination level in a fluid. The code is based on the number of particles per millilitre of fluid that are larger than 4, 6, and 14 micrometres, respectively.

Spectrometer analysis detected elevated wear metals: Copper: 65.87 ppm (vs. 50 ppm) - Aluminium: 41.7 ppm (vs. 30 ppm)- Silicon: 35.80 ppm (vs. 30 ppm) Chromium: 42.39 ppm (vs. 30 ppm). Kinematic Viscosity measured 29.9 cSt, within the acceptable range of 32 cSt $\pm$ 5%-10% at 40°C. Dissolved water content was 460 ppm, below the 800-ppm threshold, indicating some water ingress.

The wear contamination in oil indicates excessive friction and damage to the GTG components. This wear can be traced to inadequate lubrication, particle contamination, oil breakdown due to heat, oxidation, etc. The chemistry of the oil was, however, within limit as shown in Figure 1. The various colour indicators give alerts and fault alarms to maintenance and operators for quick decision making.

The Wear, contaminant and chemistry result for oil analysis after management (Table 2) showed that the sample 2 exhibited: - Particle count: 0.0/0.0/0.0, within limits- Wear metals within acceptable ranges: Copper: 0.38 ppm (vs. 50 ppm) Aluminum: 1.22 ppm (vs. 30 ppm)- Silicon: 0.62 ppm (vs. 30 ppm) Chromium: 0.0 ppm (vs. 30 ppm) Kinematic Viscosity: 26.7 cSt, within tolerance- Dissolved water: 0.0 ppm, below detection limits. These findings indicate significant improvement in the lubricant quality. Figure 2 shows that the oil is in good condition (as wear, contamination and chemistry of oil are all within range). We see that contaminants were reduced thus: Copper (99.42%), Aluminium (97.07%), Silicon (98.28%), Chromium (100%) and dissolved water content (100%).

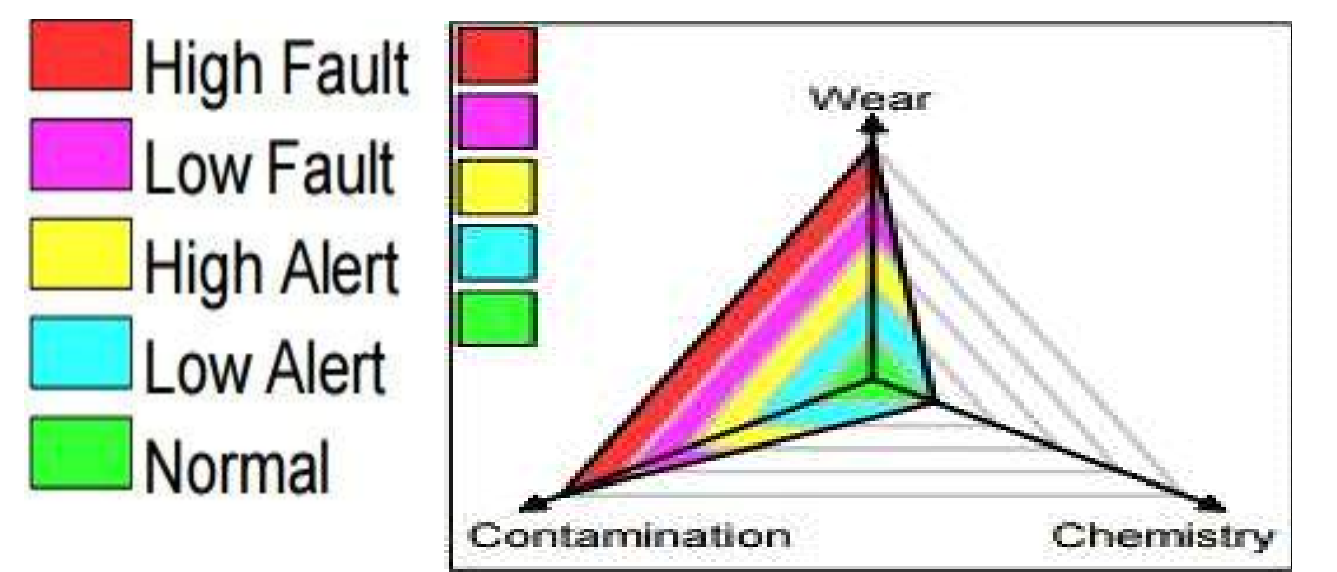


Fig. 1: Wear, contaminant and chemistry result for oil analysis before management (Sample 1) with key

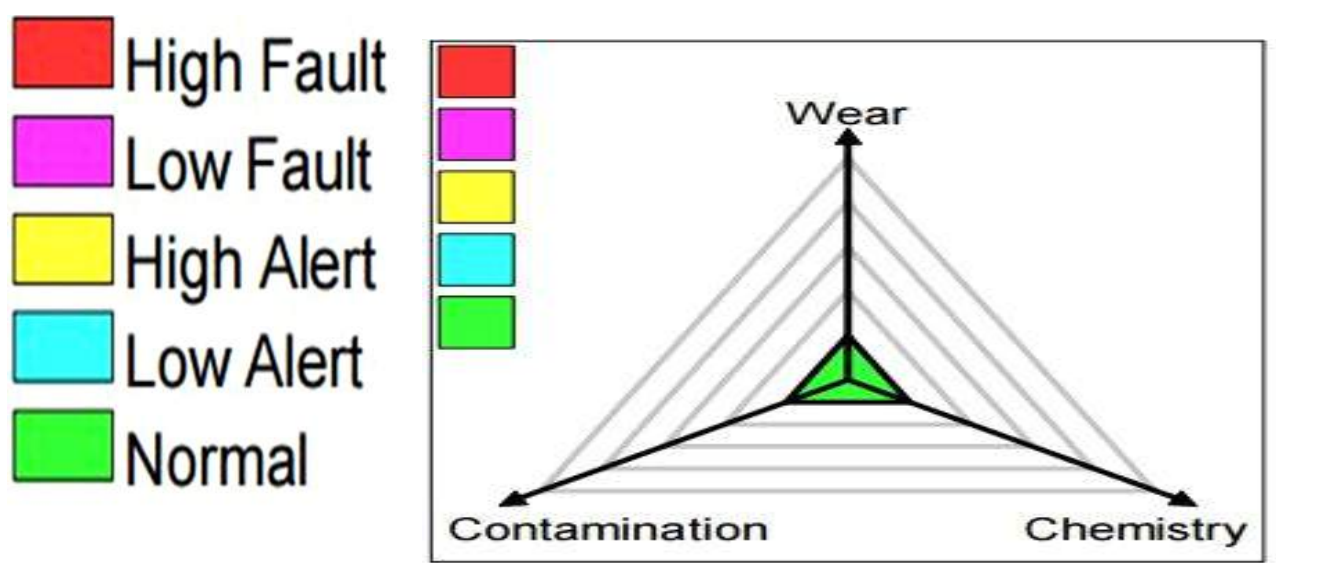


Fig. 2: Wear, contaminant and chemistry result for oil analysis after management (Sample 2) with key



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4 Conclusion And Recommendation

Effective management of lube oil contamination is essential for ensuring the performance, reliability/equipment longevity, reduced maintenance cost and efficiency of gas turbine generators. This is so because sustainable energy supply for industrial growth is tied to quality electricity supplies. Identifying and mitigating particle and water ingress is crucial for maintaining lubrication system integrity. By using the ISO 4406:1999 standard and method, we determined the particulate contamination level in the oil that reflects the level of contamination. This information was used to monitor the condition of the oil and to take corrective action. Again, by following ASTM standards for spectrometer analysis, we ensured that the analysis was performed accurately, precisely and consistently, providing reliable results that informed decision-making and maintenance activities. By understanding particle and water ingress, implementing prevention strategies, advanced filtration techniques, moisture control, ensuring constant monitoring of lube oil pressure, lube oil quality and filter differential pressure, ensuring no heat exchanger leakage, ensuring compliance to oil filter cleaning or procurement/replacement schedule, ensuring compliance to schedule sampling and lube oil analysis, installing water-absorbing filters, proper oil console covers and dehydration systems to eliminate water ingress, adherence to routine maintenance checks (predictive or/and preventive) to track wear metals and contamination and promoting operator education on the above findings; organizations can significantly mitigate the risks associated with lube oil contamination.

Ongoing and Future research should focus on correlating contamination levels with machinery performance metrics to develop predictive maintenance schedules. Research and development in this field will be necessary to address emerging challenges and support the sustainable operation of gas turbine systems across various industrial sectors.



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Assessment of the Potentials of Waste Chicken Fat Oil (CFO) and Papaya Seed Oil (PSO) Hybrid Feed-stock for Bio-diesel Production

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Abstract

This paper examines the production of hybrid bio-diesel feed-stocks through waste chicken fat oil (CFO) and papaya seed oil (PSO) to reduce food versus fuel crises. Oils were extracted (Soxhlet extraction of PSO; wet rendering of CFO), a blend was made in the ratio of 1:1, and the physicochemical properties were determined. The viscosity (45.98 mm²/s), acid value (4.39 mg KOH/kg) and molecular weight (535.84 g/mol) were also within the preferred range in line with diesel standards, and the ester value was 99.54 per cent. GC-MS identified complementary fatty acid: PSO donated a high weight of linoleic acid (14.41%) to achieve the fluidity, whereas, CFO contributed saturated esters (e.g., palmitic acid) to achieve oxidative stability. FTIR established transesterification through ester peaks (C=O 1740 1750 and C-O 1000 1200 cm⁻¹). FTIR revealed residual impurities, including O-H 3272 3749 cm⁻¹. The hybrid balanced CFO exhibited a stability (iodine value: 27.29 gI₂/100g) and PSO, a flow attribute, which presented the viability of types of sustainable feed-stock. It would thus be preferable to purify further to remove moisture and contaminants to be ASTM/EN compliant.

Keywords: Hybrid, Chicken fat oil, Papaya seed oil, Feed-stock, Bio-diesel

1. Introduction

The issue of fossil sources depletion and energy crises in recent years caused an increase in the number of studies devoted to alternative energy sources, which should replace fossil fuels (Barman et al., 2022). Vegetable oils and their derivatives are among such alternatives that show prospects (Graboski and McCormick, 1998). Their use in compression ignition engines was pioneered by Rudolph Diesel, who originally used peanut oil. Several oils (coconut, soybean, sunflower, safflower, linseed, rapeseed and palm oil) have been studied. Nevertheless, they are frequently used, resulting in injector clogging and in thickening of the crankcase oil that may affect engine performance as a result of poor atomization (Mba et al., 2021; Soo-Young, 2011).

In order to overcome these difficulties, techniques like transesterification, micro-emulsification and viscosity reduction have been devised, the most useful of them all being transesterification. This is done by



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transforming vegetable oils into alkyl esters, which are similar to diesel (Freire et al., 2012). In most cases, methanol is adopted in transesterification since it is cheap (Verulu et al., 2022; Widvan et al., 2002). What is obtained is called bio-diesel, which is renewable and can be made out of sustainable resources such as used cooking oil and animal fats, which explains why it is an appealing alternative (Umeagukwu et al., 2024; Rincon et al., 2014).

Due to the present volatility in oil markets, bio-diesel offers a great prospect to countries such as Nigeria to move on and stop depending on crude oil (Esonye et al., 2018). It is also less harmful in terms of emission of the bad pollutants, the particulate emissions, soot, and carbon monoxide are less as compared to petroleum-derived diesel, as it is oxygenated (Munack et al., 2001; Demirbas, 2009).

Various countries have different choices of oils to use in the production of bio-diesel, e.g. rapeseed and sunflower oils as a favoured oil in Europe, soybean oil in the U.S., palm oil in Malaysia and Indonesia, as well as coconut oil in the Philippines (Rashid et al., 2009). Whenever dependence is put on traditional vegetable oils, there exist concerns about food supply pressures, which affect prices and availability (Ume et al., 2024).

Research is still widening the scope of feedstocks used in the development of bio-diesel, concentrating on the waste products and animal fats to address the food-versus-fuel dilemma. Waste chicken fat and papaya seed oil are hybrid feedstocks that have a prospect as they contain beneficial fatty acids (oleic, linoleic, palmitic, stearic, cis-vaccenic, and octadecadienoic) that can be used to produce fatty acid methyl esters (FAME) (Esonye et al., 2023). This paper seeks to outline the synthesis and physicochemical properties of these hybrid oils that will help add knowledge on bio-diesel synthesis.

2. Materials and Methods

2.1 Materials

The materials that were needed in this work include a combination of glassware, analysis reagents and electronic gear. The glassware consists of conical flasks, beakers, a Soxhlet extraction apparatus, a measuring cylinder, a pycnometer, a three-neck round-bottom flask, a reflux condenser, a separating funnel, a viscometer, petri dishes, filter paper, masking tape, used spatulas, forceps and masking foil all made by Pyrex. All the reagents used are of analytical grade and provided by May and Baker, and they include, methanol, ethanol, sodium hydroxide, sodium thiosulfate, chloroform, acetic acid, potassium hydroxide, sulfuric acid, hydrochloric acid, phenolphthalein, and starch. The electronic equipment also contains a weighing scale, a hot plate in the laboratory, a heating mantle, a tabletop refractometer, a gas chromatography machine, and a Fourier transform infrared spectrophotometer.



2.2. Methods

2.2.1. Feedstock preparation

Chicken fat was collected as a waste product at the chicken market within the Abakaliki International Market in Ebonyi State. It was cleaned and filtered to get rid of any contaminants and then left to undergo wet rendering, at 50°C, for a period of 20-25 minutes to extract the oil. In the extraction of papaya seed oil, 100 g of sieved samples were put in cotton material and inserted into the thimble of a Soxhlet extractor that was joined to a 500 ml round flask that had 250 ml of n-hexane. The heating mantle was used to heat the setup and circulate water around the condenser. The extraction was done until all the oil extracted was obtained, then the spent sample was discarded and the oil -n- hexane mixture was separated using distillation in a water bath, n- hexane was allowed to evaporate, and the oil in the flask was sealed and stored in a cool and dry place. The percentage oil yield was calculated from the equation (1) below.

$$\text{Oil yield (\%)} = \frac{\text{Weight of oil}}{\text{Sample weight}} (100) \quad (1)$$

2.2.2. Physicochemical characterization of waste cooking oil, pawpaw seed oil and their blend

The obtained oils and their hybrid were characterized for moisture, free fatty acid, acid value, refractive index, peroxide value, iodine value, saponification, flash and fire point, kinematic viscosity, cloud and pour point, specific gravity, molecular weight and energy value. The oil properties as a feedstock for bio-diesel were characterized to determine its physicochemical properties by adopting the method used by Onukwuli et al. (2017) and the ASTM D6751-02 standard (ASTM, 2002).

- a) Moisture content: Moisture content was determined according to equation (2). The amount of moisture present in the oils was quantified. 5 g of the oils were weighed into a dry, clean, petri dish. The dish with the sample was introduced into the laboratory hot air oven set at 105°C. After an hour, the sample was removed from the oven and placed in a desiccator. After cooling, the final weight was taken and the percentage moisture calculated from equation (2)

$$\% \text{ moisture} = \left(\frac{\text{Weight loss}}{\text{Sample weight}} \right) 100 \quad (2)$$

- b) Specific gravity: Specific gravity was determined according to equation (3). A 50 ml pycnometer (specific gravity bottle) was initially weighed. It was filled to the mark with the sample, weighed, and calculated.

$$\text{Specific gravity} = \frac{\text{Sample mass}}{\text{Sample volume}} \quad (3)$$

- c) Refractive index: The refractive index was determined using a tabletop refractometer (HI96800) manufactured by Hanner Instruments.



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- d) Kinematic viscosity: Measurement of kinematic viscosity was done using a glass U-tube viscometer manufactured by Poulten Selfe and Lee Ltd (PSL ASTM-IP 350). Sample flow time was calculated as the time in seconds it took the sample to flow from the upper meniscus to the lower meniscus of the bulb, and it was calculated using equation (4).

$$\text{Kinematic viscosity} = ct(\text{mm}^2\text{s}^{-1}) \quad (4)$$

Where c is the viscosity constant 0.4891.

- e) Acid value: Acid value was determined according to equation (5). 0.5 g of the sample was weighed into a 250 ml volumetric flask. 20 ml of ethanol will be added. Also, 3 drops of phenolphthalein were added, and the whole solution was homogenized. It was titrated with a 1 M solution of sodium hydroxide and calculated using equation (5)

$$\text{Acid value} = \frac{(\text{Titre value})(\text{conc. of KOH}) (56.1)}{\text{Sample weight}} \quad (5)$$

Peroxide value: The peroxide value was determined according to equation (6). 0.5g of sample was weighed into a conical flask, and 25 ml of glacial acetic acid and chloroform mixed together in the ratio 2:1 was added. 1ml of 10% potassium iodide was added and shaken vigorously, covered and kept in the dark for one minute. 35ml of starch indicator was added. The whole solution was

- f) titrated with 0.02N sodium thiosulfate solution as the solution turned from pale black to white. Titration was also made for blank and calculated using equation (6).

$$\text{Peroxide value} = \frac{(100)(V_1 - V_2)(\text{Conc. of titrant})}{\text{Sample weight}} \quad (6)$$

Where V_1 is the titre value of the sample and V_2 is the titre value of the blank.

- g) Iodine value: Iodine value was determined according to equation (7). 0.5g of the sample was weighed and 15ml of chloroform added. 25ml of Wiji's solution was added and mixed vigorously. It was covered tightly and placed in the dark for thirty minutes. 20ml of 10% KI was added, and also 150 ml of distilled water. The solution was observed as it turned red. 5ml of 5% starch solution indicator was added and observed as the solution turned blue-black. The solution was titrated with 0.1N sodium thiosulfate solution until black precipitates appeared in the colourless solution. Titration was also made for the blank. Iodine value was calculated from equation (7)

$$\text{Iodine value} = \frac{(12.69)(V_2 - V_1)(\text{Conc. of titrant})}{\text{Sample weight}} \quad (7)$$

Where V_1 is the titre value of the sample and V_2 is the titre value of the blank.



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- h) Saponification value and molecular weight: Saponification value and molecular weight were determined according to equations (8) and (9), respectively. 0.5g of the sample was weighed into a conical flask, and 50 mL of 0.5N ethanolic KOH was added to the sample. The mixture was refluxed to saponify the sample. The unreacted KOH was titrated back with 0.5N hydrochloric acid using three drops of phenolphthalein as indicator.

$$\text{i) Saponification} = \frac{(V_2 - V_1)(\text{Conc. of titrant})(56.1)}{\text{Sample weight}} \quad (8)$$

- ii) Molecular weight: Molecular weight was determined according to equation (9)

$$MW = \frac{561 * 1000 * 3}{(SV - AV)} \quad (9)$$

where AV (mKOH/moil, mg/g) and SV is the saponification value (mKOH/moil, mg/g)

- (j) Ester value: Ester value is among the important parameters of estimating the quality of feedstocks to be used in bio-diesel production. It is the weight (commonly measured in milligrams of potassium hydroxide, KOH) of added base (frequently in the form of potassium hydroxide, KOH) that is needed to saponify one gram of the oil or fat. The value can offer information regarding the combined total quantity of fatty acids of the feedstock in free fatty acids (FFAs) and fatty acids in triglycerides. The ester value is higher when there is a greater amount of fatty acids that is available in order to undergo a transesterification process, which is a type of chemical reaction that produces bio-diesel when oils and fats are involved. On the other hand, a lower value of ester can indicate a high level of impurities or less fatty acid, which has a negative impact on the bio-diesel yield. This was calculated using equation (10)

$$\text{Ester Value} = \frac{100 * (IS - IA)}{IS} \quad (10)$$

Where IS represent the index of saponification and IA represents the index of FFA.

- (k) Smoke point: A mercury-in-glass thermometer was immersed in the sample in the petri dish so that the tip of the thermometer just touches the sample. The thermometer was held in position using a retort stand and clamp. The sample was placed on a laboratory heating mantle. The sample was gradually heated. The lowest temperature at which smoke is emitted from the sample is the smoke point.
- (l) Boiling point: The boiling point of the oil was determined by the following process. A 250 ml beaker was half-filled with paraffin oil. 8 ml of the test oil was poured into a 10 ml glass test tube. A mercury-in-glass thermometer was attached to the side of the test tube using a rubber band. Both are introduced into the paraffin oil and placed on a hot plate. The test tube and thermometer were held in position using a retort stand and clamp. They were placed so that they are suspended mid-way into the paraffin



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oil. Take a capillary tube of about 5cm and seal one of its ends with flame from a Bunsen burner. The open end (unsealed end) was placed into the test tube containing the sample. The hot plate was gradually heated. Note the temperature (a) at which bubbles were noticed at the tip of the capillary tube, and also the temperature (b) at which the bubble stops. The boiling point was calculated using equation (11).

$$\text{Boiling point (}^{\circ}\text{C)} = \frac{b + a}{2} \quad (11)$$

- (m) Free fatty acid: Free fatty acids (FFAs) are fatty acids that are not bound to glycerol in the form of triglycerides, and the existence of these in the feedstocks greatly affects bio-diesel production. Too many FFAs may result in reduced yields and the production of soap during transesterification, which makes the purification more difficult. Hence, the FFA content measurement serves as one of the vital needs of the feedstock suitability and the feedstock production process analysis. It was calculated using equation (12)

$$\text{Free fatty acid} = \frac{\text{Acid value}}{2} \quad (12)$$

2.2.3. Functional group and fatty acid determination of the oil

The produced oils were characterized to determine their functional group using a Fourier transform infrared spectroscope (FTIR BUCK model M530) and Gas Chromatography Mass-Spectrometer to determine the free fatty acids present in the feedstocks.

3. Results And Discussion

3.1. Physicochemical Properties

The discussion of kinematic viscosity, refractive index, acid value, free fatty acids (FFA), saponification value, moisture content, peroxide value, specific gravity, molecular weight, ester value, and the iodine value of chicken fat oil, papaya seed oil, and the hybrid mixture as shown Table 1 below is vital in citing the adoption of any of the oils in the manufacture of bio-diesel. The kinematic viscosity of chicken fat oil is high, and it is 49.491 mm²/s, which means it has a thick consistency as compared to papaya seed oil, with the value of kinematic viscosity of 45.862 mm²/s or the hybrid blend, with a value of kinematic viscosity of 45.979 mm²/s. Refractive indices are comparable with the highest one, which is chicken fat oil, 1.4667. There is a hint of superior stability of chicken fat oil (4.929 mg KOH/kg) and a maximum value (5.002 mg KOH/kg) due to papaya seed oil having more free fatty acids. The acid value of 4.387mg KOH/kg neutralizes these characteristics in the hybrid oil. Good quality of the feed-stocks is evidenced by the low FFA levels of all the samples, especially the chicken fat oil, which has a value of 1.9645 mg KOH /g. The saponification values indicate that the oil made out of chicken fat does not need as much catalyst to undergo the transesterification process (302.940 mg KOH/kg), whereas the hybrid oil contains 318.474 mg KOH/kg.



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Moisture contents are low, and chicken fat oil is 0.0790%, which is good. The peroxide value means that the chicken fat oil is a little bit beyond the ASTM standards (5.632 meq/kg), whereas the hybrid blend is acceptable (4.518 meq/kg). Specific gravities reveal that chicken fat oil has 0.9611 as compared to the hybrid (0.9462) and papaya seed oil (0.9330). This is emphasized by the molecular weights, showing that the hybrid mixture (535.838 g/mol) is more related to the diesel fuel. The estimates of the esters show that the bio-diesel presented has a high-quality potential since the hybrid blend was 99.539 per cent. The iodine value shows that all the oils are non-drying in nature, with that of chicken fat oil (27.290 Meg/100g) the lowest, which makes bio-diesel stable. On balance, the hybridization of these oils brings the positive properties together, and it is a time to point out the areas that should be purified and the ways of processing those oils should be enhanced. The values are represented in Table 1 below, which shows the physicochemical properties of the oils.

Table 1: The physicochemical properties for chicken fat oil, papaya seed oil and their hybrid.

Sample	Kinematic Viscosity @ 40°C (Mm ² s ⁻¹)	Refractive Index @ 33°C	Acid Value (MgKOH/Kg)	Free Fatty Acid Value (MgKOH/Kg)	Moisture (%)
Chicken Fat Oil	49.491	1.4667	3.929	1.9645	0.0790
Pawpaw Seed Oil	45.862	1.4648	5.002	2.501	0.2598
Chicken Fat Oil/ Pawpaw Seed Oil Blends	45.979	1.4662	4.387	2.1935	0.2304
Sample	Saponification (mgKOH/kg)	Peroxide value (meq/kg)	Specific gravity	Molecular weight (g/mol)	Ester value (%)
Chicken Fat Oil	302.940	5.632	0.9611	562.856	98.703
Pawpaw Seed Oil	322.158	2.449	0.9330	530.654	98.447
Chicken Fat Oil / Pawpaw Seed Oil Blends	318.474	4.518	0.9462	535.838	99.539

3.2. Fatty Acid Composition of Oils

The results of the waste chicken fat oil (CFO), papaya seed oil (PSO), and their hybrid mixture as bio-diesel raw materials have good prospects because their fatty acid compositions are good candidates. Important saturated fatty acids, such as n-Hexadecanoic acid (Palmitic Acid), offer oxidation stability, as unsaturated fatty acids, such as oleic acid, cis-Vaccenic acid, and linoleic acid, enhance cold flow properties and better efficiency of the fuel, which allows the bio-diesel to be processed at different temperatures. The mixture of unsaturated esters (papaya seed oil) and saturated esters (chicken fat oil) that offer great stability properties, met with an improved cold flow property attribute, thereby creating a good balance of biodiesel composition. Nonetheless, the aspect of impurities and contaminants noted in the presence of trichloron compounds, naphthalene, minor hydrocarbons, and ethers, places a certain emphasis on the importance of a more proper purification and refinement to produce acceptable quality standards of bio-diesel, and resultant achievement of the optimum fuel performance. Table 2 below shows the fatty acid composition of the oils.

Table 2: Fatty acid composition of CFO, PSO and their Hybrid.

Fatty Acid	Structure	Chicken fat oil (Area %)	Papaya seed oil (Area %)	Hybrid Feedstock (Area %)
Palmitic acid	C16:0	35.04	40.42	38.73
Oleic acid	C18:1 (n-9)	7.50	17.09	12.30
cis-Vaccenic acid	C18:1 (n-7)	12.45	0.34	6.39
9-Eicosenoic acid	C20:1 (n-9)	-	7.38	3.69
trans-13-Octadecenoic	C18:1 trans (n-5)	8.06	-	4.03
cis-13-Octadecenoic	C18:1 cis (n-5)	0.58	-	0.29
Myristic acid	C14:0	1.47	-	0.74
Palmitoleic acid	C16:1 (n-7)	1.90	-	0.95

3.3. FTIR Analysis of Chicken Fat Oil, Papaya Seed Oil and the Hybrid Oil

The FTIR spectrum of bio-diesel synthesized by the conversion of chicken fat oil corroborates the effectiveness of the process because high peaks of C=O ($1740\text{--}1750\text{ cm}^{-1}$) and C-O ($1200\text{--}1000\text{ cm}^{-1}$) are indicative of esters (transesterification reaction), and the presence of C-H stretching at 2920 and 2855 cm^{-1} is associated with aliphatic hydrocarbons. Nevertheless, the presence of O-H peaks of 3652 cm^{-1} and 3265 cm^{-1} is indicative of possible contaminations or the presence of free fatty acids which have not reacted, which implies impurity, whereas other peaks at 1982 cm^{-1} and 2102 cm^{-1} could represent incomplete reaction products. The conversion of oil to bio-diesel in papaya seed oil is successful to the extent that C-H stretching bands are observed at 2940.9 , 2892.2 , and 2847.7 cm^{-1} and C H stretching is strong at $1740\text{--}1750\text{ cm}^{-1}$. However, the presence of O-H peaks at 3295.0 cm^{-1} shows the presence of free fatty acids or water, and this requires re-purification. In the hybrid oil analysis, an ester peak is obtained at 1748.0 cm^{-1} and 1312.0 cm^{-1} , proving adult fatty acid methyl esters (FAMES); however, contaminants are also observed, such as O-H peaks at 3749.7 cm^{-1} and remnants of impurities as 2185.0 cm^{-1} , revealing the necessity of purification to improve the quality of the fuel. Figure 1a, b and c shows the FTIR Spectrum of oils Key Peaks.

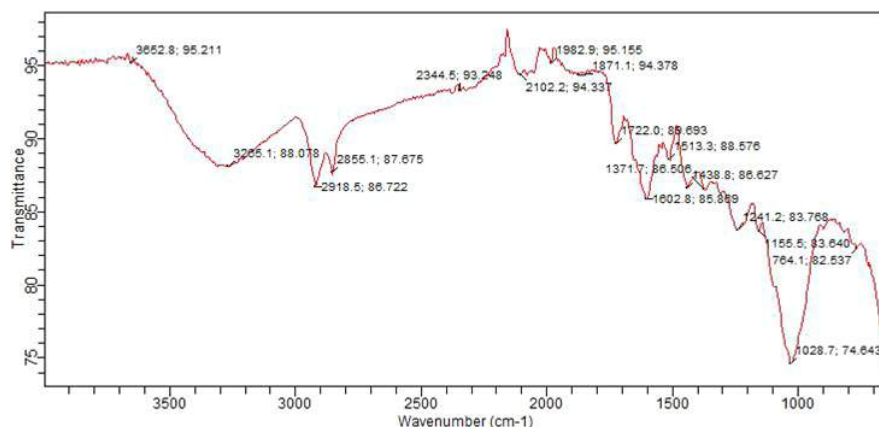


Fig. 1a. FTIR Spectrum of Chicken Fat Oil Key Peaks.

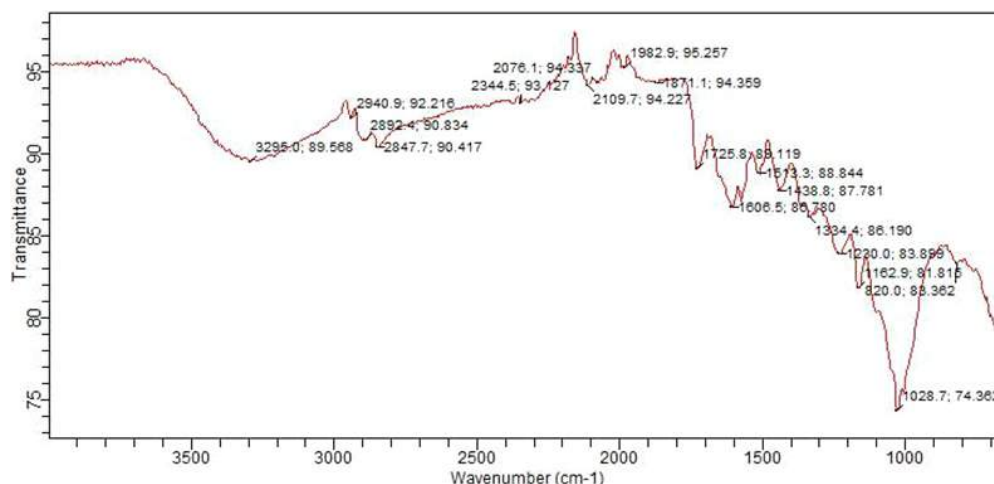


Fig. 1b. FTIR Spectrum of Papaya Seed Oil Key Peaks.

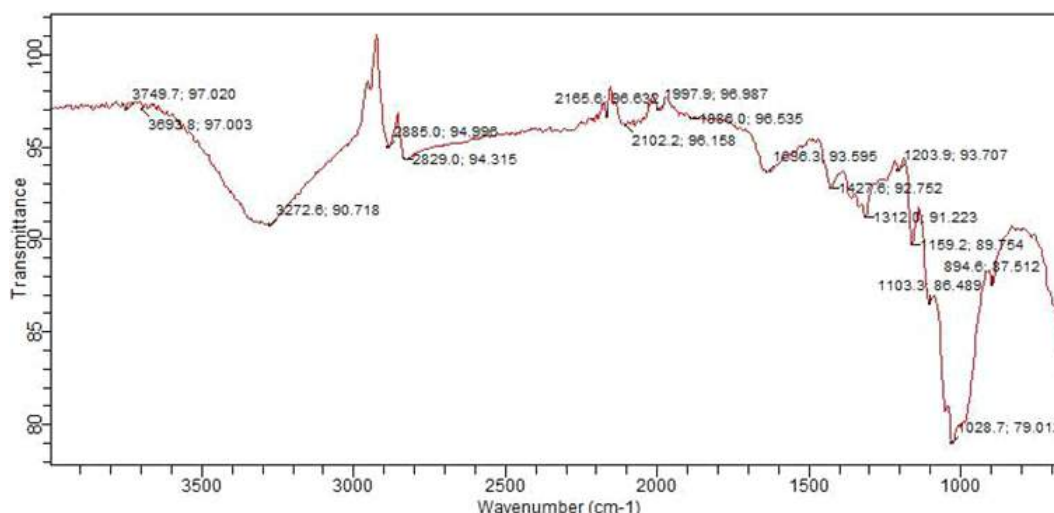


Fig. 1c. FTIR Spectrum of Hybrid Oil Peaks

4. Conclusion

Overall physicochemical profile of CFO, PSO, and their hybrid blend suggests that they may have a large potential for bio-diesel production. CFO shows much better oxidative stability, where the acid value was 3.929 mg KOH/kg, and the free fatty acid (FFA) value was low at 1.9645 mg KOH/g, although the viscosity was high at 49.491 mm²/s and the peroxide value was near ASTM limits at 5.632 meq/kg. PSO, in its turn, provides a better cold flow characteristic with a viscosity of 45.862 mm²/s but an acidity of 5.002 mg KOH/kg. These merits are well fused together in the hybrid combination because of the medium viscosity of 45.979 mm²/s, the good acid number of 4.387 mg KOH/kg and an outstanding ester figure of 99.539 per cent. GC-MS analysis reveals good fatty acid composition, where PSO is contributing 14.406 ppm linoleic acid to the total fluidity of the product, and FTIR identifies the transesterification of the process as successful. But there are still some residues of moisture and impurities, and this calls for further purification. In general, through this study, it can be emphasized that the potential of using hybrid feedstock from CFO and PSO as sustainable sources of bio-diesel is possible with due improvements to supply commercial purposes.



55TH INTERNATIONAL CONFERENCE “COAL CITY 2025”



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Effect of Crude Feedstocks Composition on the Exergy and Operational Performance of an Atmospheric Distillation Unit: A Case Study of Escravos–Forcados Blends

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Abstract

Exergy analysis is a powerful thermodynamic tool for identifying inefficiencies, supporting performance evaluation, and guiding optimization. This study presents a steady-state simulation of a Crude Distillation Unit using Aspen Plus V11 to evaluate the impact of crude feed composition on column performance. Blends of Escravos and Forcados crude oils (0:100, 30:70, 50:50, 70:30, and 100:0) were simulated and validated against literature data, showing deviations of 0.71%–6.57% in product temperatures and 0.1%–1.3% in mass flow rates. Increasing the proportion of Escravos reduced the column temperature profile, improved hydraulics, and altered energy demand: furnace duty decreased by 5.97% while condenser duty increased by 4.56%. Light product yields increased (naphtha 2%, kerosene 1.5%, diesel 3.5%, AGO 0.5%), while residue decreased by 7.1%. Stage exergy losses were lowest for the 0:100 and 100:0 feed cases but higher for blended feeds due to mixing. However, overall internal exergy loss, of which stage losses contributed 40%–45% was minimized in blended feeds. Forcados crude recorded the highest internal exergy loss (32.71 MW), while blends operated with lower losses of 31.0–30.4 MW, reinforcing the benefits of blending in reducing column irreversibility. The 70:30 blend achieved optimal performance, highlighting the importance of feedstock optimization for minimizing energy losses, improving operational efficiency, and enhancing refinery economics.

Keywords: Crude oil, Aspen Plus, Blends, Crude distillation unit, Exergy, Hydraulics

1. Introduction

As Nigeria aims to revamp its refining sector in a bid to reduce its reliance on imported petroleum products, both modular and conventional refineries are being optimized to meet its demands. As of 2024, Nigerian refining capacity is approximately 1.2MTPD with about 37 refineries already licensed in Nigeria with processing capacity ranging from 5000 bpd to 650,000 bpd per refinery. This resulted in surge in refinery capacity utilization to 65% as against 30% in 2023 (Caladium Consulting 2025). The state-owned refineries have a total capacity of 445,000 bpd; these include Port Harcourt (210,000 bpd), Warri (125,000 bpd) and Kaduna (110,000 bpd) refineries. Kaduna refinery was commissioned to supply petroleum products to Northern Nigeria in 1980 with a capacity of 50,000 bpd (fuel plant) which was later scaled up to 100,000



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bpd by addition of another 50,000 bpd (lube plant) crude train, in 1986, the capacity of the fuel plant was scaled up to 60,000bpsd through throughput optimization, resulting to a total 110,000 bpd and the feedstock to the fuel plant is a 50/50 blend of Escravos and Forcados crude (Bureau of Public Enterprises [BPE], 2006). The inefficient operations faced by refineries could also be attributed to pipeline vandalism and unrest in the Niger Delta regions, leading to a deficit in feedstock supply (BPE, 2018).

Crude oil feedstock is a complex mixture whose composition depends on its geographical origin, API gravity, sulfur content, and proportions of light and heavy components. These variations significantly affect the design and operation of crude distillation units (CDU) (Bandyopadhyay, 2002; Olakunle et al., 2011)

Petroleum offshore operational platforms operate under varying boundaries of crude oil conditions over a field's lifespan. This usually happens due to feedstock demands and topology, hence overtime as the hydrocarbon production declines or changes, composition naturally changes. Crude composition changes could interfere with the Atmospheric distillation column performance. This research focuses on the effect of feed composition changes on distillation column performance.

2. Literature Review

2.1 Overview of Crude Distillation Unit

A crude oil refinery is an integrated unit which processes crude oil, a typical multi-component mixture, into several valuable products; it contains different types of units that perform a variety of operations. The main goal is to transform and upgrade low-value feedstock (crude oil) into more valuable products, taking advantage of their differences in boiling point as well as their propensity to evaporate. The feedstock can be classified depending on its amount of light component, sulphur content, API gravity, and metals etc., as either light crude or heavy crude and as either sweet crude or sour crude (Rivero et al., 2004). Fractionation of crude oil is carried out in the atmospheric distillation tower of the crude distillation unit based on the cut-point temperature of distillate products. The distillation process is an essential separation technique widely used, and it remains the fundamental unit in chemical process industries, especially crude oil processing industries, refineries (Saxena & Saptpute, 2017). Energy requirements for atmospheric distillation consist of fuel to heat the crude oil, steam to be injected into the atmospheric tower and stripper, and energy to pump the fluids. Previous studies have revealed that up to 40% of energy consumption in a typical refinery occurs in the atmospheric distillation unit due to its relatively low thermodynamic efficiency as a result of heat losses in the furnace, condenser, and column internals. Crude blending is a widely adopted industry strategy used to modify the feed's processing characteristics. It helps refineries match feed properties with equipment capabilities and optimize product yields while minimizing energy consumption and fouling. Blending light crude such as Escravos with heavier crude like Forcados can stabilize column hydraulics, improve vapour-liquid equilibrium, and increase operational flexibility (Insight Analytical, 2022)



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Thus, understanding how feedstock variations influence energy usage, product distribution, and exergy efficiency is critical for improving refining performance. As a result of the importance of the distillation process to Chemical Process industries, its high energy demand and inefficiency, a lot of research over the years has focused towards developing energy-efficient distillation operations (Osuolale & Anozie, 2017). Column improvement conditions suggested were in terms of feed composition, feed conditioning, feed splitting, feed stage location, reflux adjustment, additional side condenser and reboiler (Olakunle et al., 2011). Meanwhile, the impact of feed types, nature, and condition on the performance of the distillation process and its thermodynamic efficiency in terms of energy requirement, consumption, and waste (loss) has not been well explored (Bandyopadhyay, 2002).

Tarighaleslam et al. (2016) performed the simulation of Tabriz refinery using two feedstock both with Light Crude API, Ahwaz-Bangestan (33.60) and NEW-CROS (32.42) and a 50%-50% blend of the two crudes was used as feedstock, the result revealed that all the three feedstocks have constant exergy loss value in the main column and constant heat load in the furnace. Odejobi (2015) simulated a crude distillation unit using Aspen Hysys, the result reveals that the minimum number of profitable trays is 40, the CDU has the lowest exergy efficiency of 52.1% and the highest irreversibility of 1.13E9 kJ/hr compared to other units in the CDU. Light crude of 34.87 API was used as feedstock. Olugbenga and Arua (2018) simulated heavy crude and obtained the expected cut using continued reflux, which improved the base case temperature of residue from 520-610 °F to 850 °F and further led to an increase in the yield of valuable products from the column. Osuolale and Anozie (2017) presented an exergy rate profile of Warri Refinery which depicts the point of inefficiencies as vapour and liquid exergy profile crossed at the feed point which resulted in a low exergy efficiency of 33% in the base case, column was optimized first by altering feed condition and further optimization of exergy rate profile using ANN yielded exergy efficiency improvement to 53%.

2.2 Exergy concept and thermodynamic analysis

Crude distillation column analysis is based on the first and second laws of thermodynamics. The first law deals with energy conversion and its limitations are addressed in the second, which presents the quantity, quality and direction of energy. A combination of both laws makes up exergy analysis, which helps to identify and quantify thermodynamic loss due to heat, mass and momentum transfer, mixing and pressure drop, which happens as a result of liquid and vapour interaction in the column. Exergy refers to the maximum useful work that can be obtained from a system as it travels reversibly from its present state to the state of equilibrium with its environment. The total exergy of a system can be mathematically expressed as seen in Equation (1) as the sum of its Chemical Exergy EX_{che} and Physical Exergy EX_{phy} (Rivero et al., 2004).

$$EX_{total} = EX_{phy} + EX_{chem} \quad (1)$$

$$EX_{phy} = m(h - h_o) - T_o(s - s_{\beta_k}) \quad (2)$$



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Equation (2) represents the physical exergy and it is based on the determination of thermodynamic state properties such as Temperature(T), Entropy(s), Enthalpy(h). While equation (3) represents the chemical exergy and the subscript denotes the reference conditions, which are at 298.15K and 1atm

$$EX_{chem} = m \left\{ \sum b_{qi} + \sum b_{chi} + RT_o \sum \ln a_i \right\} \quad (3)$$

Equation (3) above is the chemical exergy for crude oil stream due to the interaction between chemical species in a system with respect to the environment, and it refers to the maximum useful work obtained from a system as it comes into thermal and mechanical equilibrium with the environment, and without chemically reacting with it (Odejebi, 2015). Where b_{chi} refers to the standard molar chemical exergy of all non-pseudo components, b_{qi} is the standard molar chemical exergy of pseudo components I, which is further expressed as;

$$b_{qi} = NHV_k \beta_k + \sum z_m EX_{qm} \quad (4)$$

Where z_m are the mass fractions of metals, present in the streams such as Fe, Ni, V, and water and are EX_{qm} their respective specific chemical exergy values, NHV_k is the Net Heating Value of pseudo component K and β_k in equation (5) represents the chemical exergy correction factor which is a function of C, H₂, O₂, S and N₂, mass fraction as seen below (Rivero et al., 2004; Odejebi, 2015).

$$\begin{aligned} \beta_k = & 1.0401 + 0.1728 \left(\frac{zH_2}{zC} \right) + 0.00432 \left(\frac{zO_2}{zC} \right) \\ & + 0.2169 \left(\frac{zS}{zC} \right) \left(1 - 2.0628 \frac{zH_2}{zC} \right) + 0.0401 \left(\frac{zN_2}{zC} \right) \end{aligned} \quad (5)$$

Equations (6) and (7) are obtained by taking the material balance of the process stream across the boundary of the atmospheric distillation column.

$$\sum EX_{out} = EX_{Naphtha} + EX_{kero} + EX_{diesel} + EX_{Diesel} + EX_{residue} \quad (6)$$

$$\sum EX_{in} = EX_{Crude-feed} + EX_{steam} + EX_{furnace} + EX_{kero steam} + EX_{diesel steam} + EX_{AGO steam} \quad (7)$$

The exergy efficiency and the irreversibility are then calculated as indicated by equations (8) and (9), respectively.:

$$= \sum EX_{out} / \sum EX_{in} \quad (8)$$

$$I = \sum EX_{in} - \sum EX_{out} \quad (9)$$

2. Materials And Methods

The CDU model was built in Aspen Plus V14 using the steps in Figure 1. A 48-stage atmospheric distillation column, including a total condenser (Stage 1), three pump-arounds, and three side strippers (for kerosene, diesel, and AGO), was configured.

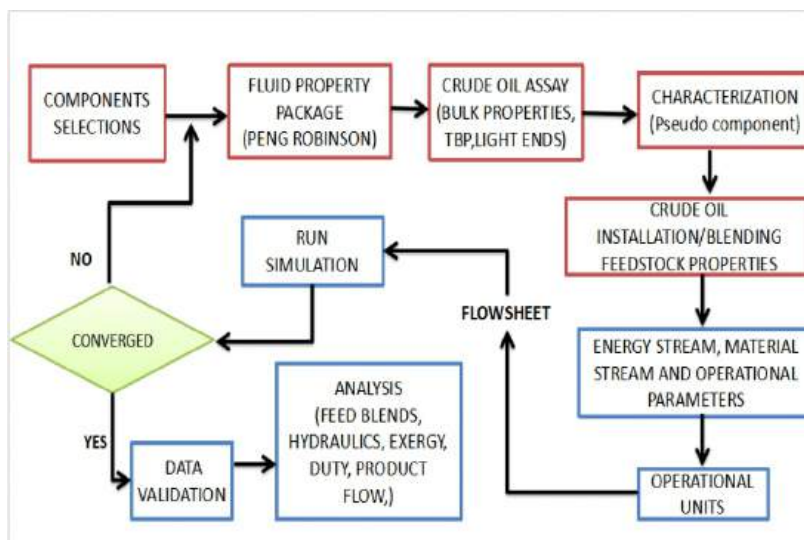


Fig. .1: Methodology.

The simulation model was done using literature data and validated with the Plant data of Kaduna Refining and Petrochemical Company (KRPC) CDU 1 ADU. The plant feedstock crude used was a blend of Escravos (API 34.17) and Forcardos (API 29.0), in a 50/50 ratio as seen in Table 1. A total flow rate of 60bpsd, and the 50/50 blend was used as base case in the simulation; other blends were created in Aspen Plus, such as 30/70 and 70/30 of Escravos and Forcardos crude. The individual feedstock, base case blend and other blends created were used as feedstock for column performance evaluation.

Operational parameters such as temperature profile, vapour-liquid hydraulics, thermodynamic analysis (exergy loss profile and exergy efficiency), furnace duty, condenser duty and product distribution were examined.

Table1: Crude oil feedstock specifications

Crude Oil type	Escravos	Forcardos
API	34.17	29
Sulphur(%wt.)	0.13	0.16
Spec. gravity	0.854	0.887
Pour point C	7	5

3.1 Process description

The feedstock is preheated by the Heat Exchanger Network (HEN), the furnace to attain column entry point temperature of about 340 °C – 380 °C, which comprises a total of 48 stages, including stage 1 which is a total condenser, that air cools overhead vapour and separates the free water vapour from Naphtha as seen in Figure 2. The column is made of Pumparounds (PA's) and side strippers, which consist of 10 stages each. The straight-run products, such as kerosene and diesel, are obtained from the side stripper by steam application to meet the purity target. The column is steam stripped and topped product leaves to VDU at the bottom stage.

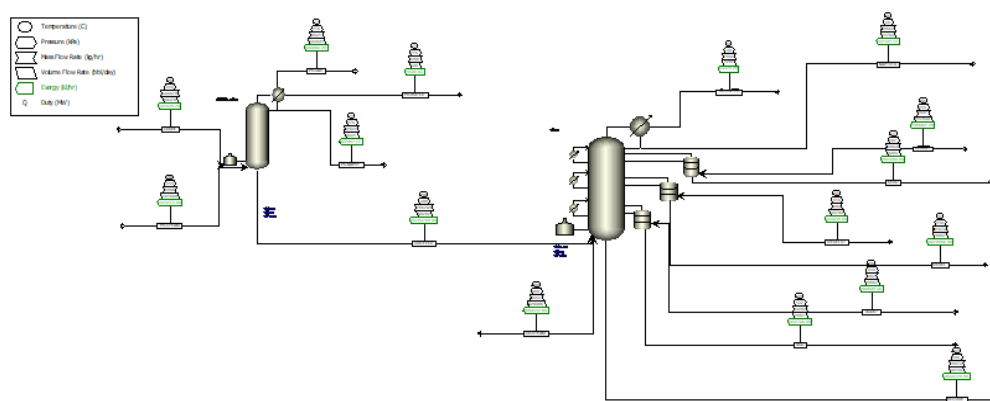


Figure 3.2: Simulated crude distillation unit.

1. RESULTS AND DISCUSSIONS

4.1 Model Validation

Tables 1 and 2 above show a comparison between Kaduna refinery CDU 1 plant data and simulation model prediction for Escravos-Forcados (50:50) blend as feedstock for temperatures and mass flow rate of products, respectively. The feedstock to the column was introduced at stage 45, counting from the up. The table indicated the simulation model compare reasonably well with deviation ranging from 0.71-6.57 percent and 0.1-1.3 percent for products temperatures and mass flow rate of products respectively, which is similar to ranges obtained by (Kekpugile & Kilsibari, 2016), deviations were ranging from 0.012 to 4.70 percent and 1.9 to 7.0 percent for temperature and product flow rate respectively using Bonny light crude as feedstock.

Table 4.1: Products temperature °C.

Tray No.	Products	Plant data	Model data	% Deviation
1	Napthta	140	139	0.71
16	Kerosene	213	227	6.57
27	Diesel	281	290	3.20
39	AGO	350	346	1.14
48	ATM Residue	354	343	3.11

Table 4.2: Products mass flowrate kg/hr.

Tray No.	Products	Plant data	Model data	% Deviation
1	Napthta	59089	59024	0.11
16	Kerosene	44913	44517	0.88
27	Diesel	92482	91802	0.74
39	AGO	13439	13261	1.32
48	ATM Residue	100930	100372	0.55

The differences could be attributed to model assumptions and limited crude assay data, although deviations are within the Standard acceptable Engineering range.

4.2 Temperature Profile

In Figure 4.1, the temperature profile of the Atmospheric distillation column simulated model in Aspen Plus using Escravos and Forcardos feedstock, individual and their blends. The lowest temperature is seen at stage one for all feedstock due to the presence of the partial condenser, and the maximum temperature of 360 °C at the feed stage (stage 45).

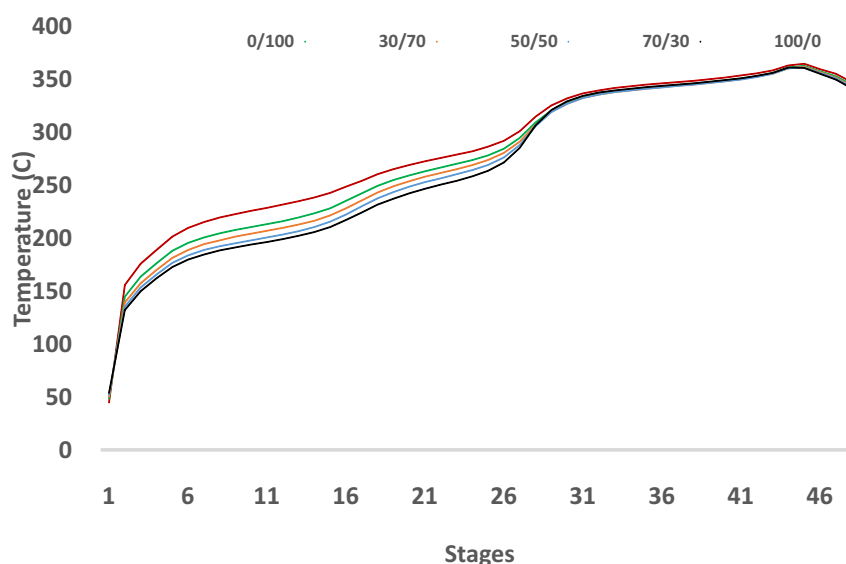


Figure 4.1: Temperature profile of different feedstock in Atmospheric distillation column.

The temperature profile increases down the column in a non-linear manner due to the presence of pump-arounds and side strippers between stages. The maximum temperature profile is seen in 100% Forcardos (0/100) feedstock profile, but as 30% Escravos is blended with Forcardos to attain Escravos/Forcardos (30/70) blend, column temperature profile drops by approximately 2.3%, further increase of Escravos crude

composition in the blend to (50/50), (70/30) and (0/100) in the feedstock results in more decline in temperature profile to 3.97%, 5.0% and 5.7% respectively. These variations can be attributed to differences in feedstock compositions. As more Escravos composition is blended with Forcardos crude, the more volatile composition in the column increases as well, which implies more liquid and vapour contact resulting in heat transfer and high vapour condensation afterwards.

4.3 Column hydraulics

A. Vapour flow rate profile

Figure 4.2 shows the vapour flow rate profile, at Stage 1; all feedstocks exhibit the lowest vapour flow rates due to the impact of the condenser, which effectively reduces the vapour by condensing the vaporized components.

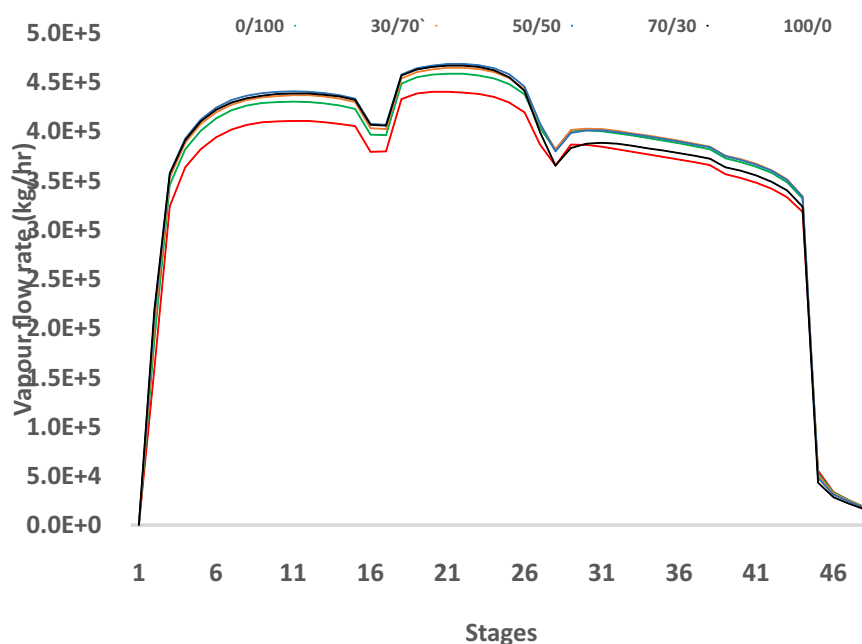


Figure 4.2: Vapour flow rate profile of different feedstock in Atmospheric distillation column.

The effects of PA1, PA2 and PA3 are seen at stages 4, 19 and 30, respectively, where liquid is withdrawn, cooled and returned to stages above the draw points. The returned cooled liquid impacts the rising vapour resulting in intermittent drops in the vapour profile at stages above the drawn stages. Also, the presence of the side stripper for products drawn at 16, 27 and 38 for SS1, SS2, and SS3, respectively, results in a sharp rise in vapour above the drawn stages due to the additional vapour from the side strippers. The same trend is observed for all the feedstock, although the effect of the feedstock composition is to play a pivotal role in influencing the vapour flow as other parameters remain constant. When 100% Forcardos is used, the vapour flow rate reaches the lowest point ($1.65\text{E}5 \text{ kg/hr}$), likely because Forcardos has a lower volatility and higher boiling point, resulting in less vaporization under the same operating conditions. As the feedstock composition shifts to a 30/70 Escravos/Forcardos blend, the vapour flow rate begins to increase by 4.5%.

This change is attributed to the higher volatility of Escravos, which evaporates more readily, hence contributing to the vapour flow rate. As the feedstock changes with an increase in Escravos composition in the blend, the vapour flow rate increased to 5.8% and 6.25% at 50/50 and 70/30 blend, respectively. At further increase to attain 100% Escravos, 100/0 as the feedstock vapour flow rate drops to 4.7%.

B. Liquid flow rate profile

The liquid flow rate profile in Figure 4.3 also shows that it is influenced by both feedstock composition and operational withdrawals and returns, which also impact product quality and energy consumption.

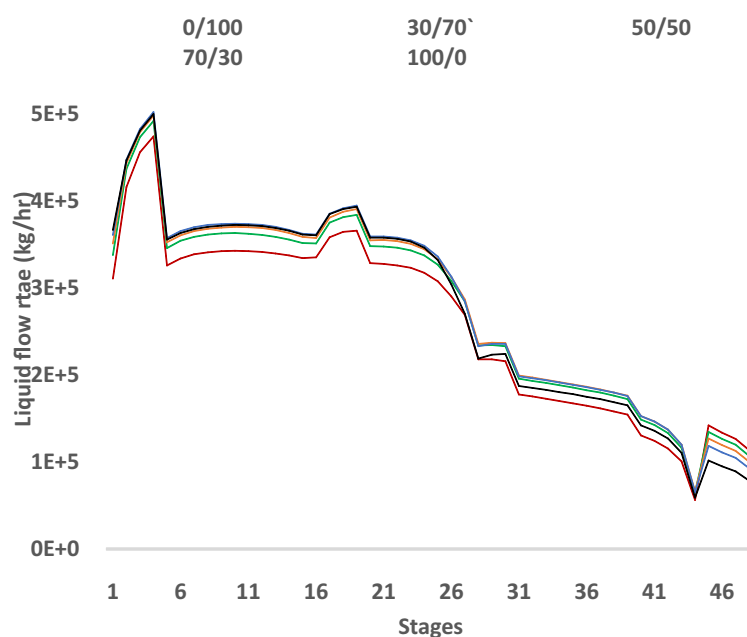


Figure 4.3: Liquid flow rate profile of different feedstock in atmospheric distillation column.

At the feed stage, the flow rate is minimal but increases towards the rectifying and stripping sections due to the feed introduction at stage 45, which enhances liquid flow in the stripping section. The flow rate rises from stage 1 to stage 4, driven by the feed liquid flow (reflux from PA1) and the reflux of condensed overhead vapour at stage 1. At stage 4, a sharp drop in flow occurs due to liquid withdrawal to PA1, which impacts stages up to stage 6. Beyond stage 6, the flow stabilizes, with additional stabilization observed at SS1 (stage 16) and stage 15, where vapour removal and the return of overhead vapor from the side stripper maintain a constant flow. The withdrawal from PA2 at stage 19, with liquid return at stage 17, causes a drop in flow down to stage 2, while SS2 withdrawal at stage 27 does not affect stage 28 due to the liquid return from PA3 at stage 30. A significant drop is observed between stages 31–33 due to the PA3 withdrawal, with the flow stabilizing afterwards until stages 37 and 38, due to the SS3 draw for Ago separation. The liquid flow rate profile also influences product quality: a lighter feedstock like 100% Escravos results in a lower flow rate due to its higher volatility, leading to more vaporization and less liquid hold-up, which can affect the separation efficiency and product purity. In contrast, blending Escravos with Forcardos in ratios such as 70-30, 50-50, and 30-70 increases the flow rate, with the 70-30 Escravos-Forcardos blend typically yielding the highest flow rate due to Forcardos' lower volatility.

C. Total liquid and vapour flow rate across the column

Figure 4.4 shows the total liquid and vapour flow rate across all stages for the different feedstocks. At 100% Forcardos, the total liquid flow and vapour flow are minimum. On blending with 30% Escravos crude, both the liquid and vapour increase as well. Further blending of 50% and 70 % Escravos kept increasing both the total vapour and liquid flow rate, respectively. At 100% Escravos, there began a decline in both total vapour and liquid flow across the column. Irrespective of the feedstock composition, the feeds maintain equilibrium liquid and vapour flow across the stages, and each feedstock and blend gives a distinct total liquid and vapour flow rate.

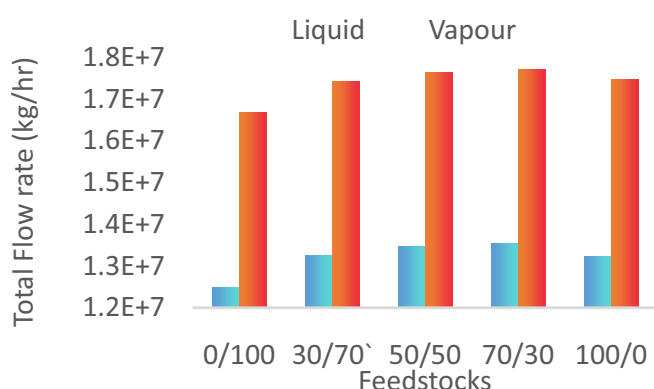


Figure 4.4: Total liquid and vapour flow rate.

4.4 Condenser and Furnace Duty

Table 4.3 shows the condenser and furnace duty for the feedstock and their blends. At 100% Forcardos feedstock furnace duty and condenser duty were 54.09MW and -30.07MW respectively, when blended with 30% Escravos crude, furnace duty decreased by 0.37%, whereas condenser duty increased by 3.89%. Further increases in Escravos composition to 50% and 70 % resulted in further decreases in furnace duty by 1.22% and 2.79% respectively, and an increase in condenser duty by 5.09% and 5.72%, respectively. At 100% Escravos furnace duty attained a least value of 50.86MW, which represented a 5.97% decline and also a decline in condenser duty to 4.79%, when compared to 100% Forcardos. The decline in condenser duty at 100% Escravos feedstock is due to more internal reflux and cooling, and the low boiling point of the feedstock.

Table 4.3: Condenser and Furnace duty.

Feed Blend (E/F)	Furnace Duty (MW)	Condenser Duty (MW)
0/100	54.09	-30.07
30/70	53.89	-31.24
50/50	53.43	-31.60
70/30	52.58	-31.79
100/0	50.86	-31.51

4.5 Products' fractional composition

Table 4.4 shows the product compositional fraction for each feedstock (Conventional and blends). As feedstock composition changes from 100% Forcados (0/100) to 100% Escravos (100/0) by the addition of Escravos in the blend, there is a subsequent gradual increase in light product compositional fraction for Naphtha, Kerosene, Diesel and AGO.

Table 4.4: Products fractional composition.

Feedstock	Naphtha	Kero.	Diesel	AGO	Residue
0/100	0.185	0.139	0.285	0.041	0.349
30/70	0.188	0.142	0.291	0.042	0.338
50/50	0.191	0.144	0.297	0.043	0.325
70/30	0.195	0.147	0.305	0.044	0.309
100/0	0.205	0.154	0.320	0.046	0.276

This is accompanied by a reduction in percentage residue as feedstock composition is altered in the same manner from 0.349 for 100% Forcados crude (0/100) to 0.276 for 100% Escravos crude (100/0). The MVC in feedstock implies that more vapour rising across the tray brings about efficient liquid and mass transfer, resulting in better separation as more Escravos crude is introduced in the feedstock blend.

4.6 Exergy Analysis

A. Exergy loss profile

Figure 4.5 depicts the exergy losses across the stages in the distillation column for the different feedstocks. For all the feedstock, a similar profile is observed except for variation in the losses per feedstock charged to the column.

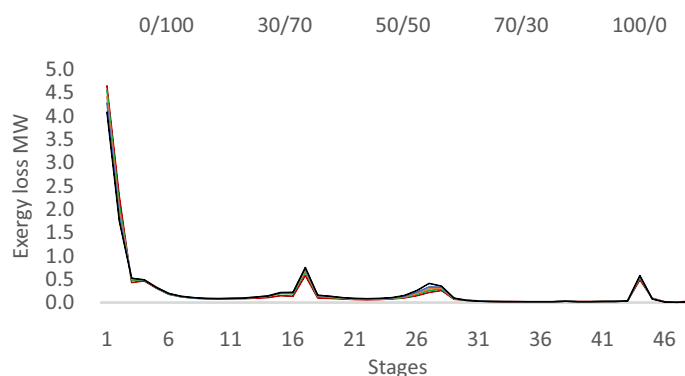


Figure 4.5: Exergy loss profile for the various feedstocks and blends



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The maximum loss is seen at the condenser between 4.08MW-4.6MW, which is a result of loss of internal heat content, Enthalpy(H) of overhead vapour in the condenser. Escravos crude (100/0) displays the least exergy loss of 4.08MW due to its low boiling point, which is also depicted by its low temperature profile; hence, less cooling is required at the condenser to meet the desired cooling specification for reflux and distillate products. As the Escravos feedstock is blended with 30% Forcardos (70/30), exergy loss increased to 4.27MW due to an increase in boiling point of the present composition, further increase of 50 %, (50/50), 70 % (30/70) and 100 % (0/100) Forcardos, resulting in increases to 4.41MW, 4.56MW and 4.6MW, respectively. At stage 2, exergy loss lies between 1.75MW and 2.24MW; it was observed to increase from 1.75MW for 100% Escravos to 2.24MW for 100% Forcardos, which could be attributed to the fact that the composition of Forcardos in the feedstock began to increase. This is due to the reflux entry on stage 2, resulting in heat transfer between the rising vapour and the cooled reflux, and mixing also happens on the stage by liquid. At stage three (3) and four (4), there is a slight observable difference in the exergy loss for the various feedstock due to the presence of PA1, while there is negligible variation in the exergy loss profile until stage 17 due to the return of cooled liquid by PA2 with a maximum loss of 0.72MW. The next variation is seen at the PA3, stage 28; beyond this point, the next variation is seen at the feed stage. At SS2, liquid is drawn for 27 and side stripped and the light ends are returned to the column responsible for the abnormal trend with stage 25-28. The above reveals that feed composition affects exergy loss profile maximally at the condenser, followed by the feed stage and the point of interaction of side strippers with the column for product draw.

B. Exergy Efficiency for ADU and Furnace

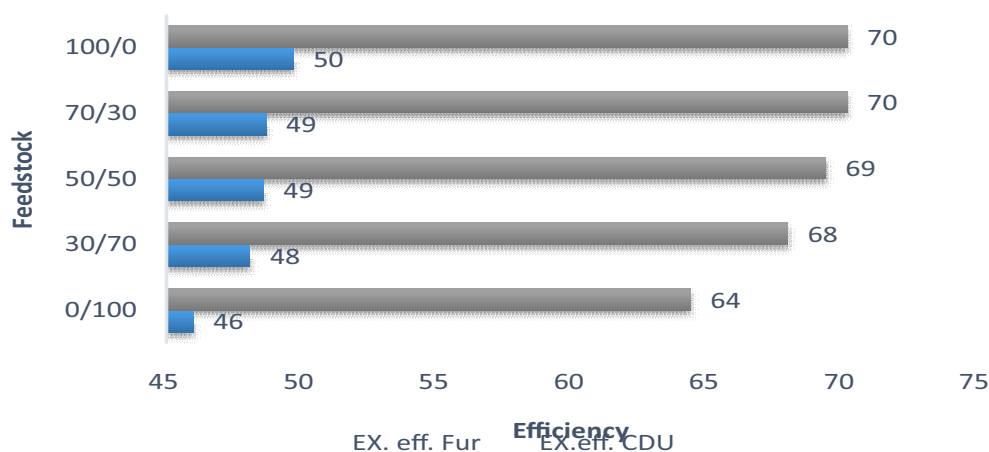


Figure 4.6: Atmospheric distillation unit and Furnace exergy efficiency of different feedstock and their blends.

Figure 9 shows the effect of different feedstock and their blends on ADU and Furnace exergy efficiency. It implies that more of the heat (Q) supplied is used to raise the feed temperature in the furnace, which is supplied to do the heating work, while most of the heat energy supplied to feedstock and ADU steam is used to carry out separation work. In 100% Escravos (100/0), the highest ADU and Furnace exergy efficiency of 50% and 70% respectively, are observed due to light feedstock and higher distillate rate, which implies better separation accompanied by lower residue rate. As 70% (70/30), 50% (50/50) and 70% (30/70) Forcardos is blended with Escravos and the feedstock composition is changed, it results in decreases in both ADU and Furnace exergy. The least ADU and Furnace exergy efficiency of 46% and 64% respectively are

observed in 100% Forcardos (0/100) due to inefficient separation in the column, accompanied by lower distillate product rate and higher residue rate. It is obvious from the result above that feed composition impacts exergy efficiency.

C. Exergy loss

Figure 4.7 shows Internal exergy loss across the column and Total exergy loss across stages

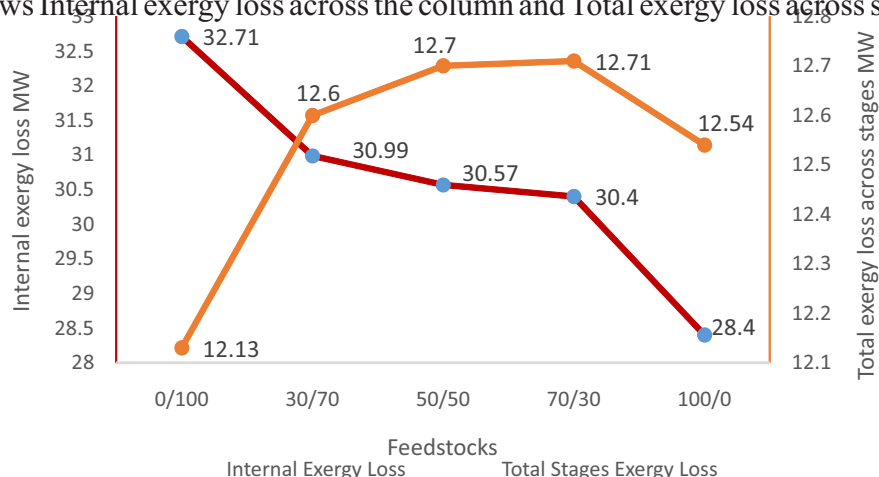


Figure 4.7: Total exergy loss for different feedstock and their blends.

Figure 4.7: Total exergy loss for different feedstock and their blends.

100% Forcardos (100/0) and 100% Escravos have 12.1 MW and 12.5 MW respectively, which represent the two lowest. By blending Forcardos crude with 30%, 50%, and 70% Escravos crude, it results in an increase in total exergy loss across the stages from 12.1 MW exergy loss at 100% Forcardos to 12.60MW, 12.69MW, and 12.71MW exergy loss, respectively. This implies that the blended feedstocks have higher exergy losses across stages due to the mixing effect that results from blending. However, when the overall internal exergy loss of the column is considered, the total exergy loss of the column contributed 40%- 45%. It was observed that Forcardos crude has the highest loss of 32.71 MW, which is higher than the blends, emphasizing the advantage of crude oil blending as it reduces overall column internal exergy loss. Hence, the 70/30 Escravos blends, amongst others, performed optimally.

2. CONCLUSION

The simulation and thermodynamic performance evaluation of the crude oil atmospheric distillation column revealed significant insights into the impact of feedstock composition on column performance. The validated simulation model demonstrated good agreement with plant data, confirming its accuracy and reliability. The results showed that a 70/30 blend of Escravos and Forcardos crude oils yielded optimal results, having the least overall internal exergy loss of 30.4% which includes its exergy loss of 12.71% across the stages of the column, and also having least furnace duty of 52.58 MW among other blends, and maximum yields of distillates accompanied by least residue fractional composition of 0.309 in products when compared with the other blends. The findings of this study emphasized that feed composition not only affects column profile, hydraulics, product yield, but also energy consumption and overall column performance. Hence, this finding can gain adequate relevance if deployed as a screening tool in the Atmospheric Distillation Column of typical refineries to optimize distillation column operation in terms of optimal feedstock blends selection so as to achieve efficient and sustainable performance.



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Techno-Economic Analysis of Co-Producing Sustainable Diesel and Bioethanol from Castor Seed in an Integrated Biorefinery

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Abstract

This study examined the techno-economic analysis (TEA) of an integrated biorefinery for the co-production of renewable diesel and bioethanol from castor seed in Nigeria. Using Aspen PLUS for process simulation and Aspen Process Economic Analyzer (APEA) for cost estimation, the study evaluates the viability of two production scenarios: (1) renewable diesel and castor seed cake, and (2) integrated renewable diesel and bioethanol. The study reveals that while both scenarios are profitable, the integrated co-production of renewable diesel and bioethanol (Scenario 2) is the most financially attractive, demonstrating a higher Net Present Value (NPV) and Internal Rate of Return (IRR), particularly with 100% equity financing. The minimum selling price (MSP) for renewable diesel and bioethanol was found to be competitive at \$0.939/kg and \$0.650/kg, respectively, under an equity-financed model. Also, sensitivity analysis identified the price of castor seed as the most critical factor influencing profitability. The findings highlight the significant potential of an integrated biorefinery approach to enhance the economic viability of biofuel production from non-edible feed-stocks.

Keywords: Renewable diesel, Bioethanol, Hydrodeoxygenation, Profitability indices, Castor seed

1.0 Introduction

The global energy sector has undergone unprecedented changes over the past 50 years, with attendant political, technological, and market-based changes that are attributed to environmental concerns and climate change arising from fossil fuel usage –(International Energy Agency, 2023). This shift is driven by the attendant effect of fossil fuels on climate change and more recent events like the Russia-Ukraine crisis, which has disrupted energy supplies, and the rising global energy demand. These activities have resulted in rising demand for energy worldwide, leading to an energy crisis, market and price instability, as well as supply risk. This is because fossil fuel still accounts for about 80% of the global energy demand (Energy Information Administration, 2024), despite its environmental effects and the call for alternative, renewable and sustainable sources of energy. As of 2022, biofuels accounted for 3.5% of global fuel consumption and are expected to reach 9% by 2030 –(International Energy Agency, 2023).

The urgent need to increase renewable energy sources in the global energy mix led to Sustainable Development Goal (SDG) 7, targeted at promoting sustainable energy and increasing renewable energy to 60% of the global energy mix by 2030 (High-Level Political Forum, 2023). To meet SDG 7, Africa cannot



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be left behind due to the energy challenges to its socioeconomic development and the fact that a sustainable source of energy is crucial to the existence of the economy and development of Africa. In Africa, there's a growing interest in biofuels development as a sustainable energy source, with countries like Nigeria exploring biofuel production (Kgathi et al., 2017). Biofuels, which are plant or agricultural-based, including biodiesel and bioethanol, are seen as effective alternatives, but their global use remains low, Africa inclusive (Rahimi et al., 2020; Energy Information Administration, 2024).

Though a renewable alternative, biodiesel possesses drawbacks such as a 20% blending limit, 15% CO₂ reduction, short shelf life, potential damage to modern or existing diesel engines without modification and a lower cetane number (50 – 60) and could produce higher levels of NO_x emissions. These limitations sparked rising interest in renewable diesel, a cleaner and more efficient alternative that is also produced from vegetable oil and used in existing engines without modifications (Gerveri et al., 2023). Economic considerations and the competition for edible oils have led to the focus on the utilization of non-edible bioenergy crops with potential for oil production and lignocellulose for bioethanol production. One major crop that has been recognized is Castor Seed (CS), which is identified as a promising non-edible crop for renewable diesel and bioethanol production in Nigeria.

Current extant literature mainly investigates either biodiesel production from castor oil or bioethanol production from castor seed cake (CSC) residues as separate studies and their TEA (Rahimi et al., 2020; Energy Information Administration, 2024). While other studies focused on hydrodeoxygenated (HDO) vegetable oil and its TEA, renewable jet fuel or sustainable aviation fuel (SAF) (Shila and Johnson, 2021), standalone hydrotreated vegetable oil (HVO) —(Hor et al., 2023; Mussa et al., 2024), and some on Biomass to Liquid (BTL) transport fuel (Dimitriou et al., 2018) and hydropyrolysis to bio-oil and fuels (Nguyen and Clausen, 2019). Though these studies provide comprehensive and valuable insights into individual conversion pathways to biodiesel and bioethanol, as well as standalone SAF and HVO, and their TEA. However, there is a lack of comprehensive studies on the integrated and concurrent production of HDO diesel and bioethanol from whole CS biomass that look at the economics and sustainability of the process, hindering the realization of potential integration benefits and overall economic viability. Hence, the study examines the TEA of co-producing HDO renewable diesel and bioethanol from whole CS via the development of a process simulation model for different scenarios to evaluate the energy efficiency, capital and production cost requirements, and profitability analysis of the scenarios with the establishment of the minimum selling price and the sensitivity to key economic factors of the scenarios. Thereby establishing the viability of the renewable diesel and bioethanol production process from whole CS.

2.0 Materials and Methods

The integrated process for the co-production of HDO renewable diesel and bioethanol from CS was simulated using Aspen PLUS V14, while APEA V14 and Microsoft Excel 2019 were used for cost



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estimation and profitability analysis. The composition of castor oil, determined experimentally using Gas Chromatography and Mass Spectrometry (GC-MS) analysis, was used to represent the triglyceride components in the simulation model (Table 1), while experimentally determined CS proximate analysis and chemical analysis of the CSC residue (after oil extraction) were used to define CS and CSC (Table 2), respectively, as nonconventional components in Aspen PLUS. Other conventional components involved in the simulation model were selected from the Aspen PLUS component database.

Table 1. Composition of extracted castor oil determined experimentally using GC-MS analysis

Triglycerides	Chemical Formular	Composition (wt.%)
Triolein	$C_{57}H_{104}O_6$	5.19
Trilinolein	$C_{57}H_{98}O_6$	3.24
Tripalmitin	$C_{51}H_{98}O_6$	0.75
Tristearate	$C_{57}H_{110}O_6$	0.59
Triricinin	$C_{57}H_{104}O_9$	86.59
Triarachidin	$C_{63}H_{122}O_6$	3.64

The Non-Random Two Liquid (NRTL) thermodynamic property method was used for the simulation model, because it gives more accurate results in handling highly non-ideal and polar compounds such as triglycerides, alcohols, etc., and is suitable for Vapour-Liquid Equilibrium (VLE) and Liquid-Liquid Equilibrium (LLE) applications (Sandler, 2015).

Table : Proximate analysis of castor seed and chemical analysis of CSC

Proximate Analysis of CS	Value	Chemical Analysis of CSC	Value
Ash Content, dry basis (%)	6.833	Cellulose, dry basis (%)	44.460
Crude Lipid, dry basis (%)	52.867	Hemicellulose, dry basis (%)	27.640
Crude Fibre, dry basis (%)	2.667	Lignin, dry basis (%)	18.340
Crude protein, dry basis (%)	14.408	Ash, dry basis (%)	6.833
Carbohydrate, dry basis (%)	23.225	Extractives, dry basis (%)	2.727

2.1 Process Simulation Model

The simulation steps entail the definition of chemical components, selection of the thermodynamic model (NRTL), modelling of the process flowsheet by setting up unit operation models and operation conditions, as well as definition of reactions involved. The major unit operations used in the simulation model are presented in Table 3.

Table 3: Aspen PLUS unit operation blocks used in the simulation model



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Unit Operations	Aspen PLUS Block	Specification
Oil Extractor	RStoic	Simplified simulation at 70°C and 1 atm
Hydrotreatment	Rplug	Rigorous simulation with kinetics reactions (Table 3), at 350°C and 50 bar
Renewable Diesel Purification	RadFrac	Rigorous multi-stage distillation model with 22 stages, Feed stage: 14 (On stage), Condenser pressure: 1.11 bar
Substrate Fermentation	BatchOp	Rigorous simulation with kinetics reactions, at 32°C and 1 atm, 2 hr batch feed time and discharge time
CSC Pretreatment	RStoic	Simplified simulation with stoichiometric reactions (Table 5), 158°C and 0 vapour fraction
Neutralization/Reconditioning Vessel	RStoic	Simplified simulation with stoichiometric reactions (Table 5), 79.85°C and 1 atm
Hydrolysis Reactor	RStoic	Simplified simulation with stoichiometric reactions (Table 5), 48°C and 1 atm
Bioethanol Bear Column	RadFrac	Rigorous multi-stage distillation model with 16 stages, Feed stage: 2 (above stage), Condenser pressure: 1.6 bar and 0.207 bar column pressure drop, Condenser temperature of 60°C and reflux ratio of 3
Bioethanol Rectification Column	RadFrac	Rigorous multi-stage distillation model with 35 stages, Feed stage: 16 (above stage), Condenser pressure: 1.5 bar, Condenser temperature: 55°C and reflux ratio of 3
Molecular Sieve Dehydration Column	Sep	Simplified separation simulation column at inlet condition
Membrane Separation	Sep	Simplified separation simulation column at inlet condition

The castor oil hydrotreatment reaction was modelled using power law kinetics reactions data adopted from Vélez-Manco (2019) and Tirado et al. (2018), for the rate-controlled hydrotreating reactions according to the rate equation presented in Equation 1, while the triglyceride hydrotreatment reaction and kinetics data are presented in Table 4.

$$r = k_o \left(\frac{T}{T_o} \right)^n \exp \left(-\frac{E}{R} \left(\frac{1}{T} - \frac{1}{T_o} \right) \right) \prod_{i=1}^N C_i^{a_i} \quad \text{Equation 1}$$

In line with the current CS production in Nigeria and in ensuring sustainability of the process, a design capacity of 10 tons/hr is considered in this study for an on-stream production of 8400 hr per year.

Table 4: Kinetic data for castor oil transesterification by heterogeneous catalysis

S/N	Stoichiometry	k_0 [kmol/m ³ .sec]	E [kJ/kmol]
1	Triolein + 3H ₂ → Tristearate	4.4E+11	162,500
2	Trilinolein + 6H ₂ → Tristearate	9.4E+09	149,900
3	Tripalmitate + 12H ₂ → 3C ₁₆ H ₃₄ + C ₃ H ₈ + 6H ₂ O	3.8E+09	147,400
4	Tristearate + 12H ₂ → 3C ₁₈ H ₃₈ + C ₃ H ₈ + 6H ₂ O	5.6E+09	149,100
5	Trirecinin + 18H ₂ → 3C ₁₈ H ₃₈ + C ₃ H ₈ + 9H ₂ O	5.6E+09	147,400
6	Triarachidate + 12H ₂ → 3C ₂₀ H ₄₂ + C ₃ H ₈ + 6H ₂ O	5.8E+09	145,700
7	Tripalmitate + 3H ₂ → 3C ₁₅ H ₃₂ + C ₃ H ₈ + 3CO ₂	1.4E+09	150,600
8	Tristearate + 3H ₂ → 3C ₁₇ H ₃₆ + C ₃ H ₈ + 3CO ₂	8.2E+09	169,200
9	Trirecinin + 9H ₂ → 3C ₁₇ H ₃₆ + C ₃ H ₈ + 3H ₂ O + 3CO ₂	8.2E+09	169,200
10	Triarachidate + 3H ₂ → 3C ₁₉ H ₄₀ + C ₃ H ₈ + 3CO ₂	8.2E+09	154,200

2.2 Process Description

Figure 1 presents the process flow diagram for the co-production of renewable diesel and bioethanol from 10 tons/hr CS. The process comprises three main sections: castor oil extraction, castor oil hydrotreatment, and bioethanol production from CSC. The castor oil extraction section begins with crushing of the seeds, followed by solid-solvent extraction using n-hexane to recover the oil. The extracted castor oil is then hydrotreated by mixing the extracted oil with hydrogen and heating it before entering the hydrotreating reactor. This process converts the oil into renewable diesel (5 MPa and 350 °C), according to the reactions in Table 4. The reactor effluent stream is then separated and purified through fractional distillation to yield renewable diesel and LPG (C₃H₈).

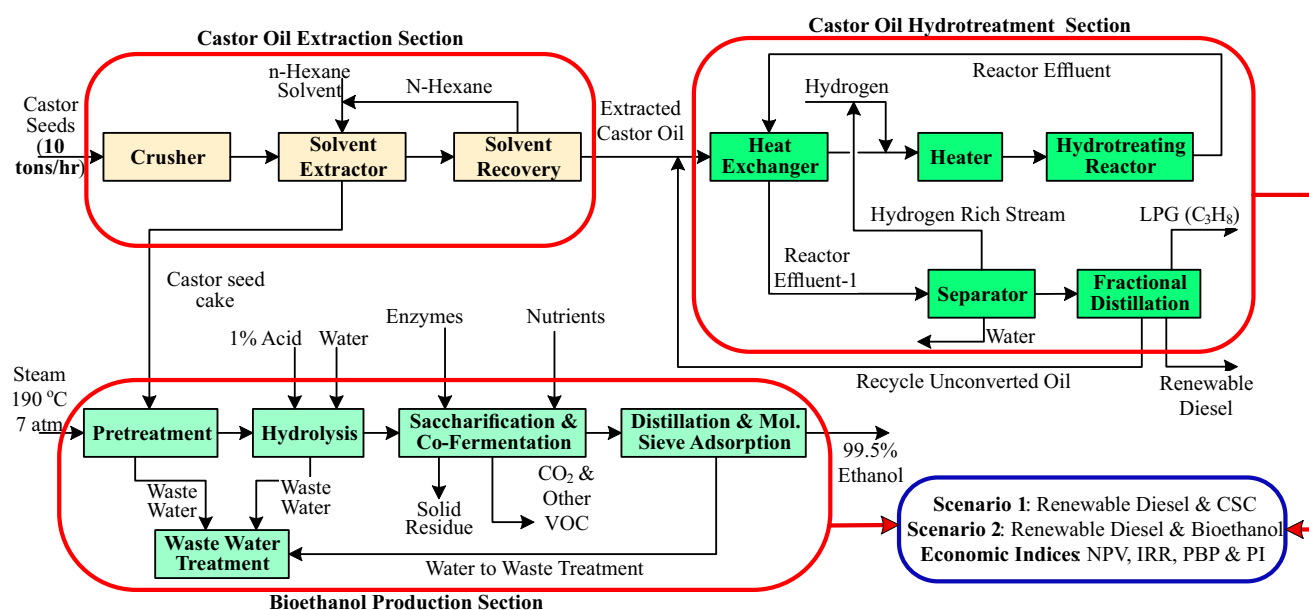


Fig. : Block flow diagram of the major process areas in the co-production process



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The CSC from the extraction process is used for bioethanol production. The CSC is first pretreated with steam and sulfuric acid to liberate C₅-sugar, followed by enzymatic hydrolysis to break down cellulose into C₆-sugar according to reactions presented in Table 5. The combined C₅- and C₆-sugar streams are then fermented using yeast to produce crude bioethanol. The fermenter was modelled as a batch reactor over 96 hours to produce bioethanol using reaction kinetics according to the Aiba-Edwards and Monod (Logistics) model. The crude bioethanol is then purified to 99.6 wt.% via distillation and molecular sieve dehydration.

Table 5: Lignocellulosic biomass (CSC) to bioethanol reactions

Reaction Type	Chemical Equation	Reactant	Conversion
Pretreatment	$(\text{Cellulose})_n + n \text{H}_2\text{O} \rightarrow n \text{Glucose}$	Cellulose	0.070
Hydrolyzer	$(\text{Cellulose})_n + m \text{H}_2\text{O} \rightarrow m \text{Glucose Oligomer}$	Cellulose	0.007
Reactions	$(\text{Cellulose})_n + 0.5n \text{H}_2\text{O} \rightarrow 0.5n \text{Cellobiose}$	Cellulose	0.007
	$(\text{Hemicellulose})_n + n \text{H}_2\text{O} \rightarrow n \text{Xylose}$	Hemicellulose	0.900
	$(\text{Hemicellulose})_n + m \text{H}_2\text{O} \rightarrow m \text{Xylose Oligomer}$	Hemicellulose	0.025
	$(\text{Hemicellulose})_n \rightarrow n \text{Furfural}$	Hemicellulose	0.050
	$(\text{Lignin})_n \rightarrow n \text{Soluble Lignin}$	Lignin	0.050
Reconditioning Reaction	$\text{H}_2\text{SO}_4 + 2 \text{NH}_3 \rightarrow \text{NH}_4\text{SO}_4$	H_2SO_4	1
Saccharification	$(\text{Cellulose})_n + m \text{H}_2\text{O} \rightarrow m \text{Glucose Oligomer}$	Cellulose	0.040
Reactions	$(\text{Cellulose})_n + 0.5n \text{H}_2\text{O} \rightarrow 0.5n \text{Cellobiose}$	Cellulose	0.012
(Enzymatic	$(\text{Cellulose})_n + n \text{H}_2\text{O} \rightarrow n \text{Glucose}$	Cellulose	0.900
Hydrolysis)	$(\text{Cellobiose})_n + \text{H}_2\text{O} \rightarrow 2 \text{Glucose}$	Cellobiose	1.000

The products yielded from the process simulation model were estimated using Equations 2 to 4.

$$\text{Oil Yield (\%)} = \frac{\text{Mass of Triglycerides}}{\text{Mass of Castor Seed}} \times 100 \quad \text{Equation 2}$$

$$\text{Renewable Diesel Yield (\%)} = \frac{\text{Mass of Renewable diesel (Hydrocarbon)}}{\text{Mass of Castor Oil Feed}} \times 100 \quad \text{Equation 3}$$

$$\text{Bioethanol Yield (\%)} = \frac{\text{Ethanol produced } \left(\frac{\text{g}}{\text{L}}\right)}{\text{Initial sugar concentration (g/L)} \times 0.511} \times 100 \quad \text{Equation 4}$$

2.3 Economic and Profitability Analysis

Two scenarios in terms of end products: 1) renewable diesel and CSC, 2) renewable diesel and bioethanol co-production, were considered for the economic and profitability analysis. The profitability of the scenarios was judged based on payback period (PBP), return on investment (ROI), IRR, NPV and profitability index (PI). The cost and economic analysis were based on the economic parameters and assumptions presented in Table 6. The estimated total project cost was imported into an Excel spreadsheet and used for profitability analysis, while material and energy balance results were imported into the Excel sheet for operating and production cost estimates.



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Table : Basis of cost estimation and economic analysis.

Parameters	Value
Project life	22 years
Plant Operating life	20 years
Engineering, procurement and construction	2 years
EPC Spending	First year: 40% and Second year: 60%
Operating days per year	345 days
Depreciation type	Straight line method
Depreciation period	15 years with zero salvage value
Income tax rate	30% (Companies Income Tax, CIT, in Nigeria)
Production volume in first year of operation	65%
Production volume in second year	95%
Ramp up production to 100%	3 rd year of operation
Equity financing (Project)	50%
Debt financing (Project)	50%
Interest rate	10%
Cost of Equity	10%
Discounted rate	Estimated Weight Average Cost of Capital (WACC)
Debt repayment period	5 years
Moratorium on debt and interest	2 years
Debt financing fee	0.5%
CSs [\$/kg]	0.312 (Nigeria Local Market)
n-Hexane [\$/kg]	0.585
H ₂ [\$/kg]	2.3
Yeast [\$/kg]	3.05
Ammonia [\$/kg]	0.362

2.4 Sensitivity of Economic Parameters

Sensitivity assessment was carried out to assess the risk and uncertainties associated with the economic assumptions made in the course of the TEA study and to determine the factors that exert the most influence on the profitability indices. The study considered a sensitivity limit of $\pm 25\%$ from the base case, and a tornado chart was used to represent the impact of the sensitivity of the response variable (net income) to varying factors in the limits of $\pm 25\%$ variations in economic parameters.

3.0 Results and Discussion

The process simulation model shown in Figure 2 was validated with previously reported experimental results and those reported by Gamal et al. (2020), as shown in Figure 3. It was observed that the simulation results compared favourably with experimental results and those reported in the literature –Caporusso et al., 2023(Gamal et al., 2020; ; Wang et al., 2024), except for HDO selectivity, which shows slight variation between reported experimental and simulation results. The noticeable variation in HDO selectivity could be attributed to variation in operating condition (350 °C and 3.5MPa) reported by Gamal et al. (2020) and that utilized for the simulation (340 °C and 5MPa). The process simulation model results compared favourably with experimental results reported in the literature, thereby indicating the validity of the simulation model for the TEA study.

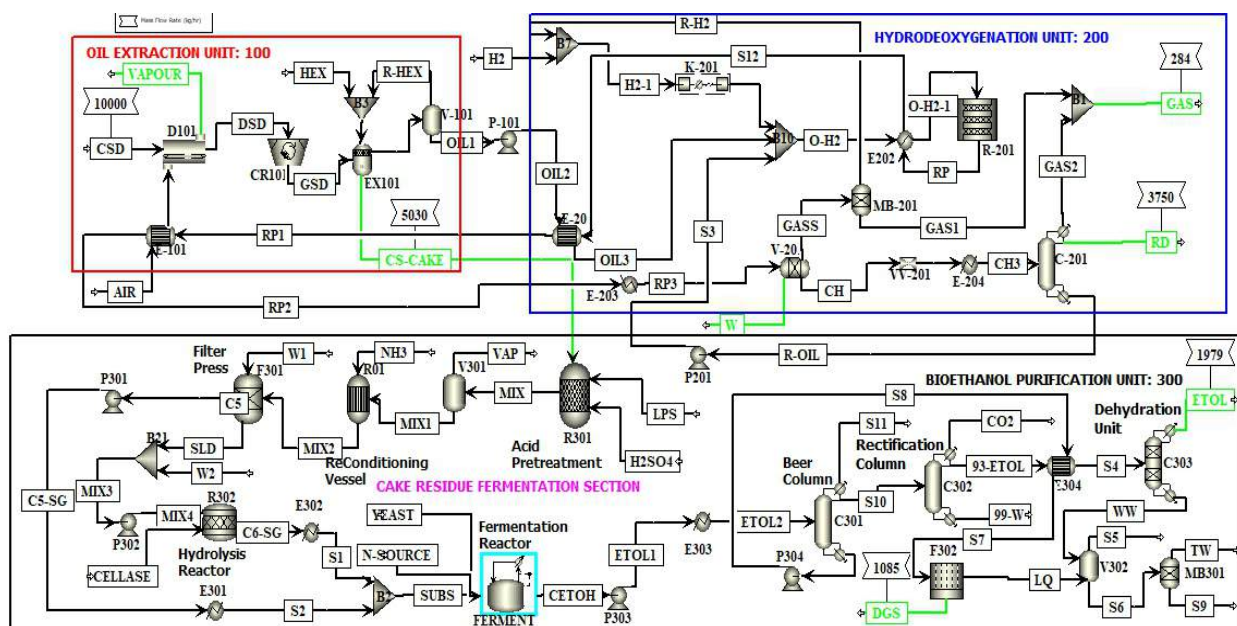


Fig. : Process simulation model of the co-production of renewable diesel and bioethanol

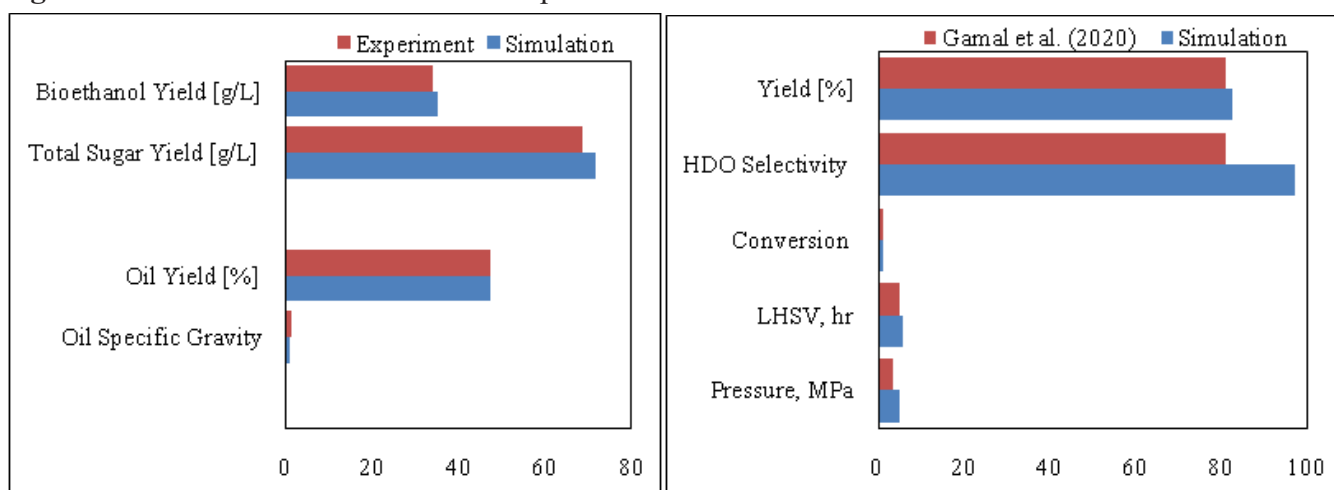


Fig. 3: Comparison between experimental and process simulation model results

3.1 Material and Energy Balance

In order to assess the economics of renewable diesel and bioethanol production from CS, an integrated renewable diesel and bioethanol production process was simulated as shown in Figure 2. The process simulation results shows that processing 10,000 kg/h. of fresh CS, which is dried to 9516.70 kg/h, yields 4587.83 kg/h oil (47.123% yield) and 5030.38 kg/h residual CSC. The hydrotreatment of the oil yields 3749.82 kg/h renewable diesel with 96.64% conversion and 96.99% selectivity for the HDO route, while the residual CSC yields 1978.59 kg/h of 99.6% bioethanol. The simulation results are consistent with results reported in previous similar studies, and the high reaction conversion and selectivity for the HDO is attributed to favourable operating conditions in this study (Mussa et al., 2024).

Table 7 presents the physico-chemical properties of the renewable diesel product ($C_{15} - C_{18}$) obtained from the simulation model in comparison to standard established diesel fuel properties. It was observed that the properties of the renewable diesel produced from the simulation model compare favourably with those of the standard value shown in Table 7.

Table 7: Physico-chemical properties of the renewable diesel

Properties	Simulation value	Standard value
Std. Liquid Density [kg/m^3]	778.39	770 – 790
Flash Point [$^{\circ}\text{C}$]	126.45	> 61
Pour Point [$^{\circ}\text{C}$]	- 20.90	-13 – -23
Higher heating value [kJ/kg]	43.93	45.62 – 46.48
Cetane Number	81.21	68 – 90
Cloud Point [$^{\circ}\text{C}$]	-2.10	-5 – -40
Kinematic Viscosity [cSt]	4.44	2 – 4

3.2 Economics and Profitability Analysis

Table 8 presents the project capital cost (CAPEX) for the different scenarios, and the results show that scenario 2 requires the highest CAPEX of \$39,978,360, while scenario 1 presents the lowest CAPEX of \$18,856,630. The high CAPEX requirement of scenario 2 is due to the higher number of unit operations present in the integrated biorefineries configuration (scenario 2), which confirms that CAPEX strongly depends on process scheme and installed capacity (Tirumareddy et al., 2022).

Also, the plant TDC share of the FCI accounted for 68.46% and 67.83% for scenario 2 and 1, respectively, which is consistent with 70.2% of FCI—(Ahire et al., 2024), 71.43% of FCI—(Cheah et al., 2017) and 55 – 75% of FCI——(Rahimi et al., 2020; Caporusso et al., 2023).

Table 8: Project capital cost estimates

Project Capital Summary		
Items	Scenario 2 Cost [\$]	Scenario 1 Cost [\$]
Total Direct Cost (TDC)	24,881,180	11,627,070
Total Indirect Cost (TIC)	11,462,780	5,515,320
Total Project/Fixed Investment (FCI)	36,343,960	17,142,390
Working Capital (WC)	3,634,400	1,714,240
Total Capital Investment (TCI)	39,978,360	18,856,630

Equally, the OPEX, RMC and TPC of the scenarios were also evaluated as shown in Table 9. It was observed that utilities cost account for 38.64% and 32.59% share of the OPEX for scenario 2 and 1, respectively. The higher utilities cost recorded for scenario 2 could be attributed to the higher utilities (heating, cooling, electricity, etc.) requirement by scenario 2 compared to scenario 1.



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Table : Project operating and production cost estimates

Cost Items	Scenario 2	Scenario 1
Parameters	Cost [\$]	Cost [\$]
Total Utilities Cost	2,630,676	1,055,441
Total Operating Cost (OPEX)	6,808,157	3,238,441
Raw Material Cost (RMC)	30,441,827	29,672,565
Total Production Cost (TPC)	37,249,983	32,911,006

Also, the TPC for scenarios 2 and 1 are \$37,249,983 and \$32,911,006, respectively, with RMC accounting for 81.72% and 90.16% share of the TPC for scenarios 2 and 1, respectively (Table 9), and castor seed is the major cost contributor to RMC for all the scenarios. The high RMC contribution to TPC is in good agreement with reported TEA conducted by –(Cheah et al., 2017) and corroborates the 40 – 90% RMC share of TPC (Tirumareddy et al., 2022), 80 – 90% for bulk chemicals and petrochemicals and around 95% for speciality chemicals (Towler & Sinnott, 2022), and is also consistent with the 80% RMC share reported from previous studies "Masoumi and Dalai, 2021(; Tibesigwa et al., 2024). The study also conforms with 76 – 88% RMC share of TPC for hydro-processed vegetable oil (Tao et al., 2017). Hence, the RMC obtained in this study, for both scenarios are consistent with those in previous studies, suggesting that RMC have a substantial effect on the biofuel production costs.

3.3 Profitability Analysis

Table 10 presents the profitability indices (NPV, IRR, PBP, ROI and PI) of the scenarios at 50% and 100% equity financing. The NPV for both scenarios are positive, indicating profitable investments at 50% and 100% equity financing structures, suggesting that the project's return will exceed the opportunity cost of the investment –(Caporusso et al., 2023). Also, the IRR, which is the discount rate at which NPV equals zero, was also evaluated and found to be 13.03% and 12.22% at 50% equity financing, and 17.10% and 16.36% at 100% equity financing for scenarios 2 and 1, respectively. This suggests that investment at 100% equity financing is more desirable and corroborate with 7.1 – 20.7% IRR reported in the literature for biofuels (Ran et al., 2024).

50% Equity (5 Years Debt Repayment at 12% Interest Rate)		
Profitability Indices	Scenario 2	Scenario 1
NPV	\$11,705,779	\$4,166,637
IRR	13.03%	12.22%
PBP	5.53	6.07
ROI	12.53%	10.92%
PI	1.32	1.24
MSP	\$0.993	\$0.993
100% Equity (0% Debt)		
Profitability Indices	Scenario 4	Scenario 2
NPV	\$18,815,524	\$7,653,602
IRR	17.10%	16.36%
PBP	4.88	5.29
ROI	14.95%	13.35%
PI	1.52	1.45
MSP	\$0.993	\$0.993

3.4 Minimum Biofuel Selling Price

The MSPs of the products for both scenarios were evaluated at 50% equity and 100% equity, and the results are presented in Table 11. Scenario 2 yields the lowest MSP of \$0.650/kg bioethanol and \$0.939/kg renewable diesel at 100% equity financing. The study established that higher debt leads to increased biofuel MSP and that the MSP for bioethanol and renewable diesel in this study were found to be economically comparable to those reported in the literature —(Ran et al., 2024).

Table 11: Minimum Selling Price of Products

50% Equity (5 Years Debt Repayment at 12% Interest Rate)		
Products	Scenario 2	Scenario 1
Solid (Cake) Residue [\$/kg]	0.102	0.102
Renewable Diesel [\$/kg]	0.965	0.968
Light Ends [\$/kg]	0.380	0.380
Bioethanol [\$/kg]	0.700	—
100% Equity (0% Debt)		
Solid (Cake) Residue [\$/kg]	0.102	0.102
Renewable Diesel [\$/kg]	0.939	0.944
Light Ends [\$/kg]	0.380	0.380
Bioethanol [\$/kg]	0.650	—

3.5 Sensitivity of Economic Parameters

Figure 4 presents the sensitivity of net income to $\pm 25\%$ variation in the selected economic factors. A 25% decrease in CS price resulted in a significant increase in net income, ranging from 274% to 669% across the scenarios. However, a 25% increase in CS price led to a severe negative impact, with net income reductions between -348% and -913% , which is consistent with literature reports that feedstock price is a major factor that impact biofuel profitability (Rahimi *et al.*, 2020; Shila and Johnson, 2021 (Rahimi *et al.*, 2020; Caporusso *et al.*, 2023; Ahire *et al.*, 2024). This finding underscores that feedstock price is a primary driver of the profitability of biofuel production. Production capacity ranked as the second most influential factor, followed by debt repayment period, project capital cost, equity ratio, and plant operational life (Figure 4), while interest rates and tax rates had the least influence on profitability.

4.0 Conclusion

This study investigates the technical and economic viability of an integrated biorefinery for the co-production of renewable diesel and bioethanol from CS. The TEA reveals that while both scenarios, producing renewable diesel and CSC (Scenario 1), and co-producing renewable diesel and bioethanol (Scenario 2), are profitable, the integrated approach (Scenario 2) offers better economic

performance. Scenario 2, which involves the co-production of both biofuels, presents the most favourable investment with higher NPV, IRR, ROI and PI at both 50% and 100% equity financing structures. The analysis also confirms that higher equity financing significantly enhances financial viability across all scenarios, resulting in lower minimum selling prices for the biofuels.

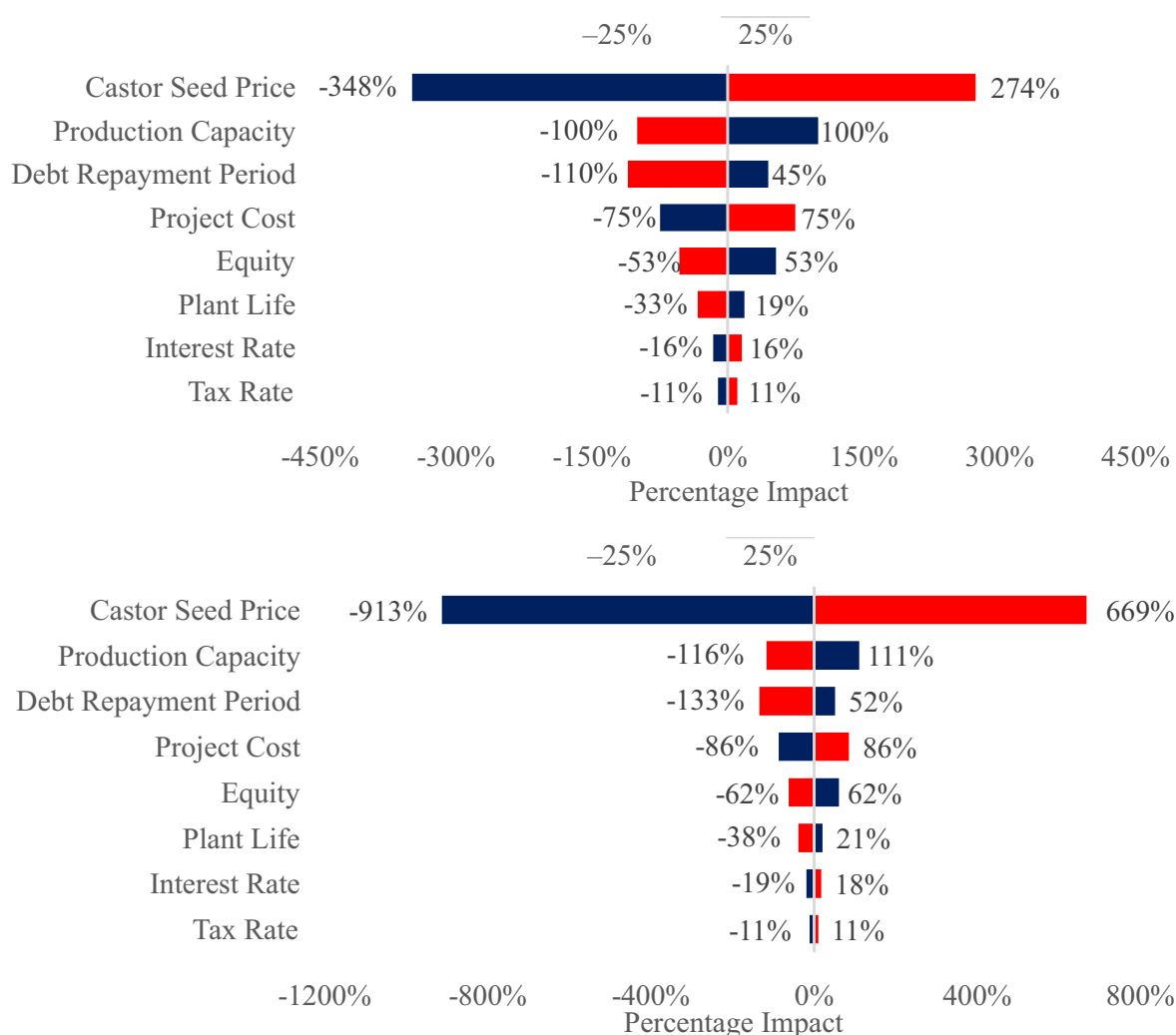


Fig. 4: Sensitivity analysis of net income to economic factors; (a) scenario 2: bioethanol and renewable diesel, and (b) scenario 1: renewable diesel and CSC Sensitivity analysis identified the price of CS as the most critical factor influencing profitability, followed by production capacity and debt repayment period, project cost, equity ratio, plant life, interest rate and tax rate in decreasing order. However, a 25% decrease in feedstock price could increase net income by up to 669%, suggesting the need to secure low-cost raw materials for commercial success. Overall, the research establishes that an integrated biorefinery model is the most competitive and financially viable option. To maximize economic viability, the study recommends focusing on reducing CS costs, increasing production capacity, and securing favourable financing with extended repayment terms.



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Exergy, Economic and Environmental Analyses of a Typical Fluid Catalytic Cracking Unit (FCCU)

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Abstract

This study focuses on the simulation, validation, and performance evaluation of a Fluid Catalytic Cracking Unit (FCCU) using real refinery data. The objectives were to validate the FCCU simulation model, conduct exergy analysis under base and alternative scenarios, and perform economic and sensitivity analyses. Simulation results showed a percentage error of 0–16% for key product properties, confirming reliability. Exergy analysis revealed total exergy destruction of 22.84 MW; 22.66 MW physical exergy, and 0.182 MW chemical exergy. Chemical exergy accounted for only 0.8% of physical exergy, rendering it negligible. Economic evaluation of the base case showed a total plant cost of 1.01 billion USD, operating cost of 381 million USD, annual net profit of 116.5 million USD, exergy loss cost of 30.01 million USD/year, rate of return of 11.49%/year, and a pay-out period of 8.69 years. Across other scenarios, total costs ranged between 1.013–1.014 billion USD, with operating costs, profits, and exergy losses showing comparable variations. Scenario 4 is the most preferred because it favours operations at a lower temperature, better overall efficiency, as well as lower total annual cost.

Keywords: Exergy Analysis, Exergy Loss, Fluid Catalytic Cracking Unit, KRPC

1. Introduction.

Fluid catalytic cracking units (FCCUs) are vital in petroleum refining, converting heavy fractions into lighter, high-value products. Despite their importance, they are among the most energy-intensive units, with energy demands ranging from 50 to 180 MJ/bbl. This is based on the energy and environmental profile of the US petroleum refining industry report (Caballero *et al.* 2014). Studies show that adopting methods such as oxy-firing can reduce power consumption by 30–50 MW compared with post-combustion technologies (Tang *et al.*, 2023). This high demand largely arises from exergy losses. Exergy (Energy = Exergy + Anergy) is the portion of energy available to do useful work, unlike anergy, which cannot be converted into work by any known means. (Rivero, 2002; Nahvi *et al.*, 2023). Physical exergy represents the maximum useful work obtainable as a stream reaches thermal and mechanical equilibrium with the environment, while chemical exergy reflects the work potential in reaching chemical equilibrium. By simulating and validating FCCU operation, this study applies exergy analysis to quantify inefficiencies and proposes scenarios for improving energy, economic, and environmental performance. Combining exergy and economic analyses for multiple scenarios, with a specific focus on Nigerian crude, and validation with plant data will be useful in a better understanding of FCCU operations. Figure 1 is a plug flow diagram (PFD) of KRPC showing the movement of process streams and equipment.

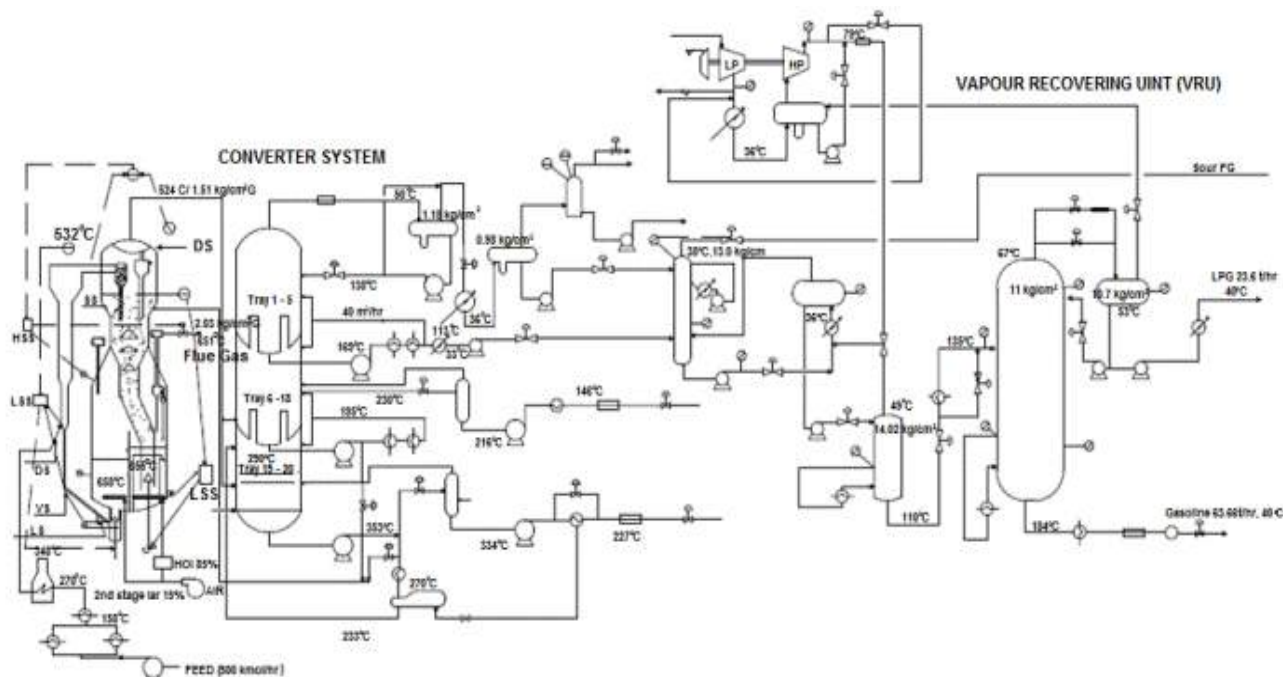


Fig. 1: Actual Process Flow Diagram (PFD) of KRPC

The most widely used cracking units are the catalytic type with a moving catalyst bed of Zeolite-Y, as this gives a higher conversion and above all a higher selectivity. The selectivity of the process is due to the particular characteristics of the catalyst. Actual design depends on refiner's operating conditions and product priority (Bhattacharyya, 2011; Helmer & Smith, 2004). Analysis of energy losses is of scientific interest and also essential for the efficient utilization of energy resources. The most commonly used method for analysis of an energy-conversion process is the first law of thermodynamics.

The basis of thermodynamics is stated in the first and second laws. The first law describes the conservation of energy, while the second law is used to describe the quality of energy and material. The term exergy was introduced by Rant in 1953. The basis of the second law analysis was made by Gouy in 1889 and Stodola in 1898, by the law, which has been named after them by Szargut, 1980. (Amir, *et al.* 2025)

Exergy analysis has been widely recommended as a powerful technique for evaluating energy utilization in chemical processes. Caballero *et al.* (2014) emphasized its ability to identify regions of energy degradation and to guide decision-making on resource allocation, optimization, and cost association. Despite its importance, many FCCU-related studies have overlooked exergy analysis and the validation of results. For instance, (Stratiev *et al.*, 2023) reported that revamping a commercial FCC unit enabled stable operation at higher throughput and raised the riser outlet temperature from 532 to 550 °C, yet no exergy evaluation was conducted. Similarly, Jarullah and Awad (2019) quantified cost savings and energy savings of 35% and 48%, respectively, but did not perform exergy or sensitivity analyses. Caballero *et al.* (2014) showed that FCC plant modifications could reduce exergy losses and achieve 9.33 GJ/h of potential energy savings,

though without economic assessment. Olakunle & Abubakar (2011) could not determine Net savings because utility costs, Heat exchanger size and cost were not available then. Nuhu *et al.* (2012) found that 67% of input energy in fractionator columns was lost, but the study suffered critical gaps—no economic evaluation, no multiple scenarios, no sensitivity analysis, absence of reactor feed temperature effects, lack of validation, and neglect of chemical exergy. Collectively, these studies highlight the potential of exergy analysis while exposing significant gaps that this work seeks to address.

Exergy analysis, when combined with environmental and economic analyses, can become a veritable tool for making recommendations that could guide design and operational changes. The Dangote Refinery has a nameplate capacity of 650, 000 barrels per day(bpd), making it the largest single-train refinery globally. This refinery has no vacuum distillation unit; instead, feedstock at 175 degrees Celsius from the crude distillation unit is preheated to 232 degrees Celsius and is then sent into the reactor/ regenerator. KRPC preheats to 332 degrees Celsius. This huge difference in driving force and temperature will undoubtedly tell on the economics of any refinery. Thus, KRPC needs to reconsider operational changes, that is, running the FCC reactor /regenerator feed temperature at a lower temperature and a possible retrofitting to improve economics.

1. Methodology

Figure 2 shows the methodology for this work. The extreme right of the figure shows clearly the scenarios and corresponding temperatures for reactor/regenerator feed.

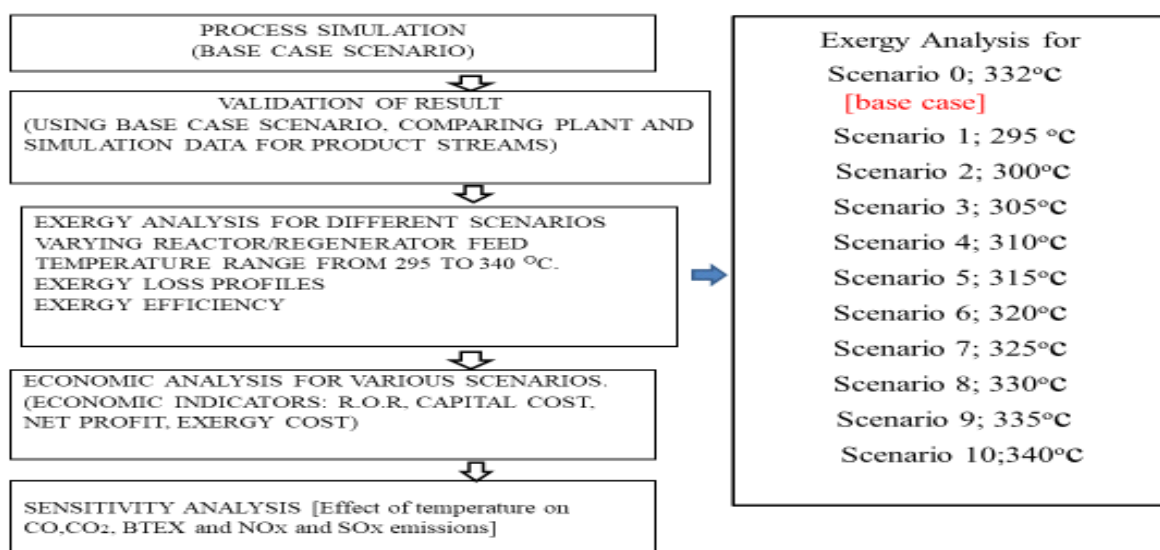


Fig. 2: Schematic diagram of the Methodology

This study adopts a computational simulation-based approach integrated with thermodynamic and economic analysis. The methodology is divided into three major phases: (1) FCC Process Simulation and Validation. (2) FCC Process Simulation and Validation. (3) Exergy Analysis. (4) Economic Analysis.



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2.1 Simulation of the FCC Unit.

- Selection of simulation Software.

Aspen HYSYS version 12.0, installed, was used for this simulation because it has thermodynamic and FCC reaction kinetics models. Aspen HYSYS is a choice simulation software because of a robust technical support base, FCC library, thermodynamic and equation of state packages associated with the software, as well as seamless integration with other software such as Microsoft EXCEL, which makes computation fast and minimize errors.

- Defining the FCC process.

The source of the crude chosen in Aspen HYSY is the Nigerian Escravos crude. While the feedstock composition, which included vacuum gas oil (VGO) was added from the Aspen HYSY Library. Catalyst ZSM, which is similar to what is used in KRPC, was selected from the catalyst library of Aspen.

- Thermodynamic models.

Equation of state (EOS) models; Peng-Robinson (PR) for vapor-liquid equilibrium was adopted. While the physical exergy was obtained directly from Aspen HYSYS after simulation, chemical exergy was calculated from elemental compositions using equation 10 for all species using Microsoft EXCELL

2.2 Model Validation

Table 1 shows the validation done comparing the product stream. Where these stream properties vary, adjustments were made to vary pressure drops (ΔP) in the simulation to reflect KRPC plant data.

Table 1: Validation of Base case scenario.



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STREAM	PARAMETER	UNIT	PLANT	SIMULATION	% ERROR
			DATA	DATA	
C3/C4	TEMPERATURE	⁰ C	40	38	5
	PRESSURE	kPa	200	208.5	4.3
GASOLINE	TEMPERATURE	⁰ C	36	34	5.6
	PRESSURE			657	16.3
Validation	(Pressure condition				
Adjustment	set to 784.5)	kPa	784.5	784.5	0
SOUR		⁰ C			
WATER	TEMPERATURE		12	10.8	10.3
	PRESSURE	kPa	441.3	208.5	52.8
LCO	TEMPERATURE	⁰ C	60	60	0
	PRESSURE				
	(HE 16E02 shell			509.4	48.4
Validation	DP120 & Tube				
Adjustment	shell DP 115)	kPa	343.2	399.4	16.3
FRAC.		⁰ C			
BOTTOM	TEMPERATURE		80	80	0
	PRESSURE				
	(Cooler 16A03)			371.3	15.9
Validation	process stream				
Adjustment	Delta p set to 10	kPa	441.3	431.3	2

- Exergy analysis
Exergy calculation framework, including mass exergy kJ/kg and mass flowrate (kg/h) for each stream, was obtained from Aspen HYSYS. The computation was done on an Excel template to obtain exergy in kW. Exergy analysis determines exergy destruction and exergy efficiencies in the FCC unit. These are calculated based on some governing equations.

2.3 Governing Equations

$$W_{ideal} = \Delta H - T_o S_G \quad (1)$$

$$\Delta H = \sum n h_e - \sum n h_i \quad (2)$$

$$S_G = \sum n \Delta S - \sum \quad (3)$$

$$\eta = \frac{W}{W_{ideal}} \quad (4)$$

$$= 1 - \frac{I \text{ Destruction}}{E_{in}} \quad (5)$$



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$$I_{\text{Destruction}} = T_o S_G \quad (6)$$

$$E_{\text{in}} = m[h_{\text{in}} - h_o - T_o (S_{\text{in}} - S_o)] \quad (7)$$

$$\Psi = h - h_o - T_o (S - S_o) \quad (8)$$

$$= m \Psi = m[h - h_o - T_o (S - S_o)] \quad (9)$$

$$EX_k^{\text{chem}} = \sum_{k=1}^n x_k^{\text{ch}} e_k^{\text{ch}} + \sum_{k=1}^n x_k^{\text{in}} \ln x_k \quad (10)$$

Where x_k is the mole fraction of component k and R is the universal gas constant taken as kJ/kmol.K ; e_k^{ch} is standard molar chemical exergy, kJ/kmol of various substances at T_o and P_o .

$$I = \sum EX_{\text{in}} - \sum EX_{\text{out}} \quad (11)$$

$$\text{Pay Back Period (PBP)} = \frac{\text{Total investment}}{\text{Net cash flow (NCF)}} \quad (12)$$

$$\text{Return on Investment (ROI)} = \frac{\text{PAT}}{\text{Total investment}} \times 100 \quad (13)$$

$$\text{Rate of return (ROR)} = \frac{\text{Income generated in a year}}{\text{Total investment}} \times 100\% \quad (14)$$

$$\text{Net profit [USD/Yr]} = \text{Total product sales} - \text{Total operations cost} \quad (15)$$

Annual cost of electricity = Annual energy consumption (kWh/yr) x Unit cost of electricity (USD/kWh)

(16)

Nigeria electricity cost is $0.15 \text{ USD/kWh} = 0.15 \times 1000 \times 8760$

$= 1,314,000 \text{ USD per MW per annum}$

Where T_o is reference temperature; S_G is entropy generation within a system; S_{in} inlet entropy; S_o outlet entropy; h_e is exit enthalpy; h_i is inlet enthalpy; Ψ is physical exergy; I is exergy destroyed; m is mass; η is efficiency; η' is second law efficiency; w_s is shaft or mechanical work; n is the number of moles or mass of a substance; Q is amount of heat of a substance; $\sum$ is summation.

2.4 Process Economics and Evaluation

The Aspen HYSYS economic analyzer is used for the process economic plant cost. For a good result, prices of hot and cold streams as well as the cost of a stand-alone FCC were specified where applicable in the journal and a reasonable estimate was given following market trends.

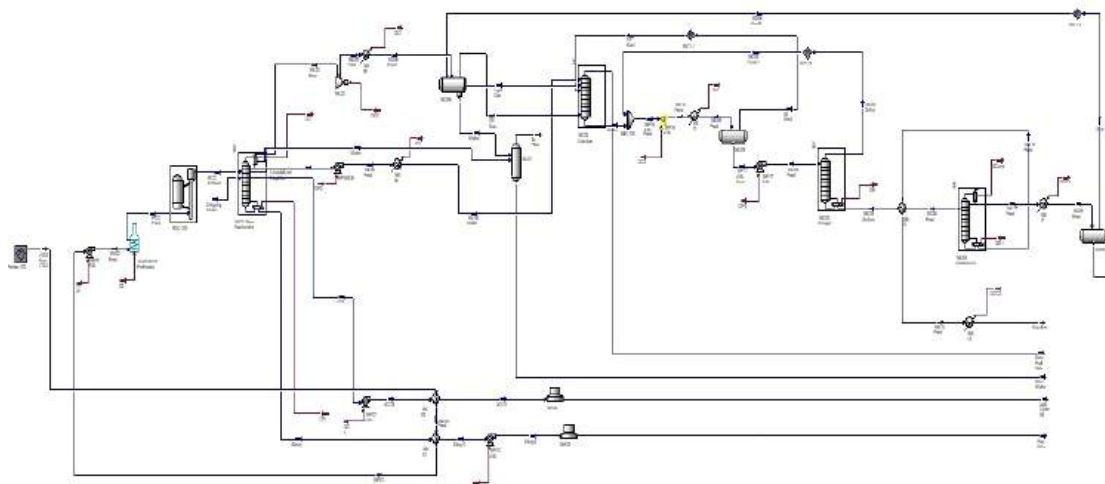


Fig. 3: PFD of Simulated FCCU

Table 2: Trends across various Scenarios

Scenarios (SC) /Temperature	Total Exergy loss	Physical exergy	Chemical exergy	Total Exergy Loss	Overall Eff	Total Annual Cost	Pay Out Period	R.O.R
				COST	(%)	COST	(YR)	(%/YR)
SC / (°C)	MW	MW	kW	(USD/YR)		(USD/YR)		
0/332(base case)	22.84	22.65	182.9	17922960.00	25.84	1013363400.00	8.69	11.49
1 / 295 °C	22.1	21.88	187.4	16792920.00	32.8	1013258200.00	8.72	11.47
2 / 300 °C	22.2	22.01	186.8	16937460.00	31.9	1013309600.00	8.56	11.69
3 / 305 °C	22.3	22.11	186.1	17082000.00	30.9	1013276300.00	8.57	11.67
4 / 310 °C	22.4	22.22	185.4	17239680.00	29.8	1013159600.00	8.59	11.64
5 / 315 °C	22.5	22.25	184.7	17397360.00	28.9	1013159600.00	8.59	11.64
6 / 320 °C	22.6	22.41	184.2	17541900.00	28	1013159600.00	8.59	11.64
7 / 325 °C	22.7	22.51	183.7	17699580.00	27.1	1013312500.00	8.65	11.56
8 / 330 °C	22.8	22.61	183.1	17857260.00	26.2	1013363400.00	8.67	11.55
9 / 335 °C	22.9	22.72	182.5	18028080.00	25.3	1013149500.00	8.7	11.49
10 / 340 °C	23	22.82	182	18185760.00	24.3	1013468000.00	8.72	11.47

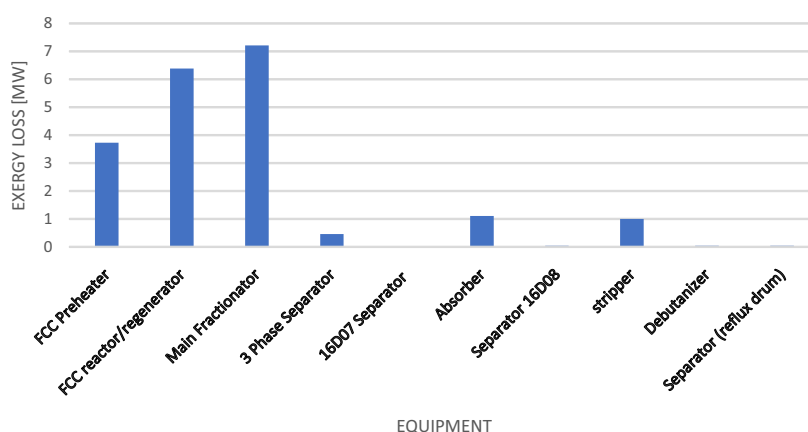


Fig. 4: Exergy losses in each equipment at base case, FCC reactor/ regenerator feed temperature of 332°C

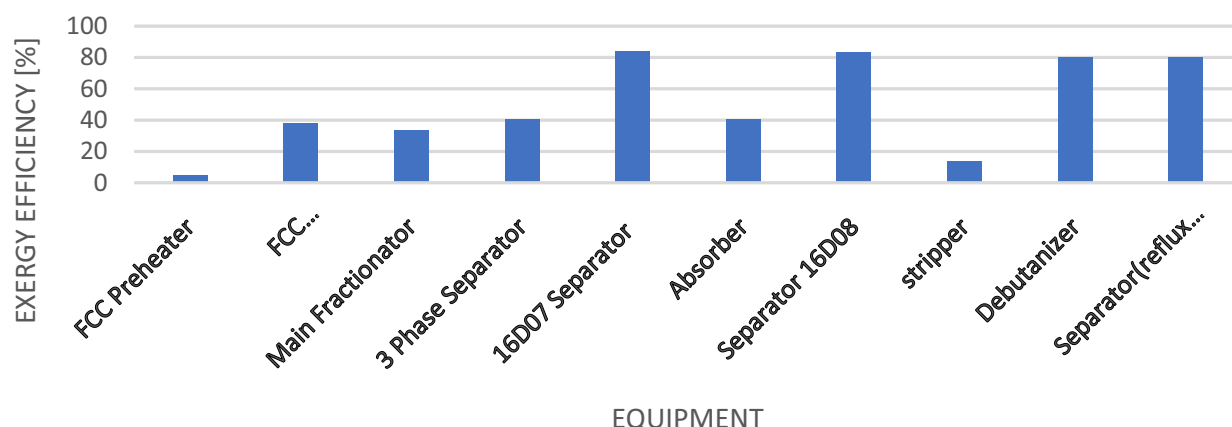


Fig. 5: Exergy Efficiency in Equipment at base case, FCC Reactor/Regenerator feed temperature of 332°C

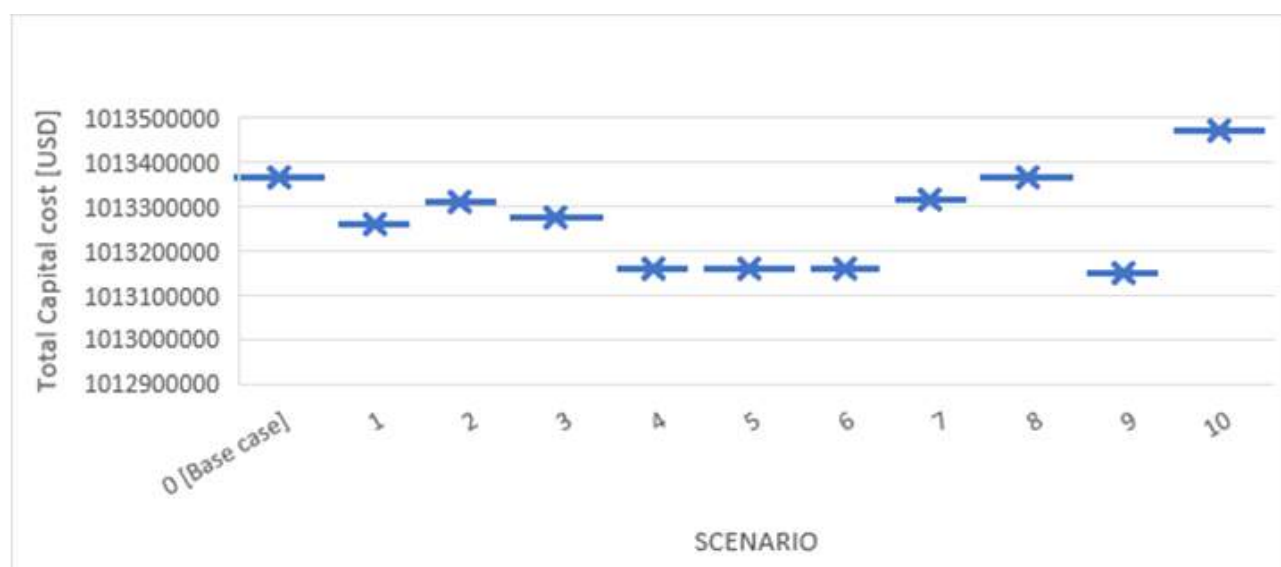


Fig. 6: Total capital cost for different scenarios

4. Results and Discussion

The FCC unit was simulated and validated, showing % error between 0 and 16 for some of the product properties. From Table 1, it is observed that 52.3 % and 48.4% errors for water and LCO were high. Some of these high pressures could be due to pressure buildups or losses, which characterizes real plant operations.

It is observed from Table 3 that physical exergy increases at higher temperature because enthalpy and entropy increase, while chemical exergy reduces at higher temperature due to more spontaneous reactions leading to a reduced maximum work extractable. Hydrocarbons may decompose partially at high temperatures, leading to their change in chemical structure; this can reduce chemical exergy. Chemical exergy is observed to be 0.8% of physical exergy, thereby making it negligible.



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Figure 4 shows Exergy losses in each equipment of the FCCU. The exergy analysis revealed a 22.84MW total Exergy loss, 18 172 620USD/Annum total exergy loss cost, which will amount to a huge financial loss and affect profitability. This is an imperative for exergy loss minimization in FCCU. Figure 5 shows the exergy efficiency of each equipment. The units with high exergy losses have lower efficiencies. Exergy losses in the main fractionator, preheater and Reactor/regenerator units have the highest exergy values of 7.21MW, 3.73MW and 6.38 MW, respectively, for the base case scenario and a similar trend is observed for other scenarios. These high exergy losses in the reactor/regenerator are largely due to chemical reaction and high energy demand in this unit. Whereas that of the main fractionator can be attributed to back mixing, heat and mass transfers. Conversely, column 16D07 Separator has a high exergy efficiency of 90% with a corresponding low exergy loss. This is because the column performs only phase separation, and there is no chemical reaction; there is also no external heating or cooling requirements.

Notably, in Table 2 is the fact that exergy continues to increase from scenario 1 to 10 with an increase in temperature. However, a system operating at a lower temperature where it is thermodynamically feasible is preferred because of the cost associated with the driving force, temperature. From Table 3, it can be seen that at higher temperatures, for example, scenario 10, the greenhouse gas emission is lowest. This will undoubtedly come with a high financial burden. Where there are huge regulations, sanctions and enforcement regarding environmental emissions the FCC may have to be run at a higher temperature so as to meet regulatory standards.

5. Conclusions.

- The FCC unit was simulated and validated, showing % error between 0 and 16 for some of the product properties; a few deviations could be attributed to pressure build-up or losses in the plant.
- Exergy analysis was performed: exergy values for all process streams calculated; the exergy analysis revealed that the total Exergy destroyed in the main fractionator, preheater and Reactor/regenerator units have the highest exergy values of 22.84 MW, 7.2MW, 3.73MW, and 6.38 MW, respectively, for the base case scenario and a similar trend was observed for other scenarios.
- Economic evaluation of the base case showed a total plant cost of 1.01 billion USD, operating cost of 381 million USD, annual net profit of 116.5 million USD, exergy loss cost of 30.01 million USD/year, rate of return of 11.49%/year, and a pay-out period of 8.69 years (8.56–8.72 years). The initial investments would be recouped in 8.56–8.72 years for all scenarios, and the product line would become profitable after that. Since the FCCU is capital intensive, this payout period may be considered reasonable.



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- The efficiency of the entire system decreases with increasing driving force and temperature. This amounts to an increase in operational cost and reduces economics. Scenarios 4, 5, 6, and 9 have the lowest capital cost; scenario 1 has the least net profit and the highest 60.6 kg/h CO₂ emissions, while scenario 10 has the least CO₂ emissions of 55.5kg/h, as shown in Table 2.
- A closer look at the base case (scenario 0) shows that the FCCU of KRPC being operated at a temperature of 332 degrees Celsius is not cost-effective. Hence, the need for operational change. Operating a thermodynamic system at a higher temperature means a higher cost implication. The newly built Dangote refinery operates at a reactor/ regenerator feed temperature of 275 degrees Celsius. The refinery also operates without a vacuum distillation unit, eliminating the crude distillation unit, thereby relying only on feed from the crude distillation unit. This means a reduction in capital cost as well as operating profitability.

Recommendation

With findings in this work, as presented in table 2 and shown in figure 6, it would be necessary to operate the KRPC FCCU at lower temperature of say 310 degrees Celsius (scenario 4) which has shown a higher overall FCC efficiency of 29.8%, lower exergy loss and as well as lower capital investment and other economic indicators which are significant in operating the FCCU profitably. Another significant consideration is to redesign the KRPC complex, taking out the Vacuum distillation unit, or to enhance the heat exchange network to minimize external heating or cooling requirement



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A Review of Advanced Technologies for Hydrogen Production: From Fossil Fuels to Renewable Pathways

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Abstract

Hydrogen is poised to be a cornerstone of the clean energy transition, particularly for decarbonizing hard-to-electrify sectors; however, its environmental value is entirely dictated by its production pathway. This review provides a comprehensive analysis of the hydrogen production landscape, revealing a critical divergence between established and emerging technologies. While thermochemical processes like steam methane reforming (SMR) currently dominate the global supply, their significant CO₂ emissions mandate the integration of carbon capture, utilization, and storage (CCUS) to create a viable transitional "blue" hydrogen stream, reducing emissions by up to 90% at an increased cost. The findings underscore that the most promising route for sustainable hydrogen is renewable-powered electrolysis, with proton exchange membrane (PEM) technology leading for its operational flexibility and solid oxide electrolysis (SOEL) for its high efficiency. Simultaneously, biomass conversion pathways, enhanced by machine learning optimization and novel processes like chemical looping gasification, offer a carbon-neutral niche for waste valorization. In contrast, cutting-edge biological and direct solar-driven pathways, such as fermentation and photoelectrochemical splitting, remain limited by scalability and efficiency barriers. The analysis concludes that a diversified portfolio, leveraging blue hydrogen in the near-term and accelerating green electrolysis and biomass pathways for the long-term, is essential. The ultimate viability of this portfolio hinges on continued reductions in capital cost, breakthroughs in catalyst and material science, and the implementation of supportive policy frameworks.

Keywords: Hydrogen production, Steam methane reforming, Electrolysis, Biomass gasification, Thermochemical cycles, Biohydrogen, Carbon capture, Renewable energy

1. Introduction

The growing global urgency to combat climate change has intensified the pursuit of sustainable, low-carbon energy carriers. Among these, hydrogen (H₂) stands out as a leading candidate, due to its high energy density by weight (120 MJ/kg) and zero carbon emissions during use, producing only water vapour. These qualities make hydrogen a highly promising alternative to fossil fuels in energy-intensive industries such as transportation, chemical manufacturing, and heavy industry (Osman et al., 2024; Pangestu et al., 2024, 2025; Singh et al., 2023; IRENA, 2021; Franco, 2025; Taghizad-Tavana et al., 2025; Lim et al., 2022;

Angelico et al., 2025; Rasul et al., 2022; Zainal et al., 2024; Sebbagh et al., 2024). However, the environmental benefit of hydrogen is entirely dependent on its production method. Currently, over 95% of the world's hydrogen is produced from fossil fuels, resulting in substantial CO₂ emissions (IEA, 2023; Salvi & Subramanian, 2015). Consequently, biomass and waste conversion to hydrogen addresses the dual challenge of waste management and clean energy production (Islam et al., 2024; Alao et al., 2022; Dhanya et al., 2020; Bhatia et al., 2018). Conventional methods like steam gasification and fermentation are well-established but face limitations in efficiency, hydrogen purity, and economic viability. To this effect, recent research has focused on overcoming these barriers through technological innovation across thermochemical, biological, and hybrid pathways.

This review synthesizes recent advances across the spectrum of hydrogen production technologies (Figure 1), evaluating their maturity, efficiency, environmental impact, and potential for scalability in a decarbonized economy. [Table 1](#) summarizes these methods, highlighting their advantages and limitations.

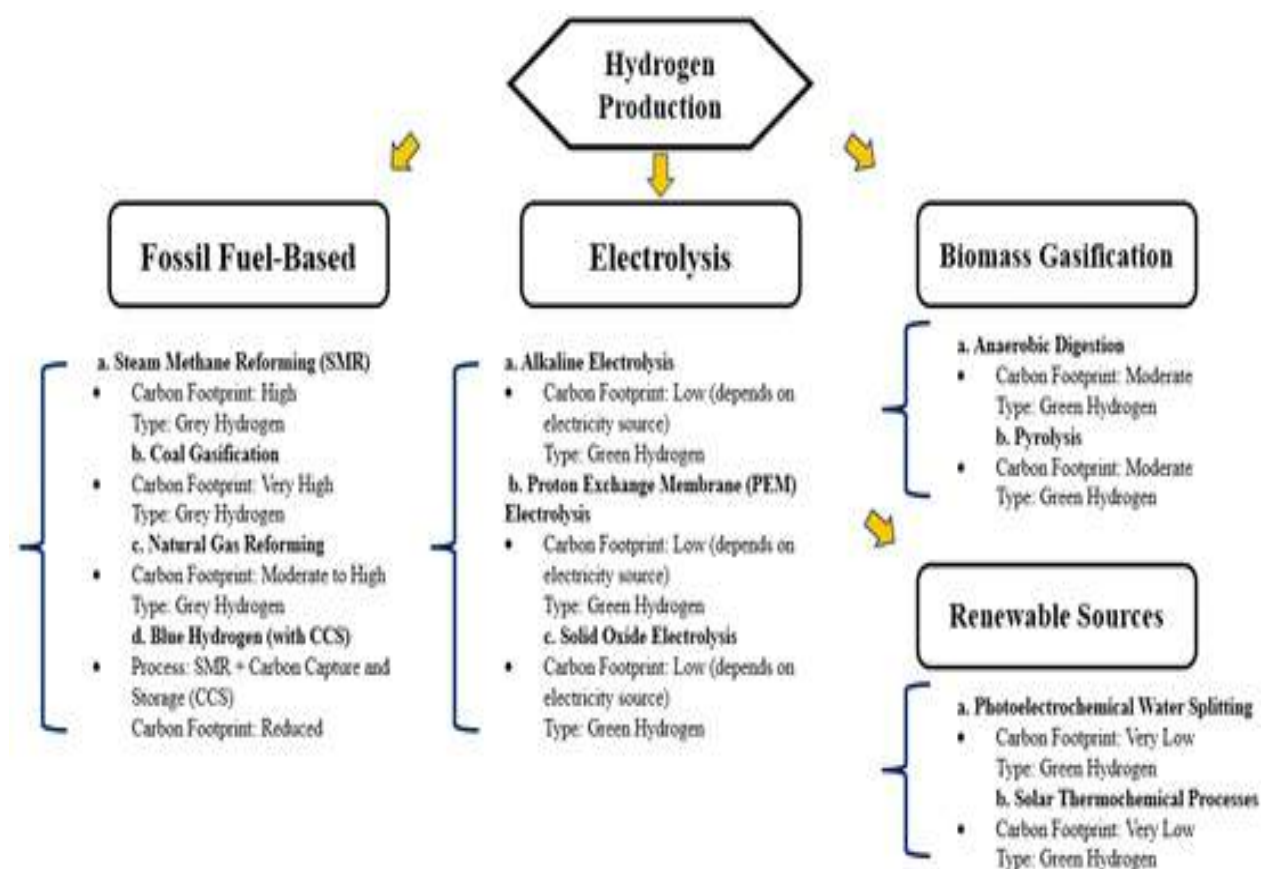


Fig. 1: Hydrogen production techniques categorized by their environmental impact and the form of hydrogen generated (Alizadeh et al. 2024).

Table 1: Recent status of several hydrogen production pathways (Pangestu et al., 2025).

Methods	Raw Materials	CO ₂ emission (kg CO ₂ e/kg H ₂)	Temperature Range	H ₂ Cost (\$/kg)	Maturity level	Ref.
Steam Methane Reforming (SMR)	Natural gas, Steam	1.5–2.0	700–1000°C	0.7–2.2	Mature, widely used worldwide	Oni et al. (2022)
SMR with Carbon capture and storage (CCS)	Natural gas, Steam	1.5–2.0	700–1000°C	1.4–3.8	Commercial stage, but limited application (CCS)	Shahid & Kim (2023)
Electrolysis	Water	0–3.5	25–200°C	3.2–7.7	Early commercial stage, high cost	Peng (2023)
Coal Gasification	Coal, Steam	19.0–23.0	700–1200°C	1.9–2.6	Mature, predominantly in China	Dai et al. (2023)
Gasification with CCS	Coal, Steam	2.0–5.0	700–1200°C	2.0–3.5	Commercial stage, but limited application (CCS)	Liu et al. (2023)
Biomass Gasification	Biomass, Steam	3.0–5.0	700–1200°C	1.9–2.6	Similar to coal gasification, mature	Zhu et al. (2024)
Methane Pyrolysis	Natural gas	0.5–16.0	500–2000°C	0.5–3.5	Early commercial stage, emerging	Pangestu et al. (2024)
Biomass Pyrolysis	Biomass	3.0–5.0	700–1500°C	1.5–2.5	Similar to biomass gasification, emerging	Veksha et al. (2023)
Dark Fermentation	Biomass, Microorganisms	0–3.0	25–70°C	N/A	Experimental stage, ongoing development	Talapko et al. (2023)
MECs (Microbial Electrolysis Cells)	Biomass, Microorganisms	0–2.0	25–40°C	N/A	Pilot scale, demonstration projects	Arun et al. (2024)



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2. Thermochemical Processes from Fossil Fuels

2.1 Steam Methane Reforming (SMR)

SMR is the most prevalent method, accounting for roughly 75% of global hydrogen production, due to its cost-effectiveness and established technology (Dufour et al., 2009; Yun et al., 2023). It involves the endothermic reaction of methane with steam over a nickel-based catalyst at high temperatures (700–1000 °C):



This is followed by the water-gas shift reaction:



The main advantage of SMR is its low cost and established infrastructure. The primary disadvantage is the high CO₂ emissions (10–12 kg CO₂ per kg H₂). Recent studies focus on integrating steam methane reforming (SMR) with carbon capture, utilization, and storage (CCUS) to produce blue hydrogen by capturing CO₂ emissions from SMR, thereby reducing its carbon footprint. Key approaches include heat integration to recover waste heat for carbon capture, shared CCUS infrastructure in cluster configurations, and comprehensive techno-economic analyses. **Khojasteh et al. (2023)** provided a techno-economic review of SMR-CCUS, highlighting that while it reduces emissions by up to 90%, it increases capital and operational costs by 30–60% and requires robust CO₂ transport and storage networks. Similarly, **Zang et al. (2024)** performed a techno-economic analysis and life cycle assessment of five natural gas reforming-based hydrogen production pathways with various CCS configurations. Their study demonstrated that a CCS system can achieve over 95% CO₂ capture at the plant level and reduce well-to-gate (WTG) greenhouse gas emissions to 3.43 kg CO₂ eq/kg H₂, representing a 63–68% reduction compared to the industrial standard. However, the levelized cost of hydrogen (LCOH) with CCS was estimated between \$1.17 and \$1.56 per kg, higher than the \$1.04/kg for the industrial standard case. Meanwhile, **Navas-Anguila et al. (2021)** revisited the role of SMR with CO₂ capture for long-term hydrogen production. They developed an energy systems optimization model to assess the potential contributions of grey and blue hydrogen in meeting Spain's hydrogen demand for fuel cell electric vehicles from 2020 to 2050. Their model included CCS retrofits to SMR and concluded that while SMR could satisfy road transport hydrogen demand in the short term (2020–2030), it is likely to be replaced by water electrolysis in the long term (2030–2050).

2.2 Coal Gasification

Coal gasification involves reacting coal with oxygen and steam under high pressure and temperature to produce syngas, which is then shifted to produce H₂ and CO₂. It is more carbon-intensive than SMR, emitting 19–23 kg CO₂ per kg H₂. The future of coal gasification is heavily dependent on the feasibility of large-scale CCUS. **Li et al. (2022)** explored advanced integrated gasification combined cycle (IGCC) plants with >95% carbon capture, noting that their economic viability is highly sensitive to carbon pricing policies.



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Comparatively, the choice between SMR and coal gasification involves a trade-off between cost, resource availability, and environmental goals. SMR is the dominant, cost-effective method, while coal gasification is pivotal in coal-rich regions. The future viability of both processes in a decarbonizing world is heavily dependent on the integration of Carbon Capture, Utilization, and Storage (CCUS) to create "blue" hydrogen (IEA, 2021; Kim & Yang, 2023). For Nigeria, **steam methane reforming (SMR) is the overwhelmingly more practical and less emissions-intensive pathway** for hydrogen production compared to coal gasification. This is due to Nigeria's abundant natural gas reserves and the lack of a significant coal industry. The emission profile of SMR, while substantial, is far lower than that of coal gasification.

3. Electrolysis: Water Splitting with Electricity

Electrolysis uses electrical energy to split water into very high-purity hydrogen and oxygen (Naimi & Antar, 2018; Chisholm et al., 2022; Zhou et al., 2018; Kelly, 2014; Chi & Yu, 2018; Rashid et al., 2015; Xiang et al., 2016; Buslaev et al., 2023). Its carbon footprint is determined by the source of the electricity.

3.1 Alkaline Electrolysis (AEL)

AEL is a mature and commercially available technology. It uses a liquid potassium hydroxide electrolyte and electrodes separated by a diaphragm. It is known for its reliability and long lifespan, but has a slower response time and lower operating current density compared to newer technologies. **Schmidt et al. (2022)** reviewed advances in electrode materials and diaphragms that are pushing efficiencies above 75% and allowing for greater operational flexibility, which is critical for integration with variable renewables.

3.2 Proton Exchange Membrane Electrolysis (PEMEL)

PEMEL uses a solid polymer electrolyte and operates at high current densities, allowing for a more compact design, rapid response, and dynamic operation. Its main challenges are the reliance on expensive platinum-group metal catalysts and the durability of the membrane (Mustapha et al., 2025). **Marocco et al. (2024)** documented recent progress in developing low-cost, high-performance non-precious metal catalysts and durable membrane materials, which are essential for reducing the capital cost of PEM systems.

3.3 Solid Oxide Electrolysis (SOEL)

SOEL operates at high temperatures (700–850°C), utilizing heat to reduce the electrical energy required for splitting water. This gives it the potential for the highest electrical efficiency of all electrolysis technologies. However, its high temperature demands create challenges with material durability and system startup time. **Lei et al. (2023)** provided a comprehensive review of material development for electrodes and electrolytes, highlighting improved performance and longevity that are moving SOEL closer to widespread commercialization.



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4. Biomass-Based Pathways

4.1 Biomass Gasification and Pyrolysis

This process converts biomass into syngas through thermochemical reactions, similar to coal gasification. It is considered carbon-neutral as the CO₂ released during production is offset by the CO₂ absorbed by the biomass during growth (Luo & Abu-Omar, 2017; Hussain et al., 2017). Ahmed et al. (2022) provided a comprehensive review on biomass gasification, detailing how varying feedstock types and gasifying agents (like steam or oxygen) significantly alter syngas composition and [hydrogen \(H₂\)](#) yields. The study identified tar formation as a major impediment, as these complex hydrocarbons can clog equipment, and proposed using advanced catalytic reforming methods, such as steam or partial oxidation reforming, to break down tars, recover chemical energy, and ultimately produce a cleaner, higher-purity hydrogen-rich syngas.

Machine learning (ML) algorithms are deployed to model complex, non-linear relationships in biomass gasification/reforming to predict product yields, optimize process conditions, and improve understanding of the process (Tuntiwongwat et al. 2025; Shi et al., 2024; Ren et al., 2023; Ceylan & Ceylan, 2021). Common ML methods used include Artificial Neural Networks (ANN), [Gradient Boosting Regression](#) (GBR), [Support Vector Machines](#) (SVM), and [Random Forest](#) (RF), which achieve high prediction accuracy for outputs like syngas composition and heating value (Santhappan et al. 2024; Mahdavi et al., 2025). Moreover, advanced techniques like [Physics-Informed Neural Networks](#) (PINN) are also used to improve model interpretability and ensure physically feasible predictions. **Dash et al. (2024)** used an artificial neural network (ANN) coupled with a genetic algorithm to optimize process parameters (temperature, equivalence ratio, catalyst loading) for maximal hydrogen production from wood chips, reducing experimental time and cost significantly.

4.1.1 Supercritical water gasification (SCWG)

SCWG is a highly promising technology for wet biomass wastes (e.g., sewage sludge, food waste, algae) as it eliminates the energy-intensive drying step required by other thermochemical processes. In supercritical conditions ($T > 374\text{ }^{\circ}\text{C}$, $P > 22.1\text{ MPa}$), water acts as both a solvent and a reactant, leading to high gasification efficiencies. Research has focused on **catalyst integration** to lower operating temperatures and pressures, thereby reducing capital costs. **Kumar et al. (2023)** demonstrated that Ru-based catalysts supported on carbon nanotubes achieved hydrogen yields exceeding 75% from microalgae at lower severities. Furthermore, **continuous-flow reactor designs**, as reviewed by **Okolie et al. (2022)**, are addressing the key challenge of reactor clogging, moving SCWG closer to commercialization.



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4.1.2. Chemical looping gasification (CLG)

CLG utilizes metal oxides as oxygen carriers to provide oxygen for the gasification reaction, eliminating the need for an energy-intensive air separation unit and producing a nitrogen-free syngas. The development of **perovskite-type oxygen carriers** (e.g., LaFeO_3 , CaMnO_3) has been a breakthrough. These materials exhibit high redox activity, stability over multiple cycles, and self-catalytic properties for tar cracking. **He et al. (2023)** reported a bimetallic Fe-Ni oxygen carrier that achieved 98% carbon conversion and a syngas yield with a H_2/CO ratio of 2.5 from pine sawdust, highlighting the potential for direct downstream synthesis.

4.1.3. Microwave-assisted pyrolysis and catalytic reforming

Microwave heating offers volumetric, rapid, and selective heating compared to conventional methods, leading to more efficient cracking of biomass and tars. The synergy between **microwave heating and engineered catalysts** is a key area of progress. **Wang et al. (2024)** developed a microwave-responsive SiC-supported Ni catalyst that acted as both a "micro-reactor" and a catalyst, dramatically enhancing tar reforming and increasing hydrogen concentration in the product gas to over 70 vol%. This approach significantly improves energy efficiency and reaction rates.

4.2 Aqueous Phase Reforming (APR)

APR is a lower-temperature process that converts oxygenated compounds in biomass-derived sugars and polyols into H_2 and CO in a single reactor (Coronado et al., 2016). APR offers an eco-friendly method for producing renewable chemicals and hydrogen from biomass feedstocks under mild conditions, distinguishing it from other methods that typically require higher temperatures or produce less sustainable products. Key advantages include the use of readily available biomass, reduced energy consumption due to lower reaction temperatures ($\sim 200\text{--}250^\circ\text{C}$), and the generation of renewable hydrogen and valuable chemicals (González-Arias et al., 2023; Davda et al., 2003; Kirilin et al., 2012). **Consequently, products derived from biomass, such as polyols (e.g., sorbitol), hydrogen, and alkanes, are nontoxic** (Davda et al., 2005). **Dash et al. (2024)** explored recent catalyst innovations, particularly with platinum and nickel-based catalysts, which have significantly improved hydrogen selectivity and yield from complex aqueous feedstocks, making APR a promising route for waste valorization.

5. Biological and Solar-Driven Pathways

5.1 Dark and Photo Fermentation

These processes use microorganisms to produce hydrogen from organic matter (Habchi et al. 2022). Often, dark fermentation is followed by photo fermentation to maximize hydrogen production from organic waste. Dark fermentation produces hydrogen and organic acids, then photo fermentation uses the acids to produce more hydrogen. While they can utilize various waste streams, they currently suffer from low conversion efficiencies and low hydrogen production rates (Modzelewska et al., 2024; Anwar et al., 2019). To improve



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biohydrogen production through sequential dark and photo fermentation of organic waste, further studies are focusing on optimizing key factors such as microbial consortia, feedstock pre-treatment, bioreactor design, and operational parameters. Researchers are also exploring hybrid systems, light perturbation techniques, and the use of nanomaterials to enhance hydrogen yields and substrate conversion. These advancements are to achieve more efficient and cost-effective biohydrogen production, supporting broader renewable energy goals. With an energy content of 143 kJ/g, hydrogen possesses a much higher energy density than methane, which has 56 kJ/g, making hydrogen a superior fuel and energy carrier (Khanal, 2008). **Kumar et al. (2024)** reviewed strategies for metabolic engineering of microbes and the design of hybrid systems that combine dark and photo fermentation to maximize substrate conversion and overall hydrogen yield from biomass.

5.2 Photoelectrochemical (PEC) Water Splitting

PEC technology seeks to directly convert solar energy into chemical energy in the form of hydrogen (H_2) using semiconductor materials within a single device (Phogat et al., 2024). Often hailed as the “holy grail” of green hydrogen production, this approach holds great promise but still faces significant challenges related to material efficiency, long-term stability, and overall cost. **Wang et al. (2023)** summarized breakthroughs in novel semiconductor materials, including metal-organic frameworks (MOFs) and perovskite-based photoelectrodes, which have demonstrated improved light absorption and charge separation properties, pushing solar-to-hydrogen efficiencies closer to the commercially viable threshold of >10%.

6. Conclusion and Future Perspectives

The landscape of hydrogen production is diverse and rapidly evolving. While SMR with CCUS offers a near-term pathway to reduce emissions from existing infrastructure, the long-term goal must be the widespread adoption of green hydrogen via electrolysis powered by renewables. Among electrolyzers, PEMEL is leading for flexible applications, while SOEL holds promise for high-efficiency, centralized production linked to industrial heat sources.

Emerging technologies like biomass gasification, APR, and PEC splitting offer niche advantages, particularly for waste utilization and direct solar conversion, but require substantial R&D to overcome efficiency and scalability barriers. Future efforts must focus on **catalyst development** (reducing or eliminating the need for precious metals in electrolyzers), **system integration** (developing sophisticated control systems to seamlessly integrate electrolysis with intermittent renewable power sources), **policy support** (implementing carbon pricing and subsidies to bridge the current cost gap between green and grey hydrogen), and **infrastructure investment** (building the necessary pipelines, storage facilities, and refueling stations to create a hydrogen economy) (Alli et al., 2024). The transition to a sustainable hydrogen future will not be reliant on a single technology but on a portfolio of solutions tailored to regional resources and economic conditions.



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Lithium as an Alternative Energy Source: A Comprehensive Review of its Role in Sustainable Energy and Industrial Development

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Abstract

This paper critically reviews the potential of lithium as a pivotal alternative energy source, focusing on its applications in sustainable energy systems and its contribution to industrial development. It explores current lithium-ion battery technologies, emerging lithium-based energy solutions, and the challenges associated with their widespread adoption, including resource availability, environmental impact, and recycling. Furthermore, the review analyzes lithium's role in supporting key industrial processes and its alignment with global efforts towards a greener economy, with specific emphasis on Nigeria's burgeoning lithium landscape within the broader African context. By examining both the opportunities and limitations, this paper aims to provide a comprehensive overview of lithium's current and future significance in the energy landscape, particularly for national industrial development and sustainable energy supply in Nigeria.

Keywords: Lithium, Sustainable energy, SMEs, National industrial development, Alternative Energy.

1. Introduction

The world's energy landscape is changing fast, driven by skyrocketing demand and the urgent need to tackle climate change. In 2024, global energy demand jumped by 2.2%, outpacing the average growth of the past decade, fueled partly by extreme weather events that strained ageing energy grids (International Energy Agency [IEA], 2024). Meanwhile, energy-related CO₂ emissions hit a new high in 2024, showing that decarbonization remains a tough challenge despite progress in renewables (IEA, 2024). The year 2025 is a turning point, with technology, policies, trade, and geopolitical shifts reshaping how we produce and use energy (World Economic Forum [WEF], 2025). The Globalia Pact, a UN initiative, pushes for a rapid phase-out of fossil fuels and a sprint toward renewables to hit net-zero, a must for fighting climate change and securing our planet's future (United Nations Department of Economic and Social Affairs [UNDESA], 2025). Extreme weather has made it clear: we need secure, resilient energy systems that cut emissions and meet bold targets, like tripling renewable capacity and doubling energy efficiency by 2030 (WEF, 2025).

Lithium is a superstar in this energy shift, especially for batteries in electric vehicles (EVs), solar storage, and wind turbine systems (U.S. Department of Energy, 2023). Alongside cobalt, graphite, manganese, and nickel, lithium is a critical battery metal, vital for the clean energy boom (Kesler et al., 2021). In 2024, the U.S. added 48.2 gigawatts of solar, wind, and battery storage, a 47% jump, showing the hunger for storage solutions (Energy Storage News, 2025). Even AI data centres, expected to eat up nearly half of U.S. electricity growth by 2030, rely on lithium batteries (Energy Storage News, 2025). Global lithium demand



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soared nearly 30% in 2024, with 90% going to batteries, and it is projected to triple by 2030, driven by cheaper renewables and policies like COP29's goal of 1,500 gigawatts of storage (IEA, 2025; Two Birds, 2025).

This paper reviews lithium-ion battery technologies (e.g., LCO, NMC, LFP) and emerging alternatives like lithium-sulfur and solid-state batteries, evaluating their performance, cost, and safety. It also examines Nigeria's lithium reserves, production, and policies, comparing them to those of other African nations, such as Zimbabwe. The objectives are to identify research gaps and technological hurdles slowing down lithium's adoption for sustainable energy, analyze Nigeria's lithium potential and policy framework, and propose strategies for a sustainable lithium supply chain to support industrial growth.

Lithium is not just about batteries; it is a game-changer for sustainable energy and industrial growth, perfectly fitting the NSChE conference theme, "The Role and Contribution of SMEs to National Industrial Development and Growth." While this paper does not focus solely on SMEs, lithium tech opens doors for new industries, like battery manufacturing and recycling, creating jobs and innovation (WEF, 2024). In Nigeria, where oil dominates, lithium could spark SME growth in places like Lagos, building batteries for solar grids or electric *keke*. The rise of AI data centres and large-scale battery systems shows lithium's steady demand, independent of electric vehicle (EV) trends, driving industrial expansion (WEF, 2024). This ties to the sub-theme "Raw Materials Development and Utilization," as Nigeria's lithium deposits (e.g., 50,000 tons in Nasarawa) need local processing and quality control to benefit SMEs (MiningCadastre, 2023).

Lithium also supports the sub-theme "Sustainable national energy supply." Lithium-ion batteries stabilize solar and wind power, crucial for Nigeria's 427,000 MWh/day solar potential, letting us store energy for markets like Sabon Gari (Energy Storage News, 2025; REA, 2023). This cuts reliance on dirty Peaker plants and boosts energy independence, vital for steady industries (IEA, 2023). Batteries respond to grid needs in seconds, making them perfect for stability (IEA, 2023). For Nigeria, lithium could replace oil as a new economic driver, with the Ministry of Solid Minerals estimating our mineral deposits at over \$700 billion (VerivAfrica, 2023). The development of the lithium-ion battery was catalyzed by foundational research on intercalation compounds, notably Whittingham's work on TiS₂ (Whittingham, 1976) and, crucially, Goodenough's discovery of the high-voltage LiCoO₂ cathode (Mizushima et al., 1980). A safe, practical device was achieved by Yoshino, who paired this cathode with a carbon anode and engineered a stable electrolyte, enabling the "rocking-chair" mechanism (Yoshino, 1985). This integration of key materials researches ultimately produced the safe, high-energy-density rechargeable battery that has become a foundational modern technology. It is a chance to build a greener economy and stabilize industries.

2. Lithium Chemistry and Energy Storage

Lithium, symbolized as Li, is the lightest known metal and belongs to the alkali metal group on the periodic table, specifically in period two, group one, with an atomic number of three. It is a silvery-white element with the highest specific heat of any solid element, and it can form strong alloys when combined with metals like copper, manganese, aluminium, and cadmium. Lithium is soluble in short-chain aliphatic amines but insoluble in hydrocarbons.

Lithium-ion battery technology has advanced significantly, with modern cells comprising cathodes (e.g., LiCoO_2 or LiFePO_4), graphite anodes, and lithium-ion-conducting electrolytes, as illustrated in Figure 1. While LiCoO_2 provides stability, LiFePO_4 offers superior cost-effectiveness, thermal tolerance (-20 – 70°C), and cycle life (>500 cycles) (Chung et al., 2020). Despite advantages like high energy density and low self-discharge, challenges such as high cost, thermal degradation, and safety risks (e.g., thermal runaway) persist, necessitating protective circuits that curb energy density (Deng, 2019). Emerging solutions like silicon-based anodes are being developed to overcome these limitations, particularly for electric vehicle applications (Manthiram, 2020)

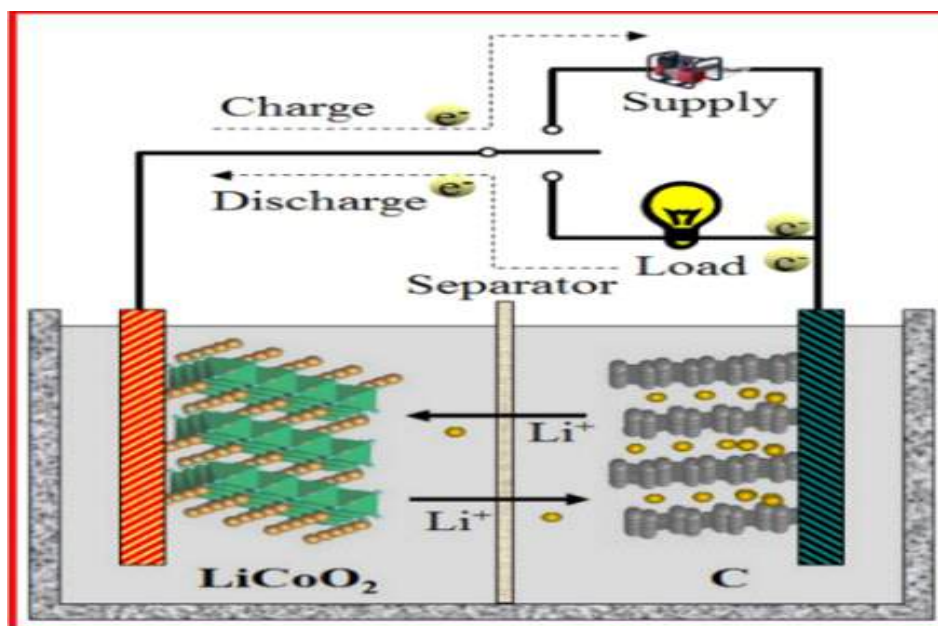


Fig. 1: Illustration to show the basic components and operation principle of a Li-ion cell.

Energy storage technologies are critical for modern applications from electric vehicles to grid-scale renewable integration. While Lithium-ion (Li-ion) batteries (see figure 1) represent a mature technology, they are approaching their practical energy density limits of 200 – 250 Wh/kg (Zhang et al., 2020). This has spurred research into next-generation alternatives. Among these, Lithium-Sulfur (Li-S) batteries are promising due to their higher theoretical energy density and lower cost, but they face commercialization hurdles from rapid capacity fade during cycling (Santhanagopalan et al., 2019).

Another major focus is solid-state battery technology depicted in Figure 2, which replaces the flammable liquid electrolyte with a solid conductor. This architecture significantly enhances safety by reducing combustion risks and potentially enables the use of lithium metal anodes for higher energy density. Solid-state batteries are also believed to offer longer cycle life and simpler packaging requirements (Jasinski, 2020; Nishio et al., 2020)

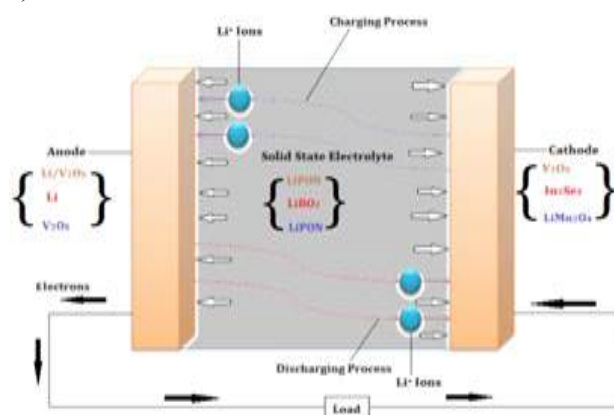


Fig. 2: A schematic representation of a representative lithium-based solid-state battery.

Lithium-air (Li-air) batteries, illustrated in Figure 3, represent a breakthrough in energy storage, offering a theoretical energy density of 5,000 Wh/kg, far surpassing conventional lithium-ion batteries (250 Wh/kg) by leveraging atmospheric oxygen as an unlimited cathode reactant (Liu et al., 2021). Their lightweight design, enabled by air-breathing cathodes, makes them ideal for electric vehicles and portable electronics, with potentially lower environmental impact. During discharge, lithium ions react with oxygen to form lithium peroxide/oxide, reversing during charging. However, practical adoption faces hurdles: limited cycle life from cathode degradation, the lack of stable electrolytes resistant to air reactions, and sensitivity to humidity/temperature (Bruce et al., 2020). While their potential is transformative, overcoming these barriers is critical for commercialization.

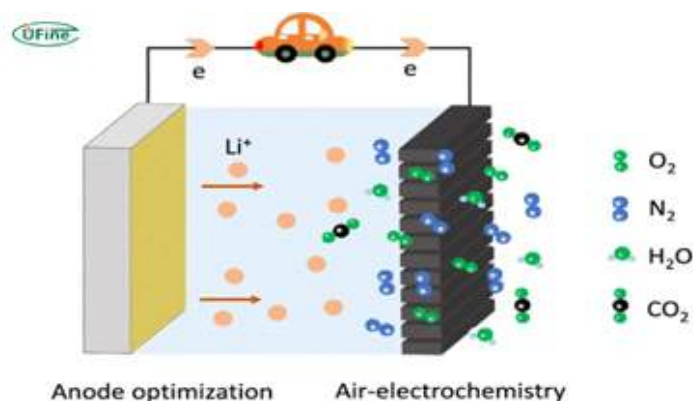


Fig. 3: Lithium-air batteries

3. Lithium as an Alternative Energy Source: Applications and Impact

The integration of lithium-ion batteries (LIBs) into renewable energy systems has revolutionized energy storage by addressing the lack of consistency in solar and wind power supply. LIBs offer high energy density, fast charge-discharge cycles, and long operational life, making them ideal for grid-scale

applications (Dunn et al., 2020). Countries such as Germany, Australia, and the United States have deployed lithium-based Battery Energy Storage Systems (BESS) to support their national grids. These systems perform functions like peak shaving, which is an energy management strategy used by commercial and industrial facilities to reduce their electricity consumption during high demand, load levelling, and frequency regulation, thus enhancing grid reliability and enabling higher renewable penetration.

In Nigeria, where grid reliability is a longstanding issue, off-grid solar systems with lithium storage are a practical solution to light up rural areas (Figure 4). For example, the World Bank-backed Nigeria Electrification Project (NEP) incorporates lithium-based storage in mini-grid installations across underserved communities (World Bank, 2022).



Fig. 4: Mini grid application in rural area

Table 1 summarizes the different battery types, benefits, level of use and their application in Nigeria.

Table 1: Summary of Lithium application systems, battery types, benefits and level of use in Nigeria.

Application	Battery Type	Benefits	Use level in Nigeria
Grid-scale storage	Lithium-ion	Grid stability, Load management	Emerging
Mini-grids	Lithium-ion (Lithium iron phosphate)	Rural electrification, low cost	Scaling
Residential systems	Lithium-ion (Nickel-Manganese-cobalt oxide)	Energy independence, cost-saving	Growing

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Lithium-ion batteries power the global electric vehicle (EV) revolution, enabling 500+ km ranges and fast charging (30-80% in 30 minutes) and powering 85% of global EVs (IEA, 2023). In Nigeria, companies like Jet Motors are introducing electric buses, potentially reducing fuel subsidies and pollution while creating jobs in charging infrastructure and maintenance, boosting economic growth. Lithium-ion technology first gained commercial prominence through its use in portable consumer electronics. From mobile phones to laptops, LIBs offer compactness, safety, and longevity. Although this application is mature, its relevance persists due to the continued demand for high-performance devices, increasing usage in smart agriculture, health monitoring, and digital education tools. Local startups in Nigeria's tech ecosystem could explore lithium-powered devices adapted to rural environments, such as rugged phones and solar-powered school tablets.

Lithium batteries are now essential in powering industrial and commercial equipment such as warehouse forklifts, mining vehicles, and backup power for telecom towers and data centres. In Nigeria, SMEs in logistics, agro-processing, and ICT can benefit from lithium-based power systems. The application of this technology would reduce generator use, making businesses operate more sustainably and profitably. Lithium technologies would open the doors to new industrial ventures such as battery packing assembly plants, recycling centres, and mining and beneficiation of local lithium ores. States like Nasarawa and Kwara have confirmed pegmatite-hosted lithium deposits (MMSD, 2023). When we responsibly explore and beneficiate them, aligning with the national Raw Materials Development policy, we can reduce import reliance and support value-chain industrialization. The Lithium battery value chain is depicted in Figure 5.

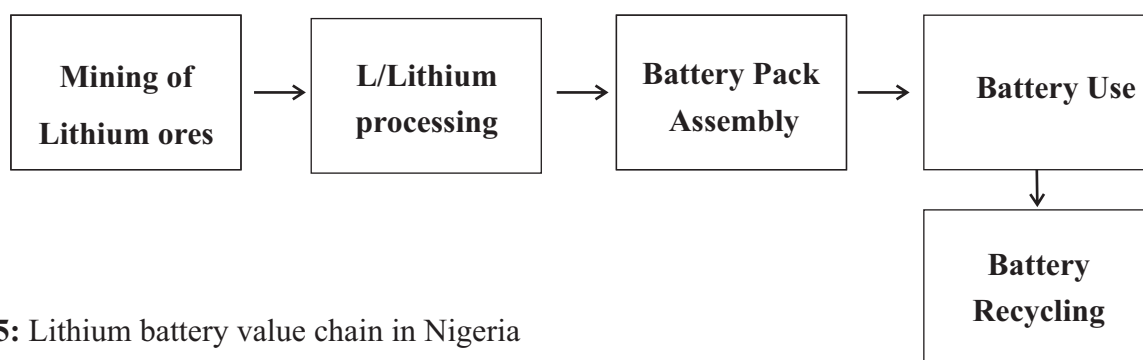


Fig. 5: Lithium battery value chain in Nigeria

Even with the potential of the application of lithium batteries to transform our lives and industrial sector, there are still some constraints inhibiting their wholesome application, which we will look at in the next chapter.

4. Challenges and Considerations for Lithium-Based Energy

While the lithium battery value chain (Figure 5) presents a clear pathway for industrial development, translating this potential into reality in Nigeria is fraught with interconnected challenges that span technical, economic, and socio-environmental domains. The first step in this journey, harnessing the domestic resource base itself, presents significant hurdles. Nigeria's identified lithium deposits, primarily located in states like Nasarawa and Kwara, with potential deposits from waste materials like produced water (which is abundant in the Niger Delta region from oil exploration) as illustrated in Figure 6, provide a foundational opportunity but also highlight the immediate challenges of resource mapping, formalization, and sustainable management.

Fig. 6: Map of Nigeria showing states with identified lithium deposits. Major known deposits in Nasarawa and Kwara are highlighted. (Adapted from Nigerian Geological Survey Agency, 2023).



A systematic analysis of these hurdles, presented in Table 2, is essential for formulating effective policies. The map in Figure 6 underscores the spatial dimension of the "Resource & Supply Chain" challenges. For instance, the environmental risks of unregulated mining in these regions, such as soil and water contamination from tailings, echo the damages seen in the Niger Delta and must be preemptively addressed through strict regulations (Adeola et al., 2024). Similarly, the high capital intensity of lithium processing, a challenge reflected in the economic category, necessitates innovative financing models to support SME participation in the value chain (Federal Government of Nigeria, 2019).

Table 2: Key Challenges for Lithium Adoption in Nigeria

Challenge Category	Specific Issues	Impact & Nigerian Context (with Sources)
Resource & Supply Chain	- Limited mapped reserves. - Artisanal mining dominance. - Lack of local processing.	Risk of remaining a raw material exporter. Inadequate quality testing labs slow local industry (Adeola et al., 2024; MiningCadastre, 2023).
Environmental & Social	- Mining waste and contamination. - E-waste from spent batteries. - Poor labor practices.	Threat of replicating environmental damage. 23,000 tons of annual e-waste with only 12% recycling (UNEP, 2023). Artisanal mining raises SDG compliance issues (United Nations, 2018).
Economic & Infrastructural	- High capital costs. - Unstable grid power. - High import duties.	Unstable grid (4-8 outages/day) disrupts manufacturing (World Bank, 2022). High costs limit affordability for a large low-income population.
Technical & Safety	- Thermal runaway risks. - Lack of local BMS expertise.	Unstable grid can damage batteries during charging. Requires targeted training and standards development.



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5. Conclusion

A growing world population implies a continuous increase in energy demand and for the energy mix. The global efforts towards increasing the generation through renewable energy sources are at an all-time high. Lithium has been shown in this study to be a viable alternative energy source. The abundance of this resource across the various parts of the country has been highlighted in this study, and this could be harnessed through various technologies, including adsorption, extraction, and ion-exchange, to name a few. More importantly, this study has highlighted that beyond the traditional deposit of lithium waste material, produced water provides a viable alternative for sourcing this important raw material. Therefore, future studies should focus on how to harness lithium from produced water.

6. Future Outlook and Recommendations

The rapid advancement of lithium battery technology is built upon a history of key breakthroughs, each addressing fundamental performance or safety gaps. The evolution of these technologies is summarized in Table 3, which highlights the progression from foundational concepts to the current research frontier.

Table 3: Key Research Focus Areas in Lithium Battery Development

Serial No.	Focus Area	Key Contribution	Gap Identified / Addressed	Reference
1	Concept & Intercalation Cathode	Pioneered the concept of Li-ion batteries using titanium disulfide (TiS ₂) as a reversible intercalation cathode.	Addressed the need for a reversible cathode but used an unstable lithium metal anode, creating a safety gap.	Whittingham (1970s)
2	High-Voltage Cathode (LCO)	Discovered Lithium Cobalt Oxide (LiCoO ₂) as a high-voltage (~4V) cathode material, dramatically increasing energy density.	Provided the high-performance cathode essential for commercial devices. The gap was the high cost and cobalt dependency.	Goodenough et al. (1980)
3	Commercial Cell Design (Carbon Anode)	Created the first safe, commercially viable prototype by pairing a carbonaceous anode with a LiCoO ₂ cathode, eliminating metallic lithium.	Solved the critical safety gap of lithium metal anodes, enabling mass production and commercialization.	Yoshino (1985)
4	Safe, Low-Cost Cathode (LFP)	Developed Lithium Iron Phosphate (LiFePO ₄), offering excellent thermal stability, long life, and low cost by eliminating cobalt.	Addressed the gaps of safety, cost, and resource scarcity associated with cobalt-based cathodes.	Goodenough et al. (1997)
5	High-Energy Cathode (NMC)	Developed the Nickel Manganese Cobalt Oxide (NMC) family, allowing for tunable performance for electric vehicles.	Addressed the gap for a versatile cathode material suitable for demanding applications.	Thackeray et al. (2001)
6	Next-Generation Safety (Solid-State)	Researched solid-state electrolytes to replace flammable liquid electrolytes, aiming for superior safety and higher energy density.	Addresses the fundamental safety gap of current Li-ion batteries. The remaining gap is in manufacturing scalability.	Various (e.g., Nishio et al., 2020)



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Building on this foundation, current research is pushing boundaries further. Solid-state batteries are emerging as a key innovation offering higher energy density, improved safety, and longer lifespans (Wellgo Battery, 2025; Coltura, 2024). Concurrent advances in silicon-carbon anodes and cobalt-free cathodes enhance performance while reducing reliance on scarce metals (IDTechEx, 2024). These innovations occur alongside a dramatic 90% cost reduction in lithium-ion batteries since 2010, accelerating the adoption of cleaner energy (IEA, 2024).

Globally, policy frameworks shape lithium energy development. The U.S. and EU offer incentives and circular economy measures (Two Birds, 2025), while Nigeria focuses on local value addition, including export bans on raw lithium (Premium Times, 2025a). However, progress is hindered by an outdated Mining Act and a lack of a Critical Minerals Policy.

For Nigeria to harness its lithium potential, key actions include detailed resource mapping (MiningCadastre, 2023; Adeola et al., 2024), addressing infrastructure gaps (World Bank, 2022), developing local processing capacity (VerivAfrica, 2023), and diversifying partnerships (African Business, 2025). These steps could unlock \$3.2B in reserves and create over 15,000 jobs (Federal Government of Nigeria, 2019). To become a key player in the clean energy sector, Nigeria must focus on local processing, strengthen governance, and establish environmental protections to avoid repeating past mistakes in the extractive industries.



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Evaluation and Optimization of Process Parameters for Biocrude Production from Sugarcane Bagasse via Hydrothermal Liquefaction

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Abstract

The underutilization of sugarcane bagasse, a common agricultural by-product, combined with the rising demand for sustainable energy alternatives, highlights the urgent need for advanced biomass conversion technologies. This research investigates the design and optimization of hydrothermal liquefaction (HTL) to convert sugarcane bagasse into biocrude oil. Sugarcane Bagasse sample was collected from Oye Emene, Enugu State and assessed for proximate analysis. Moisture content was determined according to the BS EN ISO 18134-2:2024. This provided the base data for the simulation process. The design process was facilitated through simulation and optimization employing Aspen Plus version 11 and Response Surface Methodology (RSM) via Design Expert 13 software. Critical process variables' reaction temperature, pressure, reaction time, and the feedstock-to-water ratio were systematically assessed for their impact on biocrude yield. A continuous HTL flow sheet for sugarcane bagasse was modelled in Aspen Plus, utilizing a Gibbs free energy minimization approach. The initial parameters included a mass flow rate of 300 kg/h, a moisture content of 80 wt%, a temperature of 25 °C, and a pressure of 1 bar. The resulting biocrude was identified as a complex mixture encompassing acids (e.g., acetic and levulinic acids), phenolic compounds (including 2-methoxyphenol), cyclopentanone, alcohol (3-pentene-2-ol), and various aromatic compounds like vanillin. Statistical evaluation indicated significant findings for biocrude production, with an F-value of 4.97 and a P-value of 0.0075, reflecting significance at the 0.05 level. The model displayed a strong correlation with an R^2 value of 0.91. Optimal HTL conditions for enhanced biocrude yield of 56% were identified at a temperature of 328.8 °C, pressure of 200 bar, reaction time of 34.01 minutes, and a feedstock-to-water ratio of 1, achieving a desirability of 0.788. This study enriches the understanding of biomass conversion through a detailed analysis of the HTL process using sugarcane bagasse.

Keyword: Agricultural by-product; Biocrude production; Hydrothermal liquefaction; Sustainable energy; Phenolic compounds

1.0 Introduction

The global energy demand continues to rise, propelled by industrial growth, population increases, and rapid urbanization. This growing demand, alongside the finite availability of fossil fuels, underscores the urgency for innovative and sustainable energy solutions (Adeshina et al., 2024). The transition toward renewable energy sources has gained substantial momentum in recent years, emerging as a crucial strategy for enhancing energy security, promoting environmental sustainability, and mitigating climate change. Within the renewable energy landscape, one promising avenue is the conversion of biomass, especially agricultural residues, into biofuels.

Hydrothermal liquefaction is a process that utilizes high-temperature and high-pressure water as a solvent to facilitate the depolymerization of biomass (Silva et al., 2024). Unlike dry pyrolysis methods, HTL can effectively process wet biomass without requiring extensive drying—a step that can be energy-intensive



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and economically unfavourable for traditional biomass conversion methods (Bassoli et al., 2025). The HTL process typically involves several stages, including the pretreatment of biomass, hydrothermal treatment, and subsequent separation and purification of the resulting biocrude. During the hydrothermal treatment, biomass undergoes simultaneous reactions such as hydrolysis, dehydration, decarboxylation, and condensation, resulting in the formation of diverse organic compounds (Baisch et al., 2025). The product, biocrude, contains various hydrocarbons, phenolic compounds, and other organic molecules that can be further upgraded through refining processes. In addition to serving as a renewable fuel, biocrude can also be a precursor for producing chemicals, aligning with biorefinery concepts that strive for comprehensive valorization of biomass resources (Zafeer et al., 2024).

Sugarcane bagasse, often regarded as a low-value by-product, presents unique characteristics that make it an attractive feedstock for biofuel production (Hussein et al., 2024). Composed primarily of cellulose, hemicellulose, and lignin, sugarcane bagasse provides a favourable structure for biochemical and thermochemical conversions. The high moisture content of bagasse (typically 50–60% when fresh) can pose challenges for traditional conversion methods but is advantageous for hydrothermal processes that accommodate wet feedstocks (Zafeer et al., 2024). (Ungureanu et al., 2022). Despite the increasing interest in HTL processes, significant gaps remain in the literature concerning the optimization of HTL parameters specific to sugarcane bagasse. Most studies have either focused on generic biomass or have not provided comprehensive analyses of the key variables influencing biocrude yield and quality (Kolawole et al., 2024; Ezech et al., 2024). The intricacies of the HTL process necessitate targeted research that elucidates the relationships between process parameters and product outcomes.

This research aims to address these gaps by focusing on the hydrothermal liquefaction of sugarcane bagasse. The objectives include: Characterizing the physicochemical properties of sugarcane bagasse to inform process design. Developing a detailed simulation model of the HTL process using software like Aspen Plus. Investigating the influence of critical process parameters such as temperature, pressure, and reaction time on biocrude yield (Ezech and Isah, 2024). The findings from this research hold promise for contributing to sustainable energy solutions and promoting the valorization of agricultural by-products, ultimately supporting the transition towards a more circular bioeconomy. The comprehensive analysis and insights derived from this research will serve not only to advance academic knowledge but also to inform practical applications in the biomass conversion sector. Through this work, the potential of sugarcane bagasse as a renewable energy feedstock will be illuminated, fostering further exploration and innovation in the utilization of biomass for sustainable energy production.

2.0 Materials and Methods

2.1 Materials

Sugarcane bagasse samples, Standard reference materials for calibration, Analytical balance (± 0.001 g), Muffle furnace (for proximate analysis), Desiccator (for moisture content measurement), Thermogravimetric analyzer (for proximate and ultimate analysis), Elemental analyzer (for ultimate analysis), Ceramic crucibles, Reagents for calibration and cleaning (hydrochloric acid, distilled water). Other materials that were used for this work include Aspen Plus version 11 and Design Expert 13 software and Excel

2.2 Assumptions

There are several assumptions taken during the simulation process (Tushar et al., 2024; Mousavi et al., 2023). The operation is considered to be in a steady state. The heat distribution and mixing of the input stream are uniform. In addition, the pressure drop during the process is neglected. The biomass particle sizes are assumed to be uniform. All gases were ideal.

2.3 Methodology

2.3.1 Biomass characterization

A Sugarcane Bagasse sample was collected from Orie Emene, Enugu State, and analyzed for its proximate composition. Moisture content was determined by drying the biomass at [105°C](#) until a constant weight was achieved, with the loss calculated as a percentage of the initial weight. Volatile matter was assessed using a bone-dry sample in a crucible heated at [900°C](#) for 7 minutes, with weight loss calculated accordingly. Ash content was measured by weighing the remaining residue after combusting the biomass in a [550°C](#) furnace, expressed as a percentage of the initial weight. Fixed carbon was computed by subtracting the percentages of ash and volatile matter from the bone-dry mass.

Ultimate analysis of carbon, hydrogen, nitrogen, sulfur, and oxygen was performed with a Perkin Elmer [2400](#) Series II CHNS/O analyzer, calibrated using control samples and combusting approximately [0.15 g](#) of the sample in pure oxygen. The cellulose, hemicellulose, and lignin content were analyzed following the National Renewable Energy Laboratory's protocol using High-performance liquid chromatography (HPLC-[1260](#) infinity, Agilent Technologies).

2.3.2 Modelling of process

The continuous Hydrothermal Liquefaction (HTL) of sugarcane bagasse was simulated using Aspen Plus V11, utilizing the Gibbs free energy minimization method. The initial parameters included a mass flow of [300 kg/h](#), a moisture content of 80 wt.%, a temperature of 25 °C, and a pressure of 1 bar. The biocrude was modelled as a mixture comprising acetic acid, levulinic acid, propanoic acid, various phenolic compounds (such as 2-methoxyphenol), cyclopentanone, alcohol (3-pentene-2-ol), and other aromatic compounds like vanillin and benzenecetic acid, based on GC-MS analysis (Benedetta et al., [2023](#); Ezech et al., [2025a](#)). The simulation included sixteen biocrude components, twelve aqueous components, five gaseous components, and two solid components. The aqueous phase primarily consisted of water, while the gaseous phase contained CO₂ and hydrogen. Ash served as the solid phase in the simulation.

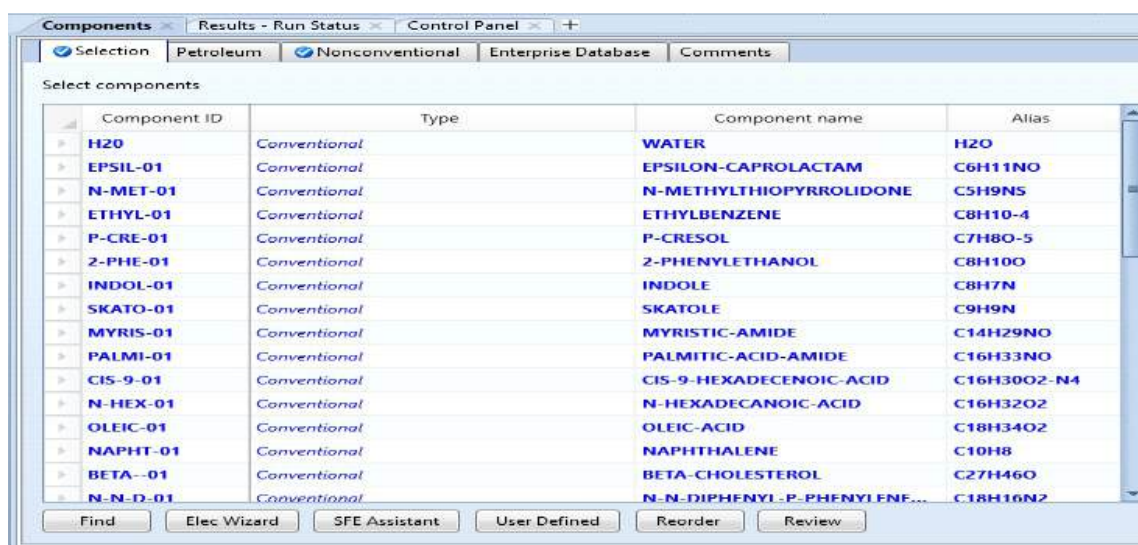


Fig. 1: Components Selection in Aspen Plus

The Soave–Redlich–Kwong equation was applied to define the physical properties of the model compounds in Aspen Plus. For non-conventional components such as sugarcane and ash, HCOALGEN and DCOALIGT models in Aspen Plus were applied to calculate their enthalpies and densities through their proximate and ultimate analyses, as presented in Table 1.

3.0 Results and Discussions

3.1 Results

3.1.1 Proximate and ultimate analysis of sugarcane bagasse

The proximate and ultimate analyses of sugarcane bagasse are essential for understanding its composition and energy potential, which serve pivotal roles in assessing its viability as a biomass feedstock for biofuel production and other applications. The results obtained from these analyses shed light on the fundamental characteristics of sugarcane bagasse, as shown in Table 1

Table 1: Proximate and Ultimate Analysis of Sugarcane Bagasse

Analysis	Components	Percentage Composition
Proximate Analysis (Dry Basis)	Volatile Matter	75.72
	Fixed Carbon	11.71
	Ash	2.27
	Moisture (moisture-included basis)	10.3
Ultimate Analysis (Dry Basis)	Carbon	49.2
	Hydrogen	4.7
	Oxygen	43
	Nitrogen	0.2
	Sulfur	0.04
	Chlorine	0.16

Source: (Author's own work from Biomass Characterization).

3.1.2 Process flow sheet

The method of Qian (2021) and Tushar *et al.* (2024) was used in the hydrothermal liquefaction of sugarcane bagasse, as shown in Figure 2. Sugarcane bagasse and water (H₂O) were mixed in a mixer (MIXER) and pressurized by a pump (PUMP). After pressurization, the stream was heated to the reaction temperature by a preheater (HEATER). The reaction pressure and temperature were initially set at 20 bar and 350 °C, respectively. Afterwards, the mixed stream was decomposed into conventional components including C, H, O, N, S, H₂O, and ASH in a yield reactor (RYIELD) and entered a Gibbs reactor (RGIBBS) to produce biocrude, solid, gaseous products and aqueous product via HTL reaction. Thermodynamic equilibrium compositions of HTL products were calculated based on the Gibbs free energy minimization principle in Aspen Plus. After the HTL reaction, the stream was cooled down and depressurized to ambient conditions (50 °C and 1 bar). Products from COOLER and VALVE subsequently entered a component separator (SEP) to obtain the oil phase (BIOCRUDE), aqueous phase (WATER), solid phase (SOLID), and gas phase (GAS). The different operation blocks used for the simulation are presented in Table 2.

Table 2: Unit operation blocks used to simulate the process

Block name	Block ID	Description
Mixer	B1	Mixer, used to mix the biomass and water
Pump	Pump	Used to increase the pressure of the inlet stream
Heater	Heater	Used to increase the temperature of the inlet stream
Yield Reactor	RYield	Used to decompose the biomass into conventional components
Gibbs reactor	RGibbs	Used to produce the biocrude and other byproducts
Separator	Sep	Used to separate the products into different streams

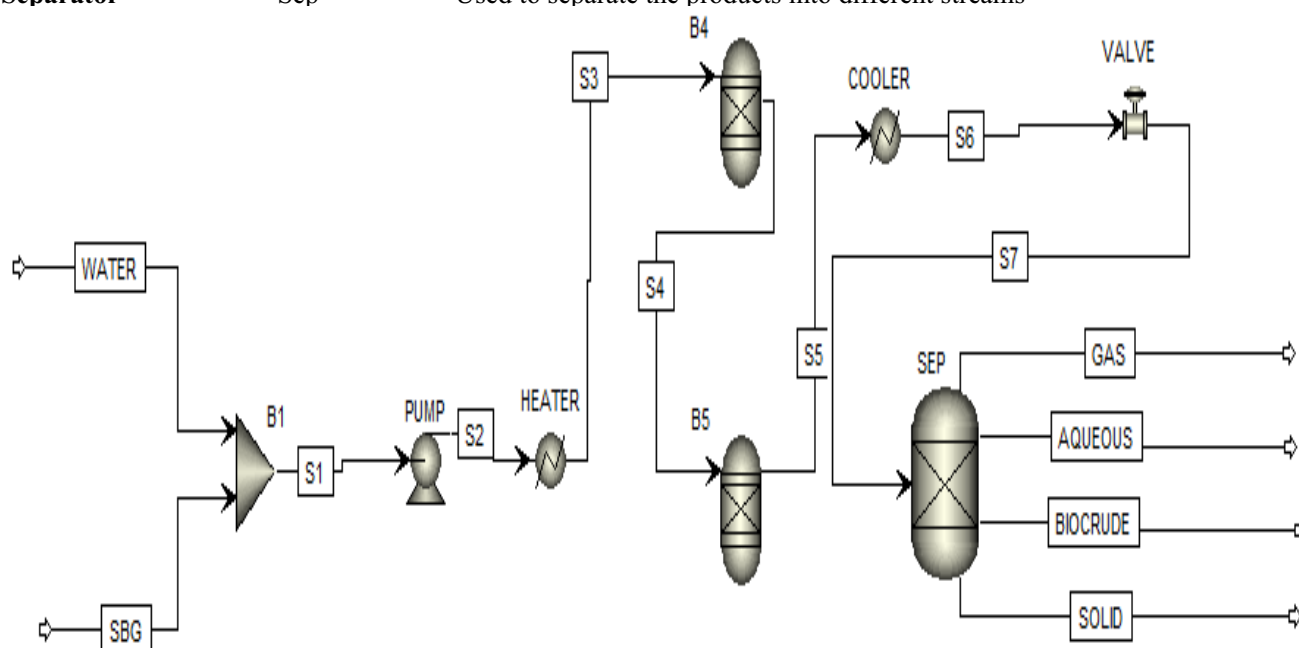


Fig. 2: Flow Sheet of Hydrothermal Liquefaction of Sugarcane Bagasse

3.1.3 Experimental design of biocrude production from sugarcane bagasse

To study the effect of the process parameters on the yield and efficiency of the produced biocrude, and to optimize the process for its production, the Response surface methodology using the Box Behnken design was implemented in Design Expert 13 software; the independent variables studied were the Reaction Temperature, Pressure, Reaction time and feedstock to water ratio. The range that was used to specify the level of the independent variables was obtained from the literature. Table 3 presents the randomly generated design table for the production of biocrude as generated from Design Expert 13 software, indicating the variables and response (biocrude yield). The result of the optimization of biocrude production from sugarcane bagasse and the characteristics of the produced biocrude are presented and discussed in this section. The design of the experiment is used to study the effect of temperature, pressure, reaction time and feed to water ratio on the yield of the produced biocrude. Table 3 shows the yield of each run from the combination of the four different factors being studied using Response Surface Methodology.

Table 3: RSM Table Showing the Yield at Different Factor Levels

		Factor 1	Factor 2	Factor 3	Factor 4	Response 1
Std	Run	A: Temperature °C		C: Reaction Time Min	D: Feedstock- water ratio	Yield %
1	1	150	100	45	2	23.06
22	2	275	200	45	1	35.875
8	3	275	150	60	3	34.635
20	4	400	150	60	2	35.475
13	5	275	100	30	2	25.725
17	6	150	150	30	2	23.55
2	7	400	100	45	2	27.015
16	8	350	200	60	1	46.575
10	9	400	150	45	1	36.985
15	10	275	100	60	2	35.915
23	11	350	100	45	3	38.205
19	12	150	150	60	2	24.285
14	13	350	200	30	2	43.55
18	14	400	150	30	2	33.445
6	15	275	150	60	1	37.265
24	16	350	200	45	3	43.905
11	17	150	150	45	3	23.935
3	18	150	200	45	2	33.115
12	19	400	150	45	3	39.24
7	20	275	150	30	3	39.535
9	21	150	150	45	1	23.815
5	22	275	150	30	1	23.805
25	23	275	150	45	2	39.38
4	24	400	200	45	2	39.435
21	25	275	100	45	1	38.42

3.2 Discussion

3.2.1 Proximate and ultimate analysis of sugarcane bagasse

The proximate analysis of sugarcane bagasse identifies four key components: moisture content, volatile matter, ash content, and fixed carbon. Our study found the moisture content to be [10.3](#), aligning with literature values. While high moisture can complicate drying and storage, it benefits hydrothermal liquefaction (HTL) processes that can use wet feedstocks directly (Dias et al., [2025](#)). The volatile matter was measured at [75.72](#), indicating the bagasse's ability to release combustible gases, making it suitable for pyrolysis and gasification. A higher volatile matter content suggests good combustion properties, enhancing energy recovery (Kpalo et al., [2020](#)). Fixed carbon, derived from the remaining composition after accounting for moisture, volatile matter, and ash, reflects the energy potential of the biomass.

Ash content analysis indicates the mineral composition of the bagasse. A low ash percentage suggests it is a good-quality feedstock with minimal adverse effects on energy systems (Garcia-Perez et al., [2023](#)).



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Ultimate analysis focuses on the elemental composition, primarily carbon, hydrogen, nitrogen, sulfur, and oxygen. With carbon content between 45% and 50%, the bagasse has strong energy potential, while its significant hydrogen content further enhances its heating value. Low nitrogen and sulfur levels indicate minimal emissions of NO_x and SO_x during combustion, which is crucial for environmental compliance. The bagasse typically contains about 40% oxygen, which affects combustion chemistry and calorific value (Onsongo et al., [2025](#)).

3.2.2 Implications for energy production

The characterization of sugarcane bagasse through proximate and ultimate analyses highlights its potential for renewable energy use. Its high volatile matter suggests easy conversion to gas or oil through pyrolysis or liquefaction, while the favourable fixed carbon ratio indicates suitability for direct combustion in industrial systems. These positions sugarcane bagasse as a strong candidate for bioenergy, aligning with the search for sustainable alternatives to fossil fuels. With its high calorific value and favourable composition, sugarcane bagasse can significantly contribute to sustainable energy solutions and reduce reliance on fossil fuels. Ongoing research could further enhance its viability for energy production, promoting a circular bioeconomy and supporting energy security in a growing global population.

3.2.3 Statistical analysis of the produced biocrude

The hydrothermal liquefaction plant for the production of biofuel from sugarcane bagasse was designed using Aspen Plus version 12. In order to study the effect of the process parameters on the yield and efficiency of the design process plant, the following factors were statistically studied using Response Surface Methodology. The results of the statistical analysis are analyzed and presented as follows.

3.2.4 ANOVA for the quadratic model for the biocrude yield

Analysis of Variance (ANOVA) is a statistical tool used to study the influence of the independent variables or factors on the response (yield) of the biocrude. Table 4 shows the ANOVA result for the yield of biocrude with respect to the different factors under consideration.

Table 4: ANOVA Table for Yield of Biocrude

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	1119.59	14	79.97	4.97	0.0075	significant
A-Temperature	347.70	1	347.70	21.60	0.0009	
B-Pressure	158.62	1	158.62	9.85	0.0105	
C-Reaction Time	33.94	1	33.94	2.11	0.1771	
D-Feedstock-water ratio	26.55	1	26.55	1.65	0.2280	
AB	1.34	1	1.34	0.0833	0.7788	
AC	1.16	1	1.16	0.0719	0.7941	
AD	0.1229	1	0.1229	0.0076	0.9321	
BC	22.99	1	22.99	1.43	0.2597	
BD	5.08	1	5.08	0.3155	0.5867	
CD	123.82	1	123.82	7.69	0.0197	
A²	108.27	1	108.27	6.73	0.0268	
B²	4.34	1	4.34	0.2697	0.6149	
C²	13.74	1	13.74	0.8536	0.3773	
D²	0.2336	1	0.2336	0.0145	0.9065	
Residual	160.98	10	16.10			
Cor Total	1280.58	24				



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The F-value is a statistical parameter that determines the level of significance of a data set. It is observed from Table 4 that the model yielded a Model F-value of 4.97, which implies the model is significant. Also, P-values are another statistical tool which measures the level of significance of the experimental data set. An experimental data set, a P-value less than 0.0500 indicates that model terms are significant. In this case of biocrude yield model, it is observed that the model has P-value of 0.0075, which is less than 0.05, therefore, it can be reported that the model for the yield of biocrude is statistically significant, other significant terms in the model are A, B, CD, A² as observed from Table 4 since their P-values are less than 0.05 as well. It is also observed, as shown in Table 5, that the R² value of the model is 0.91, which also proves the significance of the model.

Table 4 also shows the sum of squares of each of the model terms; it is observed that the temperature has the highest sum of squares value of 347.70, followed by the pressure term, having a sum of squares value of 158.62. This shows that these factors have the highest influence on the yield of the biocrude.

Table 5: Fit Statistics

Std. Dev.	8.57	R²	0.9140
Mean	68.65	Adjusted R²	0.6737
C.V. %	12.48	Predicted R²	-0.5417
		Adeq Precision	7.0815

Table 5 also presents the Adequate precision of the model. Adeq Precision measures the signal-to-noise ratio. A ratio greater than 4 is desirable. Your ratio of 7.082 indicates an adequate signal. This model can be used to navigate the design space.

3.2.5 Model equation

The model equations for the biocrude yield were generated by the design expert software after analysis of the results/ responses. The multiple regression analysis of the experimental data results in a second-order polynomial model. The equation in terms of coded factors can be used to make predictions about the response for given levels of each factor. The equation in terms of coded factors can be used to make predictions about the response for given levels of each factor. By default, the high levels of the mixture components are coded as +1, and the low levels are coded as 0. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients. This model can be used to navigate the design space. Where the yield is the response, A, B, C, and D are the coded values of the variables, including Temperature (A), Pressure (B) and Reaction time (C) and Feed to water ratio (D), respectively. The model equation is presented below.

$$\text{Yield} = 36.82 + 5.26A + 3.9B + 1.75C + 1.52D + 0.55AB + 0.52AC + 0.16AD - 2.68BC + 1.12BD - 5.37CD - 6.15A^2 + 1.09B^2 - 2.03C^2 + 0.27D^2$$

3.3 Effect of Process Parameter

To study the effect of the independent variables on the yield of the produced biocrude, the 3D surface plot from the response surface methodology was studied. The effect of each of the parameters is plotted against the yield of the biocrude. The detailed effect of the combined parameters was discussed in this section.

3.3.1 Effect of temperature and pressure on the yield of the produced biocrude

The effect of temperature and pressure on the yield of the biocrude is presented in a 3D plot shown in Figure 3a. It is observed that as the temperature is increased from 150 °C to 400 °C at constant pressure, there is an initial increase in yield which later drops as the temperature approaches 400 °C. Therefore, it can be said that Temperature significantly influences the Hydrothermal liquefaction process for the production of biocrude and determines the reaction pressure, which is generally regarded as the most important factor for HTL of biomass (Basar et al., 2021). This agrees with the findings of Qian (2021)

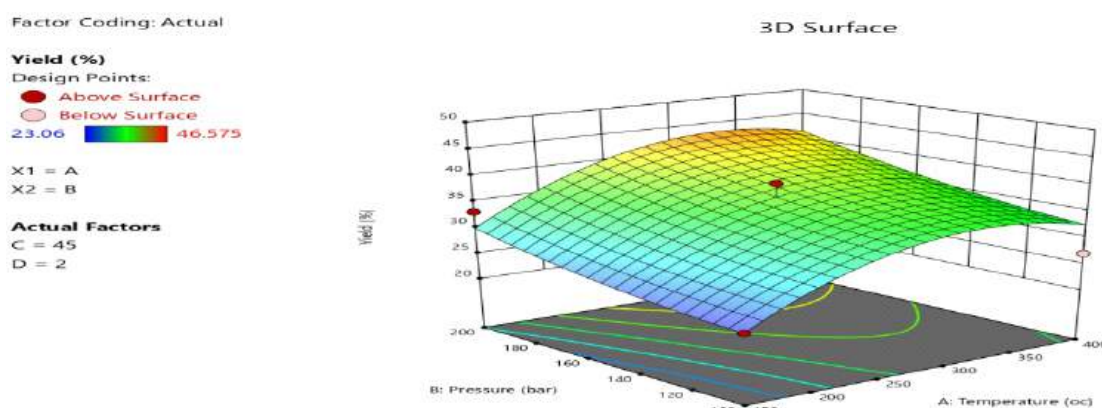


Fig. 3a: 3D Plot of Temperature and Pressure Against Biocrude Yield

It is observed that as pressure increases from 100bar to 200bar, the yield increases. This implies that a change in pressure affects the yield of biocrude. Shui et al. (2010) also found that an increase in pressure from 7 MPa to 12 MPa slightly improved the liquefied oil yield by 7 wt% during coal liquefaction. High pressure will promote the hydrolysis of sugarcane bagasse and accelerate ionic reactions during the HTL process, but excessively high pressure will generate a solvent cage effect and inhibit free radical reactions (Oliveira et al., 2024). Thus, the biocrude yields underwent little change when the pressure exceeded the critical pressure of water (22 MPa). Although few studies report the influence of pressure on HTL of sugarcane bagasse, experiments on HTL of sludge (Dolah et al., 2021), empty fruit bunch, palm mesocarp

fibre, palm kernel shell (Chan et al., 2024), and *Nannochloropsis* sp. (Nelson et al., 2023) all confirmed that once the pressure was close to or higher than the critical pressure of water, it had a negligible influence on biocrude yield. This phenomenon was consistent with the thermodynamic biocrude yield.

4.3.2 Effect of temperature and reaction time on the yield of biocrude

The effect of temperature and reaction time on the yield of the biocrude is presented in the 3D plot shown in Figure 3b. It also shows the significance of the effect of temperature on the yield of the biocrude as depicted by the shape of the 3D plot.

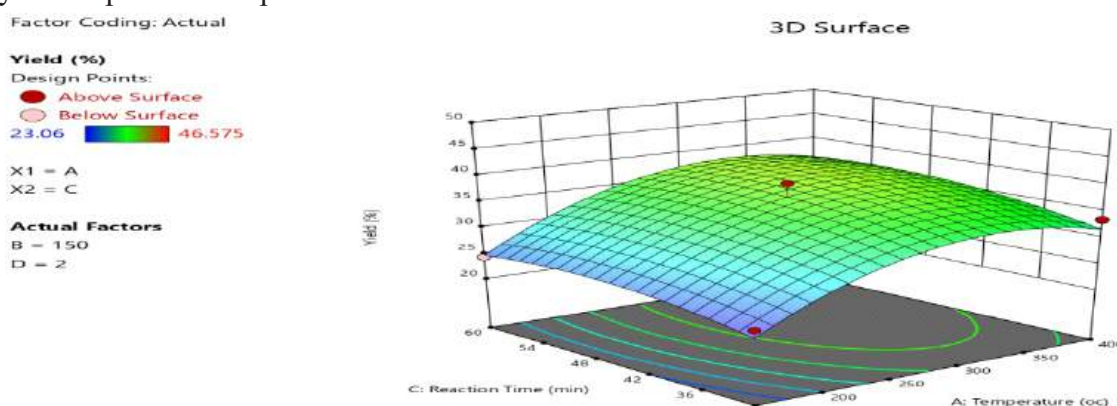


Fig. 3b: 3D Plot of Temperature and Reaction Time Against Biocrude Yield

Similarly, it is observed that an increase in the reaction time has very little effect on the yield of the biocrude, as it is observed in the insignificant change in the yield of the biocrude as the reaction time is increased from 30 to 60 minutes.

4.3.3 Effect of temperature, reaction time and feedstock to water ratio

The effect of temperature and feed-to-water ratio on the yield of biocrude is shown in Figure 3c. From the graph, it is also observed that the ratio of feedstock to water has little significance on the yield of biocrude at a constant temperature of 150 °C. This suggests that at a higher feedstock to water ratio, the effect on the yield of biocrude will be small.

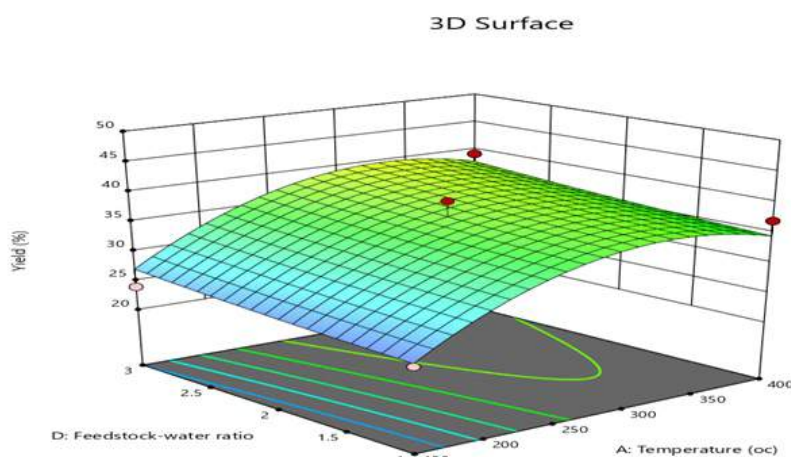


Fig. 3c: 3D Plot of Temperature and Reaction Time Against Biocrude Yield

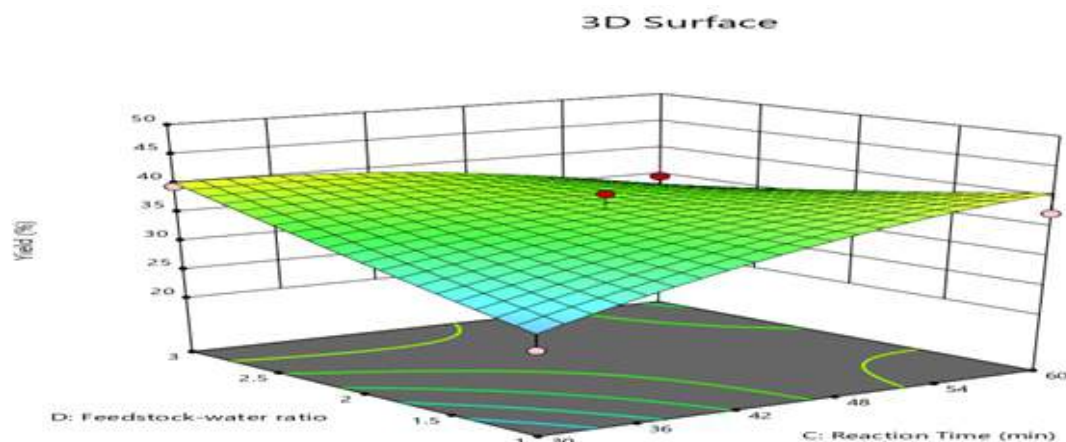


Fig. 3d: 3D Plot of Feedstock to Water Ratio and Reaction Time Against Biocrude Yield

Also, the combine effect of the feedstock to water ratio and the reaction time on the yield of the biocrude is shown in the 3D plot in figure 3d, from the 3D plot it is observed that the reaction time and the feedstock to oil ration will increase the yield of the biocrude individually, but at the highest level of the combination of both factors, a decline in the yield of the biocrude was observed. This suggests that the feedstock-to-water ratio and the reaction time have little effect on the yield of the biocrude.

4.3.4 Optimization of biocrude production

The optimization of the process was carried out using the numerical optimization tool in Design Expert 13. The independent variables: temperature, pressure, reaction time, and feedstock to water ratio, while the response was the biocrude yield. The optimum condition was found by keeping the temperature and pressure in range, while minimizing the feedstock to water ratio and the reaction time and maximizing the biocrude yield. Under these conditions, 100 possible solutions were generated. Table 6 shows the first 10 solutions. The optimum conditions are 328.806 °C, 200bar, 34.01 (min) and a Feedstock to water ratio of 1 at a desirability value of 0.788. At this optimum condition, the biocrude yield was found to be 56%

Table 6: Optimization Result for The Biocrude Production.

Number	Temperature	Pressure	Reaction Time	Feedstock-water ratio	Yield	Desirability	
1	328.806	200.000	34.011	1.000	56.332	0.788	Selected
2	328.957	200.000	33.902	1.000	56.277	0.788	
3	327.074	200.000	34.002	1.000	36.327	0.788	
4	329.716	199.997	34.074	1.000	36.363	0.788	
5	328.720	200.000	34.221	1.000	36.438	0.788	
6	328.050	199.991	33.863	1.004	36.280	0.788	
7	331.975	200.000	34.198	1.001	36.426	0.788	
8	331.119	200.000	33.656	1.000	36.148	0.788	
9	327.944	200.000	33.814	1.013	36.311	0.788	
10	329.077	200.000	33.796	1.016	36.323	0.788	



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5.0 Conclusion

This research has explored the hydrothermal liquefaction (HTL) of sugarcane bagasse, highlighting its potential as a sustainable feedstock for biocrude production. By characterizing the physicochemical properties, we laid the groundwork for process design. A simulation model using Aspen Plus helped optimize key parameters like temperature, pressure, and reaction time. Using Response Surface Methodology (RSM), we identified optimal conditions that maximize biocrude yield, which showcased a favourable chemical composition for high-quality biofuels and industrial chemicals. This work addresses gaps in HTL process optimization for sugarcane bagasse and offers a systematic approach applicable to other lignocellulosic materials. It advances the understanding of HTL and promotes the valorization of agricultural waste in renewable energy strategies, supporting the transition toward a circular bioeconomy. Future studies can build on these findings to explore scalability and HTL's integration in renewable energy production.



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Enhanced Biogas Production from Agro-Waste Through Thermophilic Anaerobic Digestion

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Abstract

This study investigated the thermophilic anaerobic digestion of palm oil sludge with snail shells as an additive to enhance biogas yield. Measured quantities of substrate and additive were mixed with distilled water in a 500 ml round-bottom flask and heated using a heating mantle. The flask was sealed with a rubber stopper connected to a gas outlet tube, and biogas was collected by water displacement. Proximate analysis confirmed the substrates as effective biogas feedstocks, while XRD, FTIR, and XRF characterization of the snail shell revealed high carbonate content, supporting its role as a beneficial additive. Optimal conditions were determined as 3.5 g additive dosage, a palm oil sludge-to-water ratio of 0.16 g/ml, a digestion time of 60 mins and a temperature of 70°C, yielding 197 ml of biogas. Process optimization using the Central Composite Design (CCD) of Response Surface Methodology (RSM) produced a statistically significant model ($p < 0.0001$) with a high coefficient of determination ($R^2 = 0.9668$). The accuracy of the model's predictions was confirmed by ANOVA. Gas chromatography showed the biogas composition as 66.8% methane and 23.5% CO₂. These results highlight palm oil sludge and snail shell as promising feedstocks for efficient and sustainable biogas production on larger scale.

Keywords: Thermophilic, Biogas, Palm oil sludge, Snail shell, Renewable energy

1.0 Introduction

Nigeria, with a population of over 200 million people, is among the most densely populated countries in Africa (Bakare, 2020). This population size, however, creates pressing challenges in both waste management and energy supply. Each year, the nation produces more than 32 million tons of solid waste, of which approximately 34–53% consists of biodegradable organic materials such as agricultural residues, food scraps, and animal manure (Onuh et al., 2020). At the same time, rapid urban growth and industrialization continue to push energy demand beyond the capacity of existing infrastructure. The country's dependence on fossil fuels, including oil, natural gas, and coal, has led to exposure to unstable global energy markets while driving greenhouse gas emissions, environmental degradation, and climate change (Okonkwo et al., 2021).



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To address both the growing waste problem and energy insecurity, research attention is shifting toward renewable energy technologies. Biogas production through anaerobic digestion is particularly promising, as this multi-stage microbial process converts organic matter in oxygen-free conditions into a methane (CH_4) and carbon dioxide (CO_2)-rich fuel (Chilakpu, 2015; Andriani et al., 2015). Thermophilic anaerobic digestion, operated at slightly high temperatures, has shown higher microbial activity, faster decomposition, and greater gas yields than mesophilic systems but is less commonly adopted due to cost and technical barriers (Khalil et al., 2019).

In Nigeria, palm oil sludge and snail shells represent underexplored feedstocks for this process. Palm oil sludge, a by-product of palm oil mill effluent, contains high levels of biodegradable organic matter but remains largely unused (Iberahim et al., 2019). Snail shells, rich in calcium carbonate (CaCO_3), are agricultural residues from snail consumption and can serve as alkaline additives to buffer pH and improve microbial stability during digestion (Zuliantoni et al., 2022).

Despite these resources, few studies have examined their combined use under thermophilic conditions or applied advanced optimization tools like Response Surface Methodology (RSM) for process improvement. This study therefore, investigates thermophilic anaerobic digestion of palm oil sludge with snail shell additive, aiming to optimize biogas yield using RSM. The findings are expected to support sustainable energy generation, improved waste management, and Nigeria's move toward a low-carbon, circular economy.

2.0 Materials and Methods

2.1 Collection and Pretreatment of Feedstock and Additive (snail shell)

8 kg of fresh palm oil sludge was obtained from a palm oil mill in Amansea, Anambra State, Nigeria, using high-density polyethylene bags. The sludge was sun-dried for 36 hours to lower its moisture content, after which 900 g was taken to the laboratory for characterization and use in the anaerobic digestion experiments.

Similarly, 5 kg of snail shells were sourced from Eke Market, Awka. The shells were initially crushed with a mortar and pestle, sieved to a size of about 5mm, and soaked in 10 L of water for three days before being thoroughly washed. Afterwards, they were sun-dried for 24 hours and further ground into a fine powder using a 2 hp electric mill. The resulting material was passed through a 500 μm mesh sieve to achieve a uniform particle size, producing 550 g of powdered snail shell for subsequent laboratory applications.

2.2. Physico-chemical characterization of substrates

The physicochemical characterization investigations conducted on Palm oil sludge are outlined in Table 1.0, along with the standard methods applied.



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Table 1.0: Standard methods for physico-chemical analyses

Tests	Standard method	References
Total solids	ASTM E1756-08(2020)	(Staber et al., 2008)
Ash content	ASTM D4906-95 (2017)	(Ismail, 2024)
Moisture content	AOAC (1990)	(Slight, 1989)
Volatile matter content	ASTM D3175-20 (2020)	(Brown, 2002)
Fixed carbon content	ASTM D3172-13(2021)	(Staber et al., 2008)
Energy value	ASTM D5865-12	(Tyrrell & Reid, 1965)

2.3. Procedure for instrumental characterization

The prepared snail shell powder was characterized using X-ray Diffraction (XRD) in Theta–Theta configuration with a reflection–transmission spinner stage. The analysis was performed over a 4°–75° 2 θ scanning range at a step size of 0.026261 and a dwell time of 8.67 seconds per step, operating at 40 mA current and 45 VA tension. Diffraction data, expressed as intensity versus angle, were used to identify mineral phases based on peak positions and X-ray counts (Owoyemi & Owoyemi, 2020). Elemental composition was determined using X-ray Fluorescence (XRF) spectroscopy on pelletized samples operated at 30 kV, following ASTM C114 standards to quantify major oxides and chemical constituents (Kolawole et al., 2017). Functional group analysis was carried out using Fourier Transform Infrared (FTIR) spectroscopy with the KBr pellet technique. Approximately 10 mg of powdered sample was blended with 500 mg of potassium bromide, compressed at 22–30 MPa, and examined with a Nicolet 6700 M spectrometer. The spectra were collected across 400–4000 cm⁻¹ at a resolution of 4 cm⁻¹, and the absorption peaks were interpreted to identify functional groups (Owoyemi & Owoyemi, 2020).

2.4. Biogas production procedure and laboratory digester setup

The thermophilic anaerobic digestion method was employed for biogas production. Finely powdered palm oil sludge was mixed with distilled water in a 500 mL round-bottom flask to form a slurry. A measured quantity of snail shell powder was added as an additive, and the mixture was stirred thoroughly with a glass rod to ensure homogeneity. The flask was placed on a heating mantle to maintain a steady thermophilic temperature, promoting efficient microbial digestion. It was sealed with a rubber stopper, fitted with a gas outlet tube, and tightly covered to prevent leakage. The produced biogas was directed through the outlet tube into an inverted, water-filled graduated cylinder placed in a trough. As gas accumulated, it displaced the water, enabling direct collection and measurement of biogas volume. The water displacement method ensured accurate monitoring, and the displaced water was recorded at regular intervals to quantify gas production (Salam et al., 2011).

2.5. Determination of Biogas Quality and Composition

Gas composition analysis was carried out using a BUCK M910 Gas Chromatograph equipped with a Flame Ionization Detector (FID) and a RESTEK MXT-1 column (15 m × 250 μ m × 0.15 μ m). The injector temperature was maintained at 280°C and operated in splitless mode with injection volumes ranging from



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0.5 to 2 μL . Helium, at 5.0 Pa·s, was used as the carrier gas at a flow rate of 40 mL/min, corresponding to a linear velocity of 30 cm/s. The oven temperature was programmed to start at 200°C, then ramped up to 330°C at a rate of 3°C/min and held for five minutes. The detector temperature was set at 320°C. Gas constituents were analyzed over a total run time of 45 minutes, and their concentrations were quantified by comparing peak areas to those of an internal standard, with results expressed in $\mu\text{g/mL}$.

3.0 Results and Discussion

3.1. Physico-chemical characterization of substrates

Table 2.0 presents the physicochemical characteristics of palm oil sludge, emphasizing its suitability for biogas generation. The moisture content, recorded at below 10%, falls within the recommended limit for long-term storage (Onuora et al., 2023). Maintaining low moisture levels prevents mould development, reduces biochemical degradation, and enhances material stability. The ash content of 7.98% reflects moderate mineral concentrations while indicating substantial organic matter availability (Onuora et al., 2023). When combined with low moisture, this composition supports improved biogas yield by providing more biodegradable material for microbial conversion. The volatile matter content, measured at 68.37%, demonstrates the high degradability of the substrate, which is essential for sustaining microbial activity during anaerobic digestion (Sambo et al., 2015). Similarly, the total solids content of 90.14% points to a significant organic load, favouring increased methane production (Godfrey, 2024). The energy value further confirms the substrate's potential for bioenergy applications (Lee et al., 2019). Meanwhile, the fixed carbon fraction, associated with lignocellulosic components, represents the remaining carbon after volatile matter release and influences the overall efficiency of the digestion process (Wan et al., 2022).

Table 2.0: Proximate Characteristics of the samples

Parameters	Palm Oil Sludge
Volatile matter content (%)	68.37
Ash content (%)	7.98
Moisture content (%)	9.86
Fixed carbon (%)	13.79
Energy value (KJ/100g)	2395.47
Total solid (%)	90.14

3.2. Instrumental characterization of snail shell (SS)

3.2.1. Phase constituent analysis using X-ray diffractometer (XRD)

The X-ray diffraction (XRD) analysis (Figures 1 and 2) revealed a dominant diffraction peak at 36.36° with an interplanar spacing of $2.471 \text{ \AA}$ and a relative intensity of 100%, confirming aragonite as the primary crystalline phase with a score of 27. Aragonite is largely responsible for the hardness and structural strength of snail shells (Owoyemi & Owoyemi, 2020). The mineral composition indicated that calcium carbonate accounted for 75.56% of the sample, primarily as aragonite, along with minor phases including lime (CaO), quartz, periclase, and orthoclase. Calcium carbonate and lime play a critical role in stabilizing anaerobic digestion by neutralizing acidic environments and reducing volatile fatty acid (VFA) accumulation (Liu et al., 2021). Furthermore, calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions act as cofactors for microbial enzymes, thereby supporting metabolic processes that enhance biogas production. Calcium-based compounds also help precipitate ammonium ions (NH_4^+) into stable salts, mitigating ammonia toxicity and improving microbial stability. Additionally, the alkaline nature of snail shells prevents excessive acidification, maintaining optimal pH conditions for microbial activity and ultimately increasing methane yields (Ning et al., 2019).

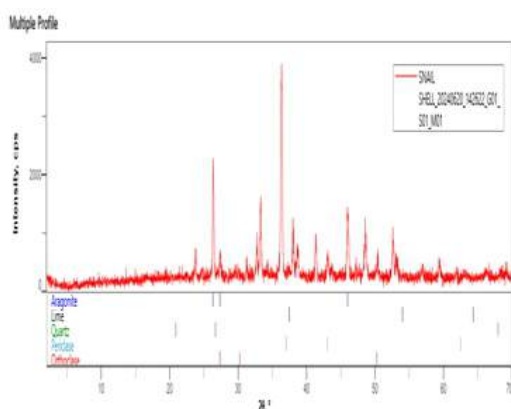


Fig 1: XRD pattern of snail shell

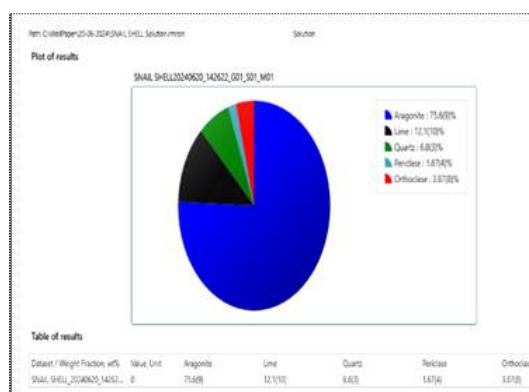


Fig 2: XRD pie chart of snail shell

3.2.2. Fourier transform infrared (FTIR) analysis of snail shell

The infrared (IR) spectrum of the snail shell sample (Fig. 3) exhibited distinct absorption peaks characteristic of CO ions present in CaCO_3 . Prominent bands appeared at 1826 , 1635 , 1374 , 1221 , 1056 , and 811 cm^{-1} , confirming the presence of carbonate ions, in agreement with findings by Udomkan and Limswan (2008). The absorption band within $1390\text{--}1416 \text{ cm}^{-1}$ corresponded to the $\nu(\text{E})$ vibrational mode of CO, while the $\nu(\text{A}_1\text{g})$ mode was absent as noted by Zuliantoni et al. (2022). Broad absorption features between $3234\text{--}3817 \text{ cm}^{-1}$ and $3400\text{--}3600 \text{ cm}^{-1}$ indicated the presence of water molecules. The $400\text{--}1800 \text{ cm}^{-1}$ region reflected CO vibrations, with a dominant C=O stretching band observed at approximately $1404\text{--}1423 \text{ cm}^{-1}$. Peaks at 811 and 1374 cm^{-1} were linked to calcite phases, with the latter also associated with the vibrational mode in aragonite. Overall, the FTIR analysis confirmed that the snail shell material was predominantly composed of calcium carbonate, with minor contributions from water and organic residues. These properties make it an effective additive for anaerobic digestion by buffering pH fluctuations and promoting stable microbial activity (Liu et al., 2021).

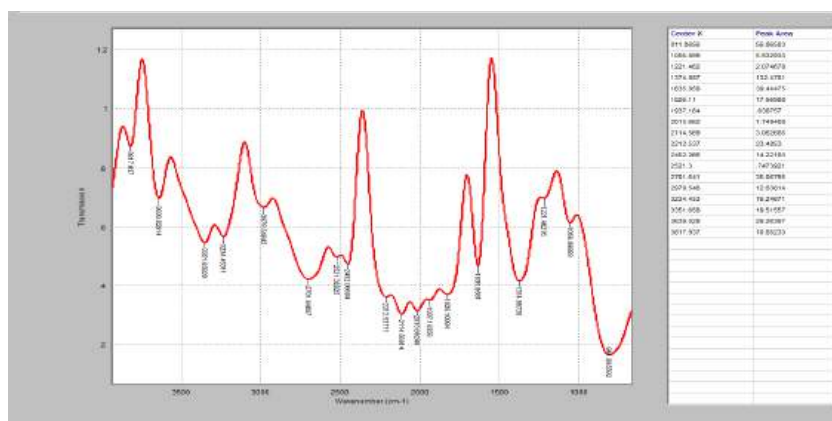


Fig. 3: FTIR spectrum of raw snail shell

3.2.3. XRF compositional analysis

Table 3.0 presents the oxide composition of snail shells as determined by Energy Dispersive X-ray Fluorescence (XRF) spectroscopy. The analysis revealed the presence of several oxides, including MnO, outlining the mineralogical characteristics of the shells and their suitability for biogas production (Owoyemi & Owoyemi, 2020). Among these, CaO recorded the highest concentration (89.884%), while PbO showed the lowest (0.002%), consistent with earlier findings. The predominance of calcium aligns with the known composition of snail shells, which primarily consist of calcium carbonate (CaCO_3) in aragonite or calcite forms. Magnesium oxide (MgO), although present in smaller quantities, is important as a cofactor for microbial enzyme activities during anaerobic digestion. Trace elements such as potassium, iron, silicon, and aluminium were also detected. While silicon and aluminium are naturally occurring with limited direct roles in digestion, potassium is a critical nutrient for hydrolytic and acidogenic bacteria, and iron facilitates electron transfer processes in methanogens, thereby enhancing methane production (Zhou et al., 2020).

Table 3.0: XRF analysis report

S/NO	Chemical Formula	Concentration (%)
1	SiO ₂	0.315
2	V ₂ O ₅	0.009
3	Cr ₂ O ₃	0.007
4	MnO	0.064
5	Fe ₂ O ₃	0.154
6	CoO	0.044
7	NiO	0.023
8	CuO	0.075
9	Nb ₂ O ₅	0.011
10	WO ₃	0.043
11	CaO	89.884
12	SO ₃	0.024
13	MgO	4.802
14	K ₂ O	0.029
15	Al ₂ O ₃	3.122
16	Ta ₂ O ₅	0.066
17	Cl	0.392
18	SnO ₂	0.617
19	SrO	0.307
20	Pb ₂ O	0.002
21	PbO	0.005

3.3. Effect of process variables on the biogas yield

Figure 4 illustrates the effect of temperature on biogas production, showing a steady increase in yield from 50°C to 70°C, where the maximum output of 197 ml was recorded. Beyond 70°C, production declined slightly, likely due to thermal inhibition of methanogenic microbes. Similar trends were reported by Zhang et al. (2020), who observed optimal gas generation between 55°C and 70°C, and by Sambo et al. (1995), who recorded peak yields near 70°C before inhibition set in. Excess heat (>70°C) can denature microbial enzymes (Ryue et al., 2020) and destabilize microbial communities (Cheng et al., 2018). Figure 5 highlights the effect of retention time. Biogas production increased from 100 ml at 40 minutes to 197 ml at 60 minutes before levelling off. The initial rise reflects active microbial metabolism, while the plateau beyond 60 minutes suggests substrate depletion and reduced microbial activity (Zhang et al., 2020; Ezekoye et al., 2011).

Figure 6 examines additive dosage, showing yield improvements as snail shell levels increased from 2.5 g to 3.5 g, after which no significant gains occurred. Snail shells likely stabilized pH and supplied nutrients supporting methanogens (Liu et al., 2021; Onuora et al., 2023; Çalhan & Ulutaş, 2023). Figure 7 shows that increasing the palm oil sludge/water ratio to 0.20 g/ml enhanced yields up to 195 ml; however, higher loadings reduced output due to volatile fatty acid accumulation and water limitation (Sambo et al., 1995; KeChrist et al., 2017). Optimal conditions were 70°C, 60 minutes, 3.5 g additive, and 0.20 g/ml palm oil sludge/water ratio, beyond which inhibition effects became evident.

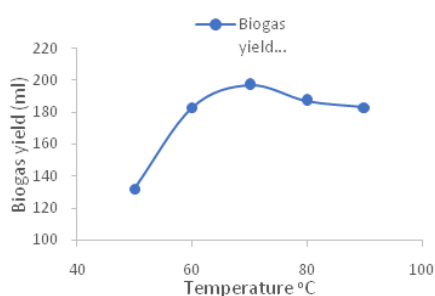


Fig. 4: Effect of temperature on the biogas yield

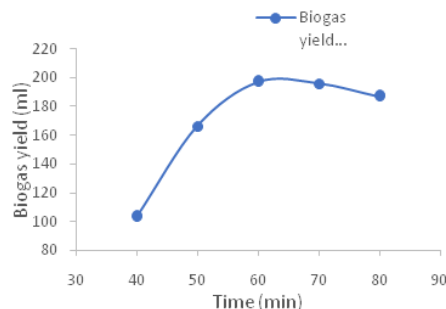


Fig. 5: Effect of time on the biogas yield

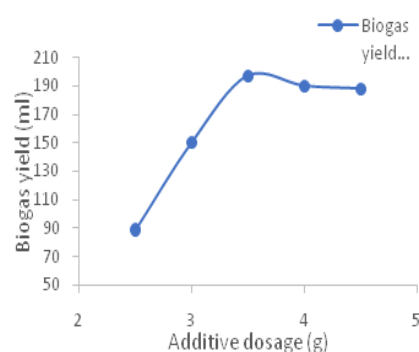


Fig. 6: Effect of Additive dosage on the yield

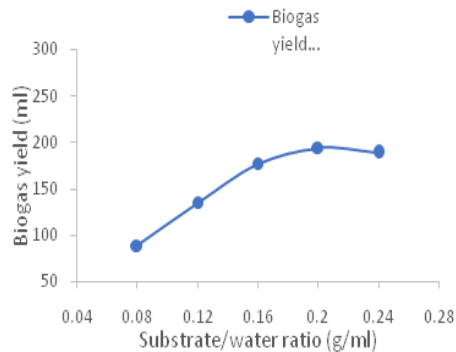


Fig. 7: Effect of palm oil sludge/water ratio on the biogas yield



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3.4. Determination of Biogas Quality and Composition Using Gas Chromatography

Biogas produced from palm oil sludge supplemented with snail shell additive was primarily composed of methane (66.81%), indicating efficient anaerobic digestion and suitability for energy recovery. Although this value is slightly below the >70% methane content typically reported for highly optimized digesters. Here, it still falls within the standard range of 50–70% for biogas quality. Carbon dioxide accounted for 23.53%, consistent with expected microbial metabolism, while the calcium carbonate in snail shells likely contributed to pH stabilization, enhancing methane conversion efficiency. The detection of acetic acid (1.78%) suggests active acetogenic pathways, with minimal residual intermediates as evidenced by trace concentrations of lactic acid (0.003%) and ethanol (0.001%). Other minor components included phenol (1.23%) and acetonitrile (0.26%), both at levels too low to inhibit microbial activity. Ethylene (3.84%) may result from incomplete degradation of complex organics. Hydrogen sulfide (2.52%) remained moderate, implying partial suppression due to the buffering capacity of snail shells. Overall, the composition demonstrates that the snail shell additive improves methane yield, gas quality, and overall digestion stability. Table 5 compares biogas composition with and without the additive under identical operating conditions, highlighting its positive impact on anaerobic digestion performance.

Table 4: Biogas from palm oil sludge using snail shells as an additive

Components	Concentration(ug/ml)	% Concentration
Lactic acid	0.0022	0.003
Methane	52.0532	66.805
Acetic Acid	1.3899	1.784
CO ₂	18.3523	23.533
Phenol	0.9606	1.233
Ethanol	0.0004	0.001
Acetonitrile	0.2032	0.261
Hydrogen Sulphide	2.9941	3.843
Ethylene	1.9627	2.519
Total	77.9187	100

Table 5: Comparative analysis of biogas quality and composition with and without additive

WITH ADDITIVE			WITHOUT ADDITIVE	
Components	Conc. (ug/ml)	% Conc.	Conc. (ug/ml)	% conc.
Lactic acid	0.0022	0.003	0.00229	0.003
Methane	52.0532	66.805	49.4505	64.224
Acetic acid	1.3899	1.784	1.4038	1.822
CO ₂	18.3523	23.533	19.2699	25.009
Phenol	0.9606	1.233	0.9746	1.265
Ethanol	0.0004	0.001	0.00044	0.001
Acetonitrile	0.2032	0.261	0.2053	0.267
H ₂ S	2.9941	3.843	3.0243	3.927
Ethylene	1.9627	2.519	1.9818	2.573
Total	77.9187	100	76.3129	100



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3.5 Optimization with Response Surface Methodology (RSM)

The Central Composite Design (CCD) of Response Surface Methodology (RSM) was employed to design the experiment (DOE) and model biogas production under anaerobic conditions. Table 6 shows biogas yields from palm oil sludge, considering variations in sludge-to-water ratio, additive dosage, temperature, and digestion time. The highest cumulative biogas yield of 197 mL was obtained at a substrate-to-water ratio of 0.16 g/mL, an additive dosage of 3.5 g, and a temperature of 70°C for 60. The Model F-value of 17420.33 indicates the model is highly significant, with a p-value < 0.0001, showing it explains most of the variation in biogas yield. There is only a 0.01% chance that such an F-value occurs due to noise. Terms A, B, C, D, AB, A², B², C², and D² are significant. The Predicted R² of 0.8889 reasonably agrees with the Adjusted R² of 0.9359, and Adeq. Precision of 18.123 indicates an adequate signal for navigating the design space.

Statistical parameters in Table 7 confirm model fitness. The R² of 0.9668 shows that 96.68% of the variability is explained by the model, affirming reliability and consistency. The sum of squares for the model source was 17420.33 with a total DF of 14, giving a mean square of 1244.31. The lack-of-fit p-value of 0.900 (greater than 0.05) indicates that the model fits the data well. Overall, the CCD-RSM model accurately predicts biogas yield, identifies significant factors, and provides a reliable framework for optimizing anaerobic digestion conditions.

Table 6: Biogas yield for pig dung under varying conditions

Run	A:POS/water ratio (g/ml)	B:Additive dosage. (g)	C: Time (mins)	D:Temperature. (°C)	Biogas yield (ml)
1	0.12	3	70	80	159
2	0.16	3.5	60	70	197
3	0.20	3	70	60	146
4	0.16	3.5	60	70	197
5	0.12	4	50	60	133
6	0.16	3.5	60	90	190
7	0.12	3	70	60	131
8	0.16	3.5	60	70	197
9	0.08	3.5	60	70	131
10	0.16	3.5	60	70	197
11	0.16	4.5	60	70	183
12	0.20	4	50	60	166
13	0.12	3	50	60	130
14	0.16	3.5	60	50	150
15	0.12	4	70	60	151
16	0.12	4	70	80	165
17	0.12	3	50	80	161
18	0.20	4	70	80	207
19	0.20	4	70	60	188
20	0.20	3	50	60	142
21	0.20	3	70	80	178
22	0.16	3.5	60	70	217
23	0.16	3.5	80	70	181
24	0.16	3.5	60	70	197
25	0.20	4	50	80	198
26	0.12	4	50	80	159
27	0.16	2.5	60	70	154
28	0.16	3.5	40	70	170
29	0.24	3.5	60	70	182
30	0.20	3	50	80	180



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Table 7: ANOVA for quadratic model of the biogas yield

Source	Sum of Squares	df	Mean Square	F Value	p-value	
Model	17420.33	14	1244.31	31.23	< 0.0001	Significant
A-POS-water ratio	4225.46	1	4225.46	106.05	< 0.0001	
B-Additive. dos.	1653.41	1	1653.41	41.49	< 0.0001	
C-time	249.12	1	249.12	6.25	0.0245	
D-temp.	3780	1	37.80	94.86	< 0.0001	
AB	439.02	1	439	11.02	0.0047	
AC	4.82	1	4.82	0.12	0.7328	
AD	25.57	1	25.57	0.64	0.4356	
BC	170.39	1	170.39	4.28	0.0564	
BD	89.13	1	89.13	2.24	0.1555	
CD	66.46	1	66.46	1.67	0.2161	
A ²	3855.21	1	3855.21	96.76	< 0.0001	
B ²	2151	1	2151	53.98	< 0.0001	
C ²	1380	1	1380	34.63	< 0.0001	
D ²	1990.15	1	1990.15	49.95	< 0.0001	
Residual	598	15	39.85			
Lack of Fit	264.35	10	26.43	0.40	0.9000	not significant
Pure Error	333.33	5	66.67			
Cor Total	18018.18	29				
Std. Dev.		6.31		R-Squared	0.9668	
Mean		171.68		Adj R-Squared	0.9359	
C.V. %		3.68		Pred R-Squared	0.8889	
PRESS		2002.64		Adeq Precision	18.123	

The regression equation in terms of coded factors is developed to establish a mathematical relationship between the response of anaerobic digestion (biogas amount) and different independent process variables as represented in Eq. (1). The equation in terms of coded factors can be used to make predictions about the response for given levels of each factor. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients.

$$\text{Biogas yield} = +200.73 + 13.27*A + 8.30*B + 3.22*C + 12.55*D + 5.24*AB + 3.26*BC - 11.86*A^2 - 8.86*B^2 - 7.09*C^2 - 8.52*D^2 \quad (1)$$

The purpose of a normal probability plot of residuals is to assess whether the residuals from a statistical model (like a regression) are approximately normally distributed. From Fig. 8, it is observed that the straight diagonal line represents a perfectly normal distribution. The data points generally follow the

diagonal line, suggesting that the residuals are reasonably close to being normally distributed. However, some deviations are present, particularly at the extreme ends.

Fig. 9 is a plot of predicted vs. actual values, which is used to evaluate the performance of a regression model. The data points are generally clustered closely around the diagonal line. This indicates that the model has a good fit and is predicting the actual values relatively well. The colours likely represent different value ranges, but the overall trend appears to be well-aligned with few potential outliers.

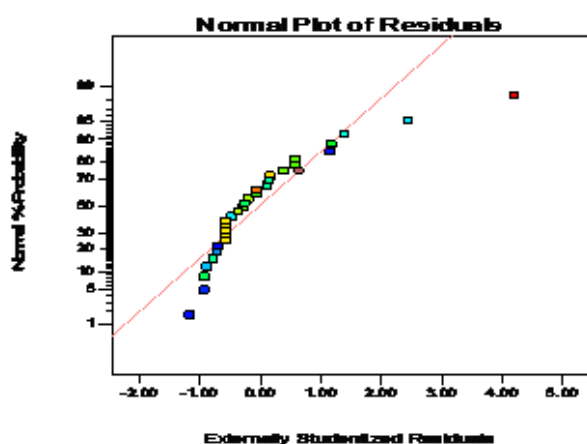


Fig 8: Normal probability plot of residual

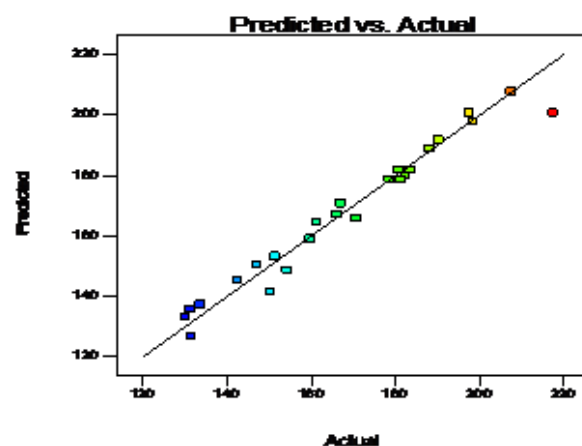


Fig 9: Graph of predicted versus actual biogas yield

Figure 10 (a,b) shows that contour plots and 3D surface plots are valuable tools for visualizing the relationships between multiple factors and a response variable in experimental design (Anderson-Cook et al., 2016). As the colour gradient changes, it indicates an increase in biogas yield. This suggests that higher additive dosages generally lead to higher yields. When the time is increased, the effect on biogas yield is noticeable until it peaks and drops gradually. At lower additive dosages, increasing time initially increases the yield, but further increases seem to have less impact. At higher additive dosages, the effect is less pronounced, with the yield remaining high across a wider range of times.

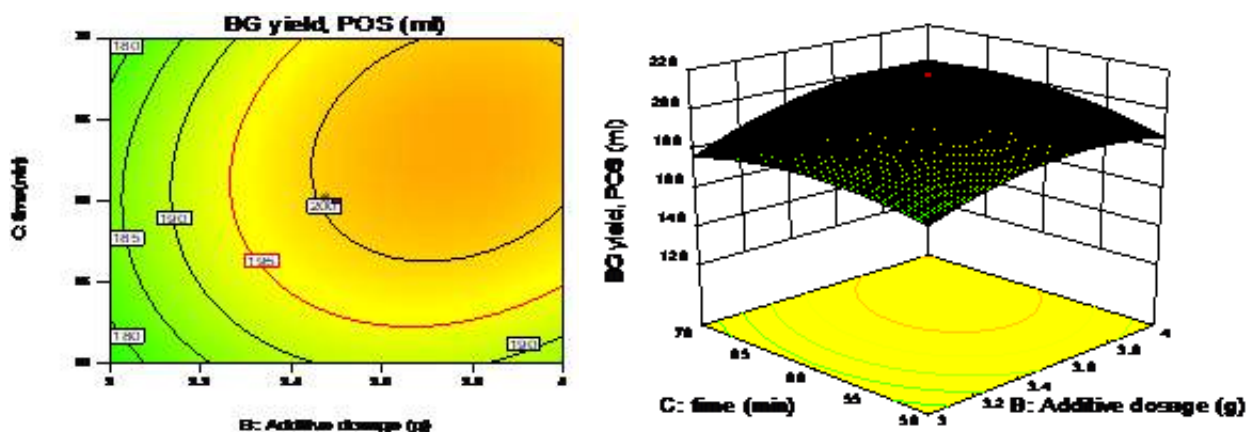


Fig.10 (a) 2D contour and **(b)** 3D Surface plots for the combined effect of time and additive dosage on the biogas yield.



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4.0 Conclusion

Thermophilic anaerobic digestion of palm oil sludge with snail shell as an additive has the potential to generate clean, renewable, and environmentally friendly energy. Proximate analysis of the palm oil sludge confirmed its suitability as a biogas feedstock due to its high organic content, considerable energy value, low ash levels, and moderate fixed carbon. However, initial moisture content may require adjustment to optimize microbial performance during digestion. XRD, FTIR, and XRF analyses revealed a high calcium carbonate content in the snail shells, making them a beneficial additive for enhancing methane yield and stabilizing digestion conditions.

Experimental results showed that the highest biogas production (197 ml) occurred under optimal conditions of 3.5 g additive dosage, a palm oil sludge-to-water ratio of 0.16 g/ml, a retention time of 60, and a temperature of 70°C. ANOVA confirmed that temperature, substrate ratio, retention time, and additive dosage significantly affected biogas output, with the model achieving strong statistical significance ($p < 0.0001$) and a high coefficient of determination ($R^2 = 0.9668$). Gas chromatography analysis indicated that the biogas contained 66.8% methane and 23.5% CO₂, demonstrating its suitability as a renewable energy source. Furthermore, the digestate generated can be used as a nutrient-rich fertilizer, supporting sustainable agricultural practices.



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C. Waste, Environmental Management and Sustainability, Biomaterials and Biosynthesis

Performance Evaluation of Wet-Air Oxidation (WAO) Method for the Treatment of Hospital Wastewater (A Case Study)

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Abstract

This research evaluated the effectiveness of the Wet-Air Oxidation (WAO) method for the treatment of hospital wastewater collected from the Rivers State University Teaching Hospital in Port-Harcourt, Nigeria. The study involved physicochemical analysis of the untreated wastewater, which revealed high concentrations of methanethiol, phenol, methanol, biochemical oxygen demand (BOD), and chemical oxygen demand (COD). The WAO process was simulated using Aspen Plus software, operating under high temperature and pressure conditions to oxidize and reduce these contaminants. Results demonstrated significant removal efficiencies, with 99% reductions in methanethiol and methanol, 96% in phenol, and 97% in both BOD and COD. Post-treatment values complied with the WHO effluent discharge standards. Sensitivity analysis further identified optimal process parameters, including temperature (150°C–320°C), pressure (10–220 bar), and a feed-to-air ratio of 1:9. The findings confirm that the WAO process is a viable and efficient method for hospital wastewater treatment, offering substantial environmental and public health benefits.

Keywords: Hospital Wastewater Treatment (HWWT), Wet-Air Oxidation (WAO), Public Health, Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD)

1. Introduction

Hospital wastewater (HWW) is a complex mix of contaminants, including pathogens, human tissues and fluids, pharmaceuticals, genotoxic substances, chemicals, heavy metals, and radioactive waste. If discharged untreated into water bodies, these pollutants can harm public health and the environment by increasing oxygen demand and nutrient levels, leading to toxic algal blooms and destabilizing aquatic ecosystems (Ugwu et al., 2019). In Nigeria, hospital effluents and public wastewater often flow into streams, rivers, lakes, and oceans, adversely affecting these environments and limiting the use of water resources for drinking, recreation, agriculture, and industry. These negative impacts are especially severe in communities lacking adequate wastewater treatment facilities (Eze et al., 2016). Hospitals in Nigeria consume substantial amounts of water daily, averaging around 100 litres per person per day, with total water usage ranging from 400 to 1,200 Liters per bed per day (Ojo & Adeniyi, 2012). This high-water consumption results in significant wastewater generation, often contaminated with microorganisms, heavy



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metals, toxic chemicals, and radioactive elements from clinical and research laboratories, medical waste incinerators, and hospital laundries. Consequently, hospital wastewater in Nigeria is a hybrid mixture of domestic, industrial, and medical research effluents (Ugwu et al., 2019). Hospital wastewater (HWW) is characterized by a wide array of emerging contaminants, including pharmaceutically active compounds, antibiotic-resistant bacteria (ARBs), antibiotic-resistant genes (ARGs), and persistent viruses (Majumder et al., 2021). These pollutants contribute to elevated levels of biochemical oxygen demand (BOD), chemical oxygen demand (COD), ammonia, and nitrogen in HWW, which are significantly higher than those found in domestic wastewater. Addressing these contaminants is critical to mitigate the environmental and public health risks associated with untreated HWW. Hanny et al. (2021) evaluated the treatment of HWW using activated sludge and constructed wetlands to remove organic matter, nitrogen, and phosphorus. Their findings revealed that activated sludge significantly reduced organic content, ammonia, and phosphate levels, demonstrating its potential as a viable treatment method for HWW. Brunner (2014) investigated the treatment of wastewater from cotton desizing operations. At a temperature of 290°C, the process reduced COD levels by more than 70 wt%, illustrating the effectiveness of high-temperature methods for industrial wastewater treatment. Tager et al. (2023) conducted a study in Lebanon employing the wet air oxidation (WAO) method simulated on Aspen Plus. This advanced oxidation process achieved high reaction conversion yields for specific contaminants, with thiols and sodium hydrosulfide reduced by 89.7% and 83.8%, respectively. The process also demonstrated significant reductions in COD (79.1%) and BOD₅ (88%), highlighting its efficacy for treating complex wastewater. Traditional treatment methods often fall short in removing hazardous components from HWW, necessitating the integration of advanced oxidation processes (AOPs). AOPs enhance the efficiency of conventional treatment systems and provide valuable insights into innovative solutions for treating complex wastewater streams. This study aimed to determine the physicochemical properties of hospital wastewater (HWW) and evaluate the performance of the wet air oxidation (WAO) method in its treatment, using a case study of Rivers State University Teaching Hospital in Port Harcourt, Rivers State, Nigeria. The WAO process employs radical chain reactions to convert organic pollutants into biodegradable substances and oxidize inorganic compounds into higher oxidation states, such as sulfides into sulfates. Operating at high temperatures (150°C–320°C) and pressures (10–220 bar), this advanced oxidation method was assessed by comparing the concentrations of key HWW components before and after treatment.

2. Materials and Methods

2.1 Materials

The materials that were employed in this study are a sample Collector, a Sampling Container, BOD Analyzer, a COD analyzer, a Mercaptan Gas Detector, a spectrophotometer, Aspen Plus (compressor, pump, mixer, heat exchanger, heater, reactor, cooler, valve, separator), and Microsoft Excel.

2.2 Methods



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2.2.1 Sample collection

The HWW sample was collected from the Rivers State University Teaching Hospital in Port Harcourt from the discharge points of the wastewater stream through grab sampling.

2.2.2 Determination of the physicochemical properties of HWW

The physicochemical properties that were determined are 5-day Biochemical Oxygen Demand (BOD_5), Chemical Oxygen Demand (COD), Methanethiol (CH_4S), Phenol (C_6H_6O), and methanol (CH_4O).

2.2.3 Determination of 5-day biochemical oxygen demand (BOD_5)

The HWW sample was collected in a bottle with a stopper and diluted with distilled water. The initial dissolved oxygen levels were measured at 20 °C using a BOD analyzer and recorded in mg/L. The sample was kept in the dark for 5 days. The final dissolved oxygen was measured and recorded in mg/L. The 5-days Biochemical Oxygen Demand was calculated in mg/L using equation 1;

$$BOD_5 = \frac{DO_i - DO_f}{P} \quad (1)$$

where:

BOD_5 = Biochemical Oxygen Demand over 5 days (mg/L)

DO_i = Initial Dissolved Oxygen (mg/L)

DO_f = Final Dissolved Oxygen after 5 days (mg/L)

P = fraction of wastewater sample volume to total combined volume

2.2.2 Determination of chemical oxygen demand (COD)

The HWW sample was collected in a beaker, and some of it was transferred into the sample cell of the COD analyzer. The reagent (Potassium Dichromate) was added to the sample cell and the COD analyzer was turned on to initiate analysis. The COD value was displayed on the screen and recorded in mg/L.

2.2.3 Determination of methanethiol (CH_4S)

The HWW sample was collected in an airtight container, followed by the calibration of the mercaptan gas detector. The mercaptan gas detector was turned on, followed by lowering the probe into the sample container to measure the concentration of methanethiol. The readings were recorded from the display in mg/L.

2.2.4 Determination of phenol (C_6H_6O)

The HWW sample was collected in a beaker and combined with a reagent such as ferric chloride, followed by proper mixing. Colour was allowed to develop in the mixture. The mixture was then transferred to a

cuvette and placed in the spectrophotometer, where the absorbance of the solution at a specific wavelength was measured. A standard curve was created, which was used in the determination of phenol content in the HWW in mg/L.

2.2.5 Determination of methanol (CH₃O)

The HWW sample was collected in a beaker and combined with a reagent such as potassium permanganate, followed by proper mixing. Colour was allowed to develop in the mixture. The mixture was then transferred to a cuvette and placed in the spectrophotometer, where the absorbance of the solution at a specific wavelength was measured. A standard curve was created, which was used in the determination of methanol content in the HWW in mg/L.

2.2.6 Aspen Plus simulation

The wet air oxidation (WAO) process for treating hospital wastewater (HWW) was simulated using Aspen Plus Version (V11) as shown in Figure 1. The simulation process began with the selection of components essential for the treatment, including methanethiol, phenol, methanol, sodium sulfate, water, and air. Following this, the appropriate property method, SRK (Soave-Redlich-Kwong), was chosen to calculate vapor-liquid equilibrium properties. This widely recognized thermodynamic model, represented by equation 2, ensures accurate predictions required for the simulation.

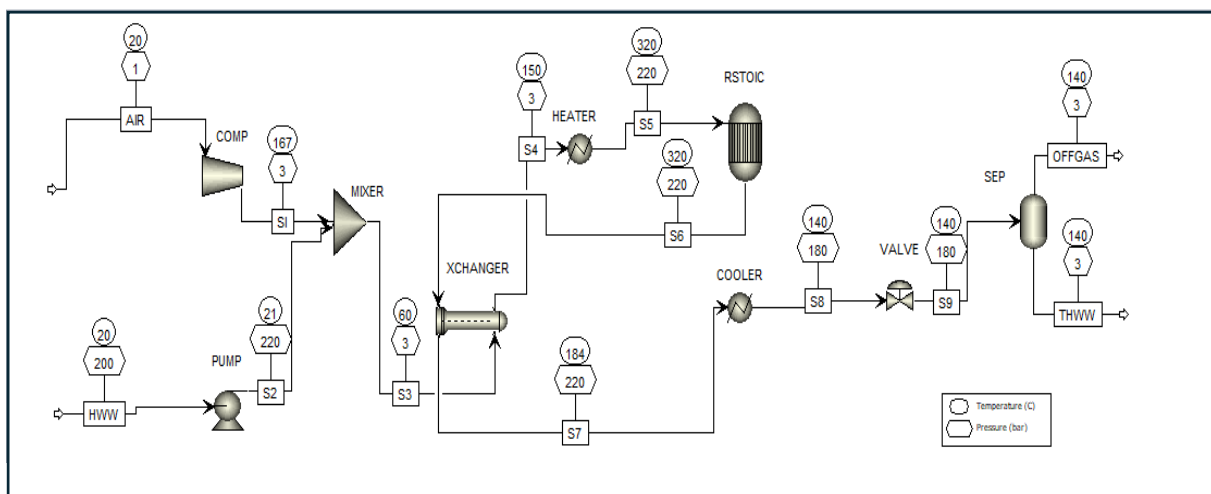


Fig. 1: PFD of WAO method for HWW treatment

$$aa(T) = bRT \cdot \left(\sum_{i=1}^{NC} x_i \frac{(aa(T))_i}{b_i RT} + \frac{G_D^E / (RT) + \sum_{i=1}^{NC} x_i \ln (b/b_i)}{\ln (u/(u + 1))} \right) \quad (2)$$

The process flow-sheet (Figure 1) was then constructed by incorporating key equipment: a pump, compressor, mixer, heat exchanger, reactor, heater, cooler, valve, and separator. Material streams were added to represent the flow of HWW and air throughout the system. The reactor's operating temperature and pressure were set at 320°C and 220 bar, conditions necessary to generate hydroxyl radicals that degrade pollutants effectively.



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2.2.2.1 Process description

The HWW feed was passed through a pump to increase its flow rate, while air was compressed to elevate its pressure. The two streams were combined in a mixer to ensure uniformity. The combined stream was preheated in a heat exchanger to approach the desired reaction temperature. It was further heated in a heater before entering the reactor, where oxidation reactions broke down organic compounds, neutralized harmful contaminants, and converted pollutants into less harmful byproducts in the presence of oxygen under elevated temperatures and pressures. The reactor effluent passed through the heat exchanger for energy recovery and was subsequently cooled before entering the separator. The separator facilitated the purification of treated HWW, discharging it along with off-gases. The simulation model was optimized by stabilizing the sodium sulfate (Na_2SO_4) composition in the gas stream. Optimization involved adjusting the feed-to-air ratio and systematically varying key parameters such as flow rate, temperature, and pressure. This approach ensured effective pollutant removal while maximizing process efficiency.

3. Results

The results of the simulation for treating pollutants in hospital wastewater (HWW) are presented below. This includes percentage reductions in pollutant levels, a comparison with World Health Organization (WHO) effluent standards, and a sensitivity analysis of the functional parameters of the process. The outcomes are summarized in Table 1 and illustrated in Figures 2 and 3 to highlight the comparative results of HWW before and after treatment using the Wet-Air Oxidation (WAO) process. **Table 1:** Comparison of the constituents of HWW before and after treatment

HWW Constituents	Amount Before Treatment (mg/L)	Amount After Treatment (mg/L)	WHO Effluent Standard (mg/L)	% Reduction (%)
CH_4S	0.258	0.00007676	-	99
$\text{C}_6\text{H}_6\text{O}$	4.53	0.15252	-	96
CH_4O	1.742	0.00152	-	99
BOD_5	839.528	21.9333	50	97
COD	1399.21	36.5555	60	97

Table 1 revealed a significant presence of organic and inorganic pollutants in the untreated HWW, aligning with findings from Majumder et al. (2021). Discharging untreated HWW with such elevated contaminant levels poses serious risks to aquatic ecosystems, human health, and the environment. However, after treatment with the WAO method, the simulation demonstrated a substantial reduction in pollutants, with a reduction of 99% in Methanethiol (CH_4S) and methanol (CH_4O), 96% reduction for Phenol ($\text{C}_6\text{H}_6\text{O}$) and 97% reduction for both BOD_5 and COD levels. These reductions indicate that the WAO method effectively mitigates both organic and inorganic pollutants, corroborating results from prior studies (Brunner, 2014; Souza et al., 2018; Tager et al., 2023).

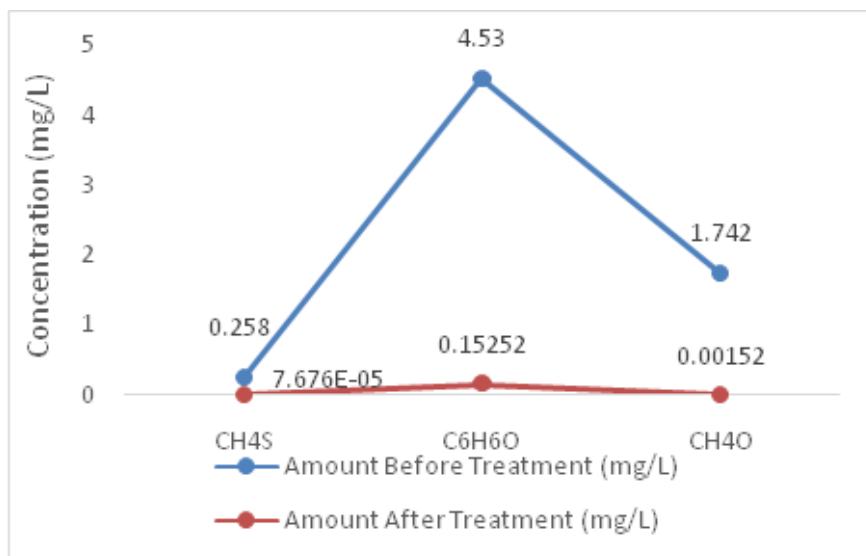


Fig. 2: HWW constituents before and after treatment

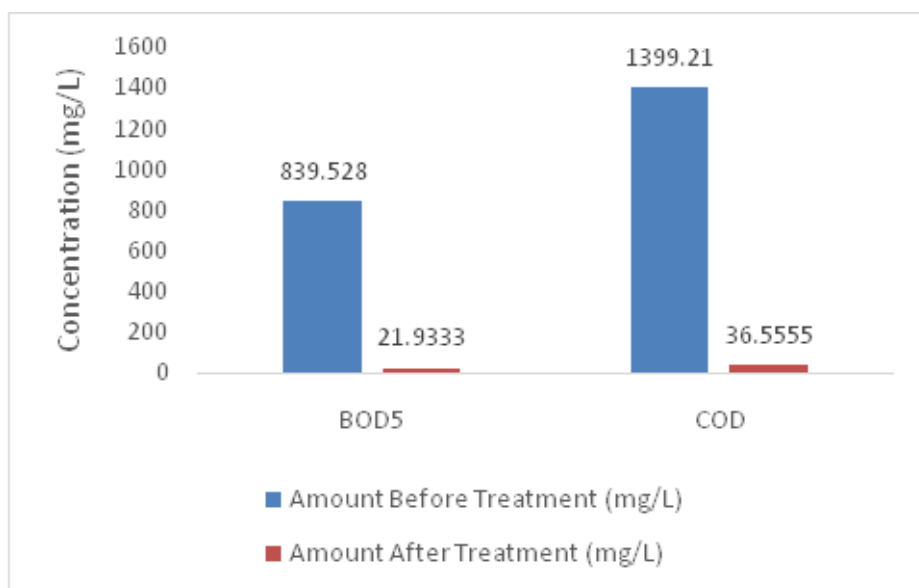


Fig. 3: Before and after treatment comparison for BOD₅ and COD

The WHO effluent standards specify maximum allowable concentrations of 50 mg/L for BOD and 60 mg/L for COD in surface water discharges (Giger et al., 2003). Post-treatment values for BOD (21.9333 mg/L) and COD (36.5555 mg/L) were well within these limits, demonstrating compliance with international environmental guidelines.

3.1 Sensitivity Analysis

3.1.1 Feed-to-air ratio analysis

Tables 2–5 show the impact of varying feed-to-air ratios on the reduction of wastewater constituents during the WAO process. Higher ratios improve the oxidation of pollutants, with significant reductions in methanethiol, phenol, methanol, BOD, and COD observed as the ratio increases. However, while ratios



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above 1:9 achieve the most substantial reductions, they also result in increased sodium sulphate (Na_2SO_4) formation, which is a result of the oxidation of the sulphur-containing compounds.

Table 2: Sensitivity analysis for flowrate (1:5)

HWW Constituents	Amount Before Treatment (mg/L)	Amount After Treatment (mg/L)
CH_4S	0.258	0.000012702
$\text{C}_6\text{H}_6\text{O}$	4.53	0.2524
Na_2SO_4	3.893	9862.02
CH_4O	1.742	0.00252
BOD5	839.528	36.2971
COD	1399.21	60.4951

Table 3: Sensitivity analysis for flowrate (1:7)

HWW Constituents	Amount Before Treatment (mg/L)	Amount After Treatment (mg/L)
CH_4S	0.258	0.00009568667
$\text{C}_6\text{H}_6\text{O}$	4.53	0.19013
Na_2SO_4	3.893	9895.96
CH_4O	1.742	0.0019
BOD ₅	839.528	27.3417
COD	1399.21	45.5694

Table 4: Sensitivity analysis for flowrate (1:11)

HWW Constituents	Amount Before Treatment (mg/L)	Amount After Treatment (mg/L)
CH_4S	0.258	0.00006408667
$\text{C}_6\text{H}_6\text{O}$	4.53	0.12734
Na_2SO_4	3.893	9929.91
CH_4O	1.742	0.00127
BOD5	839.528	18.3121
COD	1399.21	30.5202



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Table 5: Sensitivity analysis for flowrate (1:13)

HWW	Amount Before Treatment	Amount After Treatment
Constituents	(mg/L)	(mg/L)
CH ₄ S	0.258	0.00005500667
C ₆ H ₆ O	4.53	0.1093
Na ₂ SO ₄	3.893	9939.61
CH ₄ O	1.742	0.00109
BOD ₅	839.528	15.7176
COD	1399.21	26.1961

Additionally, Table 6 demonstrates that higher feed-to-air ratios reduce the Na₂SO₄ mass fraction in the off-gas, highlighting effective oxidation and pollutant neutralization. Managing Na₂SO₄ emissions is vital because excessive sulfate in off-gas can contribute to secondary pollution and operational inefficiencies.

Feed-to-Air Ratio	Amount of Na₂SO₄ in Off Gas (mass fraction)
1:1	1.34641×10^{-8}
1:2	1.31296×10^{-8}
1:3	1.29309×10^{-8}
1:6	1.26417×10^{-8}
1:7	1.25895×10^{-8}
1:8	1.25481×10^{-8}
1:9	1.25145×10^{-8}

3.3 Temperature Variation

The reactor temperature was varied between 200°C and 300°C while maintaining constant pressure and flow rate. As shown in Table 7, no significant changes were observed in the concentrations of HWW constituents after treatment, with the post-treatment values remaining consistent with those obtained in the standard WAO process. Similarly, the reactor pressure was adjusted within the range of 100 bar to 200 bar, while keeping temperature and flow rate constant. The results, presented in Table 8, exhibited the same trend as the temperature adjustments, showing no additional changes in pollutant levels.



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Table 7: Variation of temperature (200 °C, 250 °C, and 300 °C)

HWW	Amount Before Treatment	Amount After Treatment
Constituents	(mg/L)	(mg/L)
CH ₄ S	0.258	0.00007676
C ₆ H ₆ O	4.53	0.15252
Na ₂ SO ₄	3.893	9916.32
CH ₄ O	1.742	0.00152
BOD ₅	839.528	21.9333
COD	1399.21	36.5555

Table 8: Pressure variation (100 bar, 150 bar, and 200 bar)

HWW	Amount Before Treatment	Amount After Treatment
Constituents	(mg/L)	(mg/L)
CH ₄ S	0.258	0.00007676
C ₆ H ₆ O	4.53	0.15252
Na ₂ SO ₄	3.893	9916.32
CH ₄ O	1.742	0.00152
BOD ₅	839.528	21.9333
COD	1399.21	36.5555

These findings confirm that the recommended operating ranges of 150°C to 320°C for temperature and 10 bar to 220 bar for pressure, as suggested by Tager et al. (2023), are optimal for the efficient performance of the WAO method.

4.0 Conclusion

Characterization and treatment of Hospital Wastewater (HWW) using the Wet-Air Oxidation (WAO) method was carried out in this research. Laboratory analysis identified significant concentrations of methanethiol, phenol, methanol, BOD₅, and COD, indicating a high presence of organic and inorganic pollutants in the untreated wastewater. The WAO process, simulated using Aspen Plus, achieved substantial reductions in these pollutants, with BOD₅ and COD levels meeting WHO effluent discharge standards. Sensitivity analysis determined the optimal operating conditions: temperature, pressure, and feed-to-air ratio that enhanced pollutant removal efficiency. Furthermore, an economic feasibility analysis confirmed that the WAO method is a cost-effective solution for large-scale HWW treatment. This research significantly contributes to the understanding of advanced wastewater treatment technologies, demonstrating the effectiveness of WAO in removing diverse contaminants from hospital effluents. The identification of optimum operating parameters provides a practical framework for maximizing treatment efficiency while minimizing costs. These findings support the development of sustainable, environmentally friendly, and economically viable solutions for managing hospital wastewater, addressing critical environmental and public health challenges.



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Comparative Evaluation of Palm Kernel Shell-Based Adsorbents Activated with Lime, Lemon, ZnCl_2 , and HNO_3 for Heavy Metal Removal from Pharmaceutical Effluent

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Abstract

The study explores the capacity of palm kernel shell adsorbents that were activated through the combination of green and chemical agents in eliminating toxic heavy metals from pharmaceutical effluent. PKS samples were collected from a palm kernel mill in Enugu State, Nigeria, and treated with distilled water, sun-dried, and activated using lime, lemon, and potash (natural activation), as well as zinc chloride (ZnCl_2) and nitric acid (HNO_3) for chemical activation. The samples were carbonized at 800°C and impregnated with the respective activating agents. Tests of adsorption were realized with 10 grams of each activated carbon and 50 millilitres of pharmaceutical effluent. The effluents were examined after some time of agitation by Atomic Absorption Spectrophotometry (AAS) for residual concentrations of lead (Pb), arsenic (As), cadmium (Cd), and chromium (Cr). Results showed that effluent concentrations of Pb, As, Cd, and Cr (1.268 ± 0.003 , 0.056 ± 0.000 , 0.676 ± 0.000 , and $0.397 \pm 0.001 \text{ mg/L}$, respectively) were initially far above WHO acceptable levels. Following treatment, the highest removal efficiency was exhibited by HNO_3 -activated PKS for Pb ($1.124 \pm 0.000 \text{ mg/L}$ adsorbed), ZnCl_2 -activated PKS for maximum As removal ($0.029 \pm 0.005 \text{ mg/L}$), and potash-treated PKS for Cr adsorption ($0.280 \pm 0.000 \text{ mg/L}$). All modified PKS adsorbents showed a remarkable superiority over normal charcoal under most conditions, indicating their prospects as low-cost, sustainable materials for treating pharmaceutical wastewater. These findings highlight the effectiveness of natural and chemical activation of PKS for enhancing the adsorption of heavy metals and warrant its use in green effluent detoxification technology.

Keywords: Pharmaceutical effluent, Heavy metal removal, Palm kernel shell (PKS), Activated carbon, Eco-friendly adsorbents, Chemical activation, Wastewater treatment.

1. Introduction

The rapid growth of pharmaceutical industries worldwide, particularly in urban areas of developing nations, has brought about significant benefits to global health. However, this growth has also introduced pressing environmental challenges, notably in the management of industrial wastewater. In many low- and middle-income countries, pharmaceutical effluents are often discharged untreated or inadequately treated, posing severe environmental and public health risks. Pharmaceutical wastewater frequently contains complex mixtures of complex organic contaminants and hazardous heavy metals, including lead (Pb),



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cadmium (Cd), chromium (Cr), and arsenic (As). These metals are non-biodegradable and tend to bioaccumulate in living organisms, leading to serious consequences such as neurotoxicity, renal impairment, and carcinogenicity (Verlicchi et al., 2012; Awokunmi et al., 2021; Nurchi et al., 2020). Once released into water bodies, they not only degrade aquatic ecosystems but also contaminate drinking water supplies and enter the food chain.

To address heavy metal pollution, conventional treatment methods such as chemical precipitation, membrane filtration, and ion exchange have been extensively used. However, these technologies are often expensive, energy-intensive, and may result in secondary pollution due to chemical sludge generation (Fu and Wang, 2011). This has prompted a search for cost-effective, environmentally friendly, and sustainable alternatives for wastewater treatment—particularly in resource-constrained settings. In this context, biosorption using agricultural waste materials has emerged as a promising solution. One such material is the palm kernel shell (PKS), a lignocellulosic waste by-product of the palm oil industry. PKS is abundantly available in sub-Saharan Africa and Southeast Asia, and is well-suited for adsorption applications due to its high carbon content, surface area, and porosity (Tan et al., 2017). These properties make it a viable low-cost precursor for the production of activated carbon and other adsorbent materials. The adsorptive efficiency of PKS can be significantly enhanced through activation processes that increase surface functionality and pore volume. Two primary categories of activating agents have been explored: chemical activators, such as zinc chloride (ZnCl_2) and nitric acid (HNO_3), which are known to create extensive pore structures and introduce functional groups on the adsorbent surface (Mohammed et al., 2022) and green/natural activators (lime and lemon juices) which provide sustainable and safer alternatives to harsh chemical treatments (Bello et al., 2019). While numerous studies have demonstrated the effectiveness of activated carbon in removing heavy metals, comparative assessments of chemically and naturally activated PKS using the same base material are scarce in the literature. Moreover, most prior research has focused on single-metal solutions under ideal laboratory conditions, neglecting real-world pharmaceutical wastewater, which contains multiple co-existing metals and competing ions. Despite the growing interest in biosorbents, there remains a lack of comparative studies on the performance of green vs. chemical activation of PKS for heavy metal removal. Limited focus on real pharmaceutical wastewater, which poses more complex adsorption challenges than synthetic metal solutions. This study aims to develop PKS-based adsorbents activated with both green (lime and lemon juice) and chemical agents (ZnCl_2 and HNO_3) and to compare their performance in the removal of Pb, Cd, Cr, and As from pharmaceutical effluents, thereby providing insight into the environmental sustainability and cost-effectiveness of using PKS as a biosorbent in low-income settings.

2. Materials and Methods



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2.1 Materials and Sample Collection

Palmkernel shellsampleswere obtained fromthe palmkernel millatUmuodu village, Uwani Amokwe in Udi Local Government Area of Enugu State, Nigeria. The required reagents for the activation process include: potash, lime, lemon, zinc chloride, nitric acid. These are bought from Ogbete market, Enugu State, Nigeria.

2.2 Methods

2.2.1 Sample preparation

Palm kernel shell (PKS) sample was treated with distilled water several times to get rid of any unwanted dirt and impurities. After which it was sun-dried.

2.2.2 Preparation of activated carbon

In this research work, activated carbon was prepared using two different processes which are: the Natural and the Chemical processes. For the Natural process, lime, lemon, and potash were used as reagents, for the chemical process, zinc chloride (ZnCl_2) and Nitric acid (HNO_3) were used as reagents. 200g of palm kernel shell were measured and placed in different containers. For the natural process, 0.5L of lime, lemon and potash were added to the palm kernel shell separately. For the chemical process, 0.5L of dilute zinc chloride and nitric acid were added to the palm kernel shell separately, it was allowed to stay for up to 24hours,beforesievingthesamplesand drying it in an oven for 1 hour. After drying the samples were placed on heat resistant material (ceramics crucible plate) in a furnace at the temperature of 800°C for 1 hour. After which it was allowed to cool, and it was washed with warm water and sun-dried.

2.2.3. Impregnation Process

The carbonized samples were impregnated with 0.5L of lime, lemon, potash, zinc chlorideand nitric acid,respectively,for24 hours and washed to neutral with warm water and dried in an oven at 100°C for 1 hour.

2.2.4. Absorption studies

The five absorbent samples were used concomitantly with standard activated charcoal. A known quantity (10g) of each of the sampleswas weighed in a 200ml conical flask, and 50ml of the pharmaceutical effluent was added, and it was put in an incubator (rotary shaker at 120 rpm)for 1 hourat 37 C. After 1 hour ofbeen agitated, the samples were filtered using Whatman No. 1 filter paper. The concentrations of these heavy metals in the untreated effluent and filtrates were measured using an Atomic Absorption Spectrophotometer

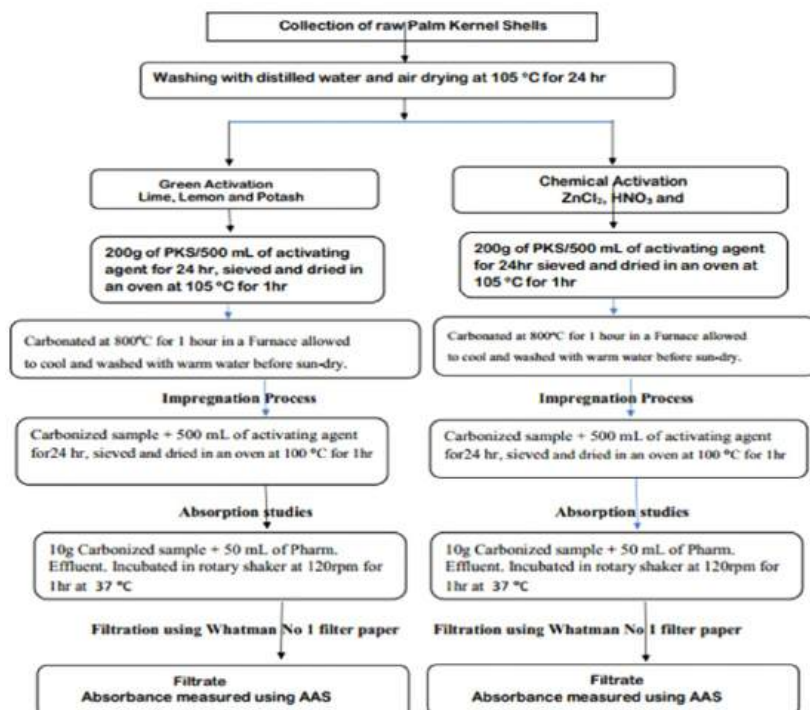


Fig. 1: Flow chart of activated PKS and its application in the treatment of pharmaceutical effluents.

3.0. Result and Discussion

Table 1: Concentrations of Toxic Heavy Metals in Pharmaceutical Effluent

S/N	Metal	Initial Concentration (mg/L)	Who Standard Limit (mg/L)
1	Lead(Pb)	1.268 ± 0.003	
2	Arsenic(Ar)	0.056 ± 0.000	0.01
3	Cadmium(Cd)	0.676 ± 0.000	0.003
4	Chromium(Cr)	0.397 ± 0.001	0.005

The results in Table 1 show that the pharmaceutical effluent contains significantly elevated concentrations of toxic heavy metals. Lead (Pb) was recorded at 1.268 ± 0.003 mg/L, cadmium (Cd) at 0.676 ± 0.000 mg/L, chromium (Cr) at 0.397 ± 0.001 mg/L, and arsenic (As) at 0.056 ± 0.000 mg/L. These values exceed the World Health Organization (WHO) permissible limits for drinking water: 0.01 mg/L for Pb and As, 0.003 mg/L for Cd, and 0.005 mg/L for Cr (WHO, 2017).

Lead had the highest concentration among the metals analyzed, pointing to extensive use of lead-containing raw materials or catalysts in drug production. Cadmium and chromium concentrations were also



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relatively high, which may be attributable to additives or corrosion of metallic equipment used in manufacturing processes (Awokunmi *et al.*, 2021). Arsenic, although lowered in intensity, was still higher than acceptable, demonstrating contamination possibly by solvents or process water used in the industry. Such high quantities can result in severe harm to public health and the environment. Lead and cadmium can lead to brain and kidney damage, especially among children. Arsenic and chromium prolonged exposure are associated with cancer and gene mutations (Nurchi *et al.*, 2020; Jaishankar *et al.*, 2014). These harmful substances can build up in fish and other aquatic organisms and enter the food chain if they get into water, worsening environmental risks in the long run. However, similar studies in Nigeria and other developing countries have reported heavy metal levels in pharmaceutical or industrial effluents that exceed permissible standards. For instance, Ogbeide *et al.* (2015) found Pb and Cd levels in pharmaceutical effluents from Lagos exceeding WHO limits by over 50 times. Likewise, studies by Oluyemi *et al.* (2008) observed toxic metal contamination in industrial areas of southwestern Nigeria, aligning with the findings in this current study.

Table 2: Concentration of Toxic Heavy Metal in the Pharmaceutical Effluent after Treatment

S/N	Metal	Initial Conc	Lime	Lemon	Potash	ZnCl ₂	HNO ₃	Standard Charcoal
1	Lead(Pb)	...	0.578 ± 0.022	0.267 ± 0.028	0.334 ± 0.039	0.198 ± 0.034	0.144 ± 0.027	0.189 ± 0.030
2	Arsenic (Ar)	0.056 ± 0.000	0.007 ± 0.020	0.017 ± 0.022	0.010 ± 0.039	0.027 ± 0.030	0.12 ± 0.023	0.015 ± 0.022
3	Cadmium (Cd)	0.676 ± 0.000	0.045 ± 0.021	0.016 ± 0.024	0.023 ± 0.032	0.014 ± 0.030	0.022 ± 0.023	0.047 ± 0.033
4	Chromium (Cr)	0.397 ± 0.000	0.023 ± 0.022	0.078 ± 0.023	0.117 ± 0.032	0.015 ± 0.031	0.045 ± 0.023	0.023 ± 0.034

Table 3.2 gives the concentrations of lead (Pb), arsenic (As), cadmium (Cd), and chromium (Cr) in pharmaceutical wastewater after treatment using adsorbents from palm kernel shells activated with various agents: lime, lemon, potash, ZnCl₂, HNO₃, and normal charcoal. The data indicate tremendous reductions in all treatments from the initial concentrations. Among these, lead recorded the highest reduction, particularly with HNO₃ (0.144 ± 0.027 mg/L) and ZnCl₂ (0.198 ± 0.034 mg/L) activation. Arsenic levels dropped below the WHO level with lime (0.007 ± 0.022 mg/L) and potash (0.010 ± 0.039 mg/L). Cadmium was reduced to the lowest value using ZnCl₂ (0.014 ± 0.030 mg/L). Chromium was eliminated to a significant level with ZnCl₂ (0.015 ± 0.031 mg/L) and lime (0.023 ± 0.022 mg/L).

The various extents of heavy metal reduction can be attributed to the variation in chemical properties of the activating agents and impacts on the surface characteristics of the palm kernel shell (PKS) adsorbents. Acid-activated adsorbents (like HNO₃ and ZnCl₂) are capable of developing larger porosity and surface functional groups with higher capacity for metal ion adsorption (Foo and Hameed, 2012). Lime and potash, as alkaline materials, also shift surface charge to enhance cationic metal adsorption (Kurniawan *et al.*, 2006). Eco-friendly compounds like lemon juice (containing citric acid) moderately enhanced removal, especially for Pb and Cr. Effective reduction in the concentrations of metals lower than WHO limits—attests to the effectiveness of PKS-based adsorbents, especially those activated using ZnCl₂ and



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HNO₃. This suggests their potential use as low-cost and environmentally friendly alternatives to commercial activated carbon for effluent detoxification (Inyinbor *et al.*, 2018). However, residual concentrations of Pb and Cr in some treatments exceeded WHO standards suggesting the need for optimization or sequential treatment. Adewuyi and Pereira (2017) also observed over 85% removal of Pb and Cd using ZnCl₂-activated biomass. In another investigation, acid-treated PKS was used by Okoye *et al.* (2020) to eliminate Cr and Cd from tannery effluent with great efficiency, similar to what was observed here. The current investigation is in line with these in demonstrating that chemical activation significantly enhances the performance of bio-adsorbents.

Table 3: Concentration of toxic Heavy metal Absorbed after Treatment

S/N	Metal	Initial Concentration (mg/L)	Lime	Lemon	Potash	ZnCl ₂	HNO ₃	Standard Charcoal
1	Lead	1.001 ± 0.000	0.69 ± 0.000	1.001 ± 0.005	0.934 ± 0.004	1.07 ± 0.000	1.124 ± 0.000	1.001 ± 0.000
2	Arsenic	0.056 ± 0.000	0.049 ± 0.001	0.039 ± 0.000	0.046 ± 0.001	0.029 ± 0.005	0.044 ± 0.000	0.041 ± 0.000
3	Cadmium	0.676 ± 0.000	0.631 ± 0.000	0.66 ± 0.000	0.653 ± 0.003	0.662 ± 0.001	0.654 ± 0.000	0.629 ± 0.000
4	Chromium	0.397 ± 0.001	0.374 ± 0.008	0.319 ± 0.000	0.28 ± 0.000	0.382 ± 0.000	0.352 ± 0.000	0.374 ± 0.000

Table 3.3 shows the amount of toxic heavy metals (lead, arsenic, cadmium, and chromium) adsorbed by palm kernel shell (PKS) activated with different activating agents.

The Quantity adsorbed is determined as the initial concentration minus the residual concentration after treatment, based on the assumption that the higher the value, the better the removal. Pb adsorption was best with HNO₃-activated PKS (1.124 ± 0.000 mg/L), followed by ZnCl₂ (1.07 ± 0.000 mg/L). Arsenic (As) was best absorbed by PKS activated with ZnCl₂ (0.029 ± 0.005 mg/L). Cadmium (Cd) had no considerable difference in treatments because all the adsorbents adsorbed within the range of 0.629 to 0.662 mg/L. Chromium (Cr) was best adsorbed by potash-activated PKS (0.280 ± 0.000 mg/L), followed by lemon-activated PKS (0.319 ± 0.000 mg/L).

The efficiency of metal uptake is closely tied to both the activating agent employed and its specific interaction with the PKS matrix. Acidic activators such as ZnCl₂ and HNO₃ are particularly notable for significantly increasing the surface area and fostering a microporous structure rich in active sites (Foo and Hameed, 2012). This structural enhancement directly facilitates greater adsorption of cationic metals like Pb²⁺ and Cd²⁺, primarily via ion exchange and electrostatic interactions. Interestingly, cadmium adsorption appears relatively uniform across all activation treatments, implying either rapid saturation of available PKS binding sites or an inherent tendency toward monolayer coverage, regardless of the activation strategy applied. In contrast, the adsorption behaviour of chromium and arsenic—both of which exist as



55TH INTERNATIONAL CONFERENCE “COAL CITY 2025”



oxyanions under certain pH conditions—is more nuanced. These elements tend to interact more efficiently with positively charged or chemically distinct functional groups present on the PKS surface, and the expression of these groups is contingent upon the choice of activating agent (Kurniawan *et al.*, 2006). This highlights the context's complex, agent-dependent nature of metal adsorption processes.

The high adsorption rates show that chemically treated PKS can potentially be a good adsorbent in the cleanup of waste. In general, HNO₃- and ZnCl₂-activated PKS are efficient in eliminating lead and arsenic and can be used in wastewater treatment of industrial and pharmaceutical waste. However, the narrow differences in cadmium removal imply that we may have to improve or augment other treatment processes for certain metals. These findings agree with reports from Inyinbor *et al.* (2018) and Adewuyi and Pereira (2017), in which ZnCl₂-activated biomass proved to have good capacity for the adsorption of Pb and Cd. Okoye *et al.* (2020) also illustrated enhanced removal of Cr from industrial effluent through the use of acid-modified PKS, in line with present findings on chromium adsorption. In addition, the similarity of PKS-based adsorbents to commercial charcoal (as noted from the 'Standard Charcoal' column) further supports their prospects for application as low-cost and environmentally friendly alternatives.

4. Conclusion

The study investigates the ability of palm kernel shell (PKS) adsorbents, activated using a combination of green and chemical agents, to remove toxic heavy metals from pharmaceutical wastewater. After the treatments, HNO₃-activated PKS achieved the highest Pb removal (1.124 ± 0.000 mg/L adsorbed), ZnCl₂-activated PKS demonstrated the greatest As removal efficiency (0.029 ± 0.005 mg/L), while potash-treated PKS was most effective for Cr adsorption (0.280 ± 0.000 mg/L). Overall, the modified PKS adsorbents outperformed conventional charcoal in most cases, underscoring their potential as affordable and eco-friendly materials for pharmaceutical effluent purification. These results confirm that both natural and chemical activation of PKS significantly improve heavy metal adsorption, supporting its application in sustainable wastewater detoxification processes.

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Conflicts of Interest

The authors declare no conflict of interest.

Declaration of competing interest.

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.



55TH INTERNATIONAL CONFERENCE “COAL CITY 2025”



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Fertilizer Value of Bio-Synthesized Solids Produced from Anaerobic Digestion Treatment of Petroleum Wastewater

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Abstract

Petroleum wastewater was treated in anaerobic thermophilic and mesophilic bioreactors. This yielded important products: biogas, a substitute for natural gas, and bio-synthesized solids (bio-solids), the solid residue produced from the biological treatment of petroleum wastewater. The concentration of nitrogen (in the form of free ammonia) in the bio-solids was 2,857,000 mg/kg for thermophilic (50–75 °C) bio-solids and 3,571,500 mg/kg for mesophilic (28–37 °C) bio-solids. The concentration of phosphorus in the bio-solids was 624.0 mg/kg for thermophilic bio-solids and 286.20 mg/kg for mesophilic bio-solids. Potassium concentrations were 280.65 mg/kg for thermophilic bio-solids and 314.20 mg/kg for mesophilic bio-solids. The thermophilic bio-solids are classified as class A bio-solids because faecal coliforms were eliminated at high temperature. A bio-solid is classified as class A if it contains a faecal coliform density below 1000 Most Probable Number per gram (MPN/g) of total solids (dry weight). The mesophilic bio-solids were classified as class B, having a coliform density of 1000 MPN/g total solids (dry weight). Due to their high concentrations of nitrogen, phosphorus, and potassium (NPK), the bio-solids can be used as fertilizers. Nigerian farmers, the government and the private investors should be informed about the advantages of bio-solids over chemical fertilizers.

Keywords: Anaerobic digestion, Thermophilic bio-solids, Mesophilic bio-solids, Petroleum wastewater, Fertilizer value.

1.0. Introduction

Over the centuries, Nigerian farmers have yearned for a better fertilizer and soil conditioner that has advantageous qualities for land application compared to chemical fertilizers. Technical Science Research (2024) stated that nutrient recycling is a crucial process that helps keep the ecosystem running smoothly. It involves the breakdown of organic materials (dead plants, animals and waste products) by decomposers, e.g. bacteria and fungi, turning them into simpler forms that plants and animals can absorb again.

Fehily (1999) stated that nutrient recycling is integral to all-natural processes. Plants absorb nutrients from the soil and incorporate them into their tissues. Humans consume this plant tissue either directly, through fruits, vegetables, and cereals, or indirectly, through dairy and meat products. Not all nutrient value in food is utilized by humans; the unused portion enters the wastewater stream via human and animal waste disposal. Wastewater treatment produces a solid product containing these unused nutrients. The nutrient recycling cycle is completed when these unused nutrients are returned to the soil, replenishing nutrients removed by plants, as illustrated in Figure 1.

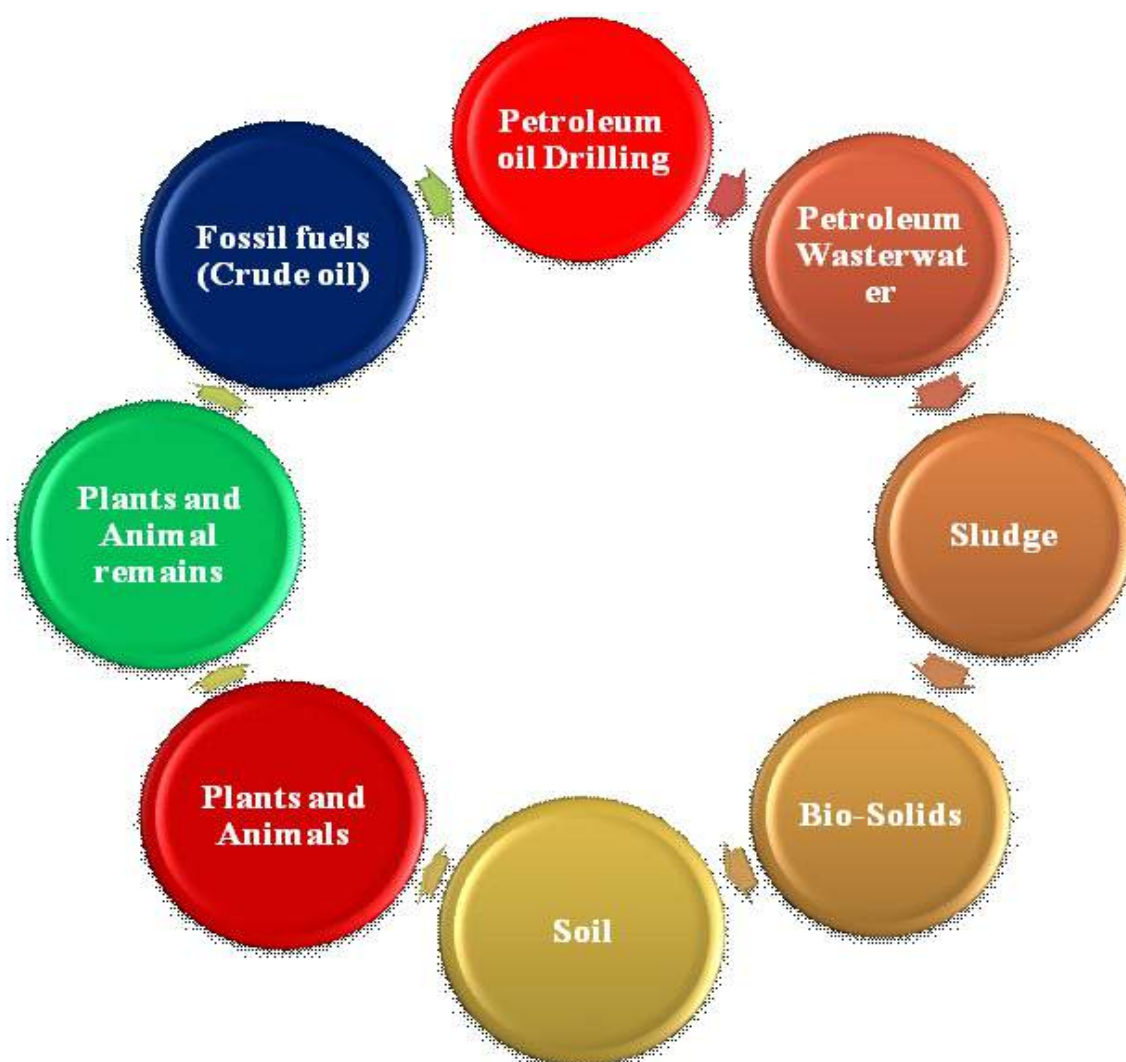


Fig. 1: Nutrient cycle

The only wastewater treatment method that produces a substantial quantity of sludge is the biological anaerobic digestion treatment. The biological treatment of the sludge yields biogas and bio-solids. Anaerobic process is a process that occurs in the absence of oxygen. This process takes place in an anaerobic reactor.

National Non-Food Crops Centre (NNFCC) (2011) defined an anaerobic reactor as a vessel in which processes occur by which micro-organisms break down biodegradable material in the absence of oxygen. The solid product (sludge) produced could be broken down by micro-organisms to bio-solids, which are useful as fertilizer or soil conditioner after heavy metals and faecal coliforms are removed.

Anaerobic sludge treatment is the most sustainable option for sludge treatment since bio-solid production transfers nutrients from food back to the soil, alongside biogas production as a sustainable energy source. Petroleum wastewater treatment involves the biological treatment of water produced during petroleum oil drilling with anaerobic bacteria to generate biogas and bio-solids. The bio-solids are of different classes.



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Class A bio-solids result from thermophilic sludge digestion (50 °C – 75 °C) and have low pathogen content compared to class B bio-solids, allowing their use with unrestricted public contact. Class B bio-solids result from mesophilic sludge digestion (28 °C – 37 °C) and contain faecal coliform densities above 1000 MPN/g of total solids on a dry weight basis (Tchobanoglous et al., 2004). Class A bio-solids have coliform densities below 1000 MPN/g of total solids on a dry weight basis.

Bio-solids produced from wastewater treatment sludge are rich in nitrogen, phosphorus and potassium (NPK), organic matter, and trace metals. Trace metals are extracted to regulatory limits, as they are not recommended for land application. FEPA (2002) mandates that faecal coliform counts must be reduced to an acceptable limit of 50 MPN/100 mL for land application. Passing bio-solids produced from anaerobic digestion of petroleum wastewater through a microwave drier effectively destroys faecal coliforms. Girovich (1996) gave the NPK value of a common chemical fertilizer as 8-8-8 (8% nitrogen, 8% phosphorus, and 8% potassium), which can be equated to the class A bio-solid from the anaerobic treatment of petroleum wastewater studied with several advantages.

Barb (2016) stated that bio-solids improve the tilth of heavy soils, enhance drainage, increase water retention, reduce erosion, and promote water conservation. The organic matter content in bio-solids improves sandy soil structure and fosters better relationships between soil microorganisms and plant roots, thus enhancing healthy and optimal plant growth.

Barb (2016) further noted that organic nitrogen in bio-solids is initially bound in complex molecules that require mineralization and nitrification to become available to plants. This delayed release means nitrogen is available throughout the growing season when plants need it most, making bio-solid fertilizers often more effective than inorganic sources. About 15 % of the total nitrogen becomes available in the first year, with smaller amounts in subsequent years. Organic nitrogen mineralizes over time to plant-available forms and supports subsequent crops, so applying low quantities is advised to prevent nitrogen buildup.

Wisconsin Wastewater Operative Association (WWOA) (2024) stated that quantified mineralization rates of bio-solids are determined by the amount of plant available nitrogen (PAN) released when bio-solids are land applied. This technical paper studies the production and application of bio-synthesized solids, which are used as fertilizer or soil conditioner, as well as the advantages of the bio-solids over chemical fertilizers. Process design, equipment design and process modelling are the limitations of this study.

2.0. Materials and Methods

2.1. Materials

Materials used include: Petroleum wastewater obtained from Agip oil Company, Hydrochloric acid, GBC Avanta Atomic Absorption Spectrophotometer, Boric acid, Ammonia, Jenway 6305 UV Visible Spectrophotometer, Potassium dihydrogen orthophosphate (KH_2PO_4), Conical flask, Hydrogen trioxonitrate (v) acid, Trioxochlorate (v) acid, Distilled water, Lauryl Tryptose Broths (LTB), Test tubes, Wooden applicator stick, water bath, Microwave generator, metallic hydroxides, microwave dryer and Activated alumina.

2.2. Methods

American Public Health Association (APHA) (2001) standard experimental methods were used for the determination of the fertilizer value of the bio-solids.

2.2.1. Anaerobic production of bio-solids

The solid residue obtained from wastewater treatment (sludge) was processed to reduce or eliminate pathogens and odours, resulting in a product (bio-solid) that is harmless to the environment upon disposal and non-toxic to personnel on exposure. Figure 2 shows the block flow diagram for the treatment of petroleum wastewater to obtain bio-solids via anaerobic processes.

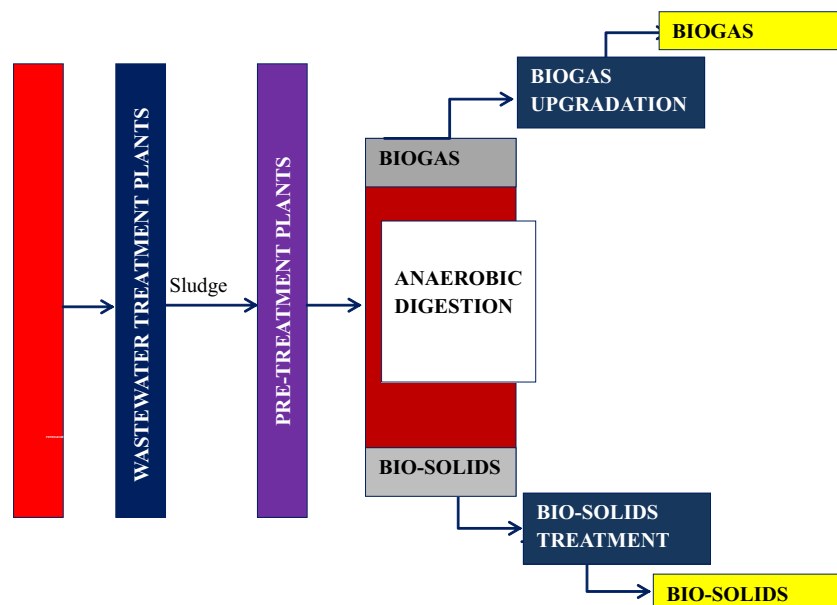


Fig. 2: Block-Flow for the Anaerobic production of Bio-Solids

2.2.2 Measurement of nitrogen content in the bio-solids

A weighed sample of bio-solids was titrated against hydrochloric acid, with colour changes indicating the endpoint. The concentration of nitrogen (free ammonia) was calculated based on the titration volume using equation (1):

$$\frac{\left[\text{Weight of sample} \right] \times \left[\text{Volume of digest used (aliquot volume)} \right] \times \left[\text{Conversion factor from gram to miligram} \right]}{\left[\text{Titre value} \right] \times \left[\text{Volumetric equivalent of Hcl used in relation to nitrogen} \right] \times \left[\text{Total volume of Biosolids (Digest)} \right]} \quad (1)$$

The results in mg/L were converted to mg/kg.

2.2.3. Measurement of phosphorus content in the bio-solids

Bio-solid samples were weighed using a chemical balance, and analyzed for absorbance using a UV-visible spectrophotometer. Concentrations were derived from a standard calibration curve of KH_2PO_4 using equation (2).

$$\left[\text{Gradient of standard graph of concentration of } \text{KH}_2\text{PO}_4 \text{ versus absorbance} \right] \times \left[\text{Absorbance of the Biosolids} \right] \quad (2)$$



The results in mg/L were converted to mg/kg.

2.2.4. Measurement of potassium ion concentration in the bio-solids

1 gram of the bio-solid was weighed into a clean 250 mL conical flask. 10 mL of HNO_3 was added to 5 mL of HClO_3 . This solution was then heated until it became a clear solution. The digest was allowed to cool to room temperature and then diluted to 50 mL with distilled water.

The wavelength of the GBC Avanta atomic absorption spectrophotometer was selected to 766.5 λ , which is the wavelength for potassium. The air and acetylene flows were adjusted to give optimum flame conditions, and the hollow cathode lamp was given adequate time to stabilize. The bio-solids sample solution was aspirated into the flame of the GBC Avanta atomic absorption spectrophotometer under the same conditions as the standards.

A calibration curve was plotted from the standard range after setting the top standard to a suitable scale deflection and the 0 PPM standard to zero. The blank values were subtracted and corrected to dry weight values, and the concentration of potassium was read from a printout obtained from the spectrophotometer. The experiment was carried out for both mesophilic and thermophilic bio-solid samples.

2.2.5. Measurement of concentration of faecal coliforms in the bio-solids

The Lauryl Tryptose Broth (LTB) media was prepared and dispensed into test tubes. The test tubes were arranged in four rows of five tubes each and the wastewater was inoculated. The inoculated tubes were incubated at 35°C. Each tube was swirled gently after 24 hours and examined for growth and gas production.

One confirmatory tube was inoculated for each tube that produced growth and gas, and the tubes that showed growth and gas production were shaken gently. Using a sterile 3.5 mm diameter wooden applicator stick, growth was transferred from each tube that showed growth and gas production to the corresponding confirmatory test tubes. All the confirmatory test tubes were placed in a 44.5°C water bath within 30 minutes of inoculation and incubated for 24 hours with the water level above the media in the immersed tubes. After incubation, each tube was examined for growth and gas production. Records were made of the tubes that showed growth and gas production, and the ones that did not. The Most Probable Number (MPN) per gram of total solids (dry weight) was calculated from the number of confirmatory tubes that showed growth and gas production.

$$\text{Coliform Bacterial Count} = \frac{1}{\text{DF}} \times \text{Average Plate Count} \times \frac{1}{\text{VCF}} \quad (3)$$

Where DF is the Dilution Factor and VCF is the Volume Correction Factor

2.2.6. Measurement of heavy metals

The bio-solids were prepared for metal ion analysis by acidification with 1 mL concentration of hydrochloric acid. The wavelength of the GBC Avanta Atomic Absorption Spectrophotometer was selected to match that of the metal whose concentration was to be measured. The air and acetylene flows were adjusted to give optimum flame conditions, and the hollow cathode lamp was given adequate time to stabilize. The bio-solids sample solution was aspirated into the flame of the GBC Avanta atomic absorption spectrophotometer under the same conditions as the standards. A calibration curve was plotted from the standard range after setting the top standard to a suitable scale deflection and the 0 PPM standard to zero. The blank values were subtracted

and corrected to dry weight values and the metal concentrations were read from a printout obtained from the spectrophotometer.

2.2.7. Removal of heavy metals from the bio-solids

The bio-solids were passed through microwaves from a microwave generator. The microwaves broke the bonds that held the heavy metals to the molecules of the bio-solids. This helped the easy precipitation of the heavy metals with 0.0018 mL of metallic hydroxides. The hydroxides, bio-solids and heavy metals were separated by filtration.

2.2.8. Destruction of faecal coliforms in the bio-solids

The bio-solids produced from anaerobic digestion of the wastewater were passed through a microwave drier. The microwaves destroyed faecal coliforms in the bio-solids.

3.0. Results and Discussion

3.1. Fertilizer Value of the Bio-Solids

The results of the measurement of the concentration of nitrogen (in the form of free ammonia), Phosphorus and Potassium ion concentration (NPK) in the bio-solids gave the fertilizer value of the bio-solids.

3.1.1. Concentration of nitrogen in the bio-solids

The calculations for the nitrogen content of the bio-solids are presented in Appendix A. The calculations for the concentration of nitrogen in the bio-solids calculated using equation (1) show that the bio-solids contain a substantial amount of nitrogen.

3.1.2. Concentration of phosphorus in the bio-solids

The concentration of phosphorus in the bio-solids calculated using equation (2) shows that the bio-solids contain a substantial amount of phosphorus. Concentration of phosphorus is given by the product of the gradient of concentration versus absorbance graph (Figure 3) and the absorbance of the bio-solids sample.

Table 1 below is obtained by measuring the absorbance of the bio-solids sample using a spectrophotometer and multiplying it by the gradient of Fig. 3 to get the concentration of phosphorus in the bio-solids sample. Table 1 shows that the concentration of Phosphorus increases with the absorbance.

Table 1: Concentration of Phosphorus in the Bio-Solids at various Absorbance

Gradient of graph (Fig. 3)	Absorbance of Bio-Solid Sample	Concentration (mg/mL)
0.002	0.06	0.00012
0.002	0.128	0.000256
0.002	0.212	0.000424
0.002	0.312	0.000624
0.002	0.395	0.00079
0.002	0.449	0.000899

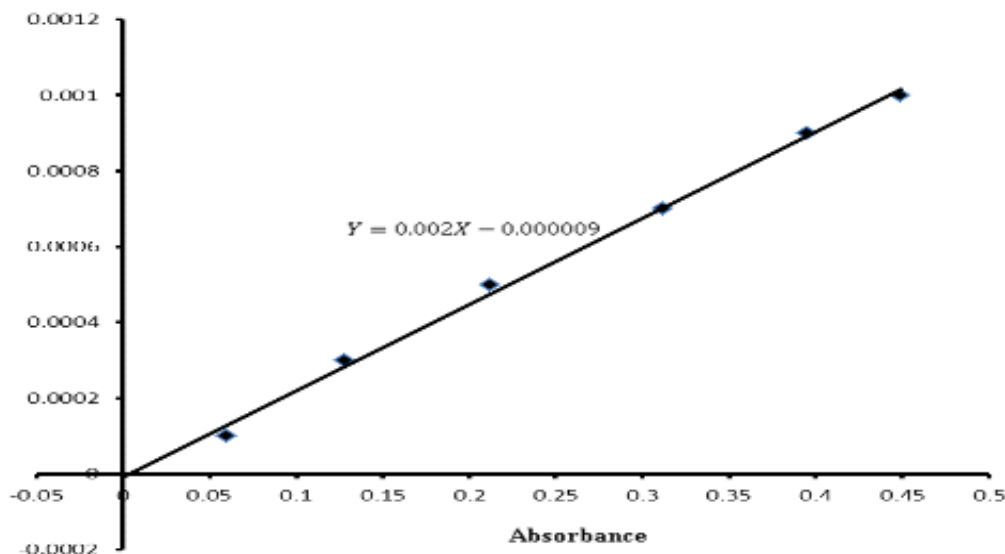


Fig. 3: Concentration of phosphorus in the bio-solids at various absorbance

Fig. 3 shows that concentration of phosphorus is directly proportional to the absorbance. The gradient of the graph of phosphorus concentration in the bio-solids versus absorbance gave 0.002.

3.1.3. Concentration of potassium in the bio-solids

Table 2: Concentration of Potassium in the Bio-Solids

Day	Mesophilic (28 °C)	Thermophilic (75 °C)
5	6.284 mg/L	5.613 mg/L
	280.65 mg/kg	314.20 mg/kg

The bio-solids contain a high concentration of Potassium. This contributes to the high fertilizer value of the bio-solids.

3.1.4. Concentration of faecal coliforms in the bio-solids

The presumptive test result showed the absence of growth and the absence of gas. Confirmatory test showed the absence of growth and the absence of gas. Failure to produce gas confirmed a negative reaction and hence the absence of faecal coliform in the thermophilic bio-solids. Concentration of faecal coliform in thermophilic bio-solids = 0 MPN/g.

The procedure was undertaken at 75°C for thermophilic bio-solids and 28°C for mesophilic bio-solids. Calculations for the concentration of faecal coliforms in the bio-solids are available in the Appendix.

3.1.4.1. Components in the bio-solids and their fertilizer value

Table 3: Fertilizer value of bio-solids produced from anaerobic digestion treatment of the petroleum wastewater



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Component	Thermophilic (75 °C)	Mesophilic (28 °C)
Nitrogen	2,857,000 mg/kg	3,571,500 mg/kg
Phosphorus	624.0 mg/kg	286.0 mg/kg
Potassium	280.65 mg/kg	314.20 mg/kg
Fecal Coliforms	0 MPN/g	1000 MPN/g

Table 3 shows that the bio-solids can be used as fertilizer since it is rich in nitrogen, phosphorus and potassium. The thermophilic bio-solids are classified as class-A bio-solids as they contain no faecal coliforms. USEPA (2014) stated that a bio-solid sample is classified as class-A bio-solid if it contains a fecal coliform density below 1000 MPN/g total solids (dry weight). Faecal coliforms were destroyed by passing the bio-solids through microwave radiation. Table 4 shows a comparison of crop performance for bio-solids and chemical fertilizers.

Table 4: Comparison of crop performance for bio-solids and chemical fertilizers

Years Crop		93 Corn	94 Sorghum	95 Soyabeans	96 Wheat
% Moisture	Fertilizer				
	Bio-Solids	15.7	13.7	10.30	11.50
	Chemicals	17.1	13.8	10.30	12.20
Test Weight (Pounds per Bushel)	Fertilizer				
	Bio-Solids	57.3	60.3	56.40	60.40
	Chemicals	56.2	59.8	56.40	60.20
Yield (Pounds per Acre)	Fertilizer				
	Bio-Solids	101	155	16.0	47
	Chemicals	96	120	15.0	35

Source: (Barb, 2016)

It was found that crops or plants fertilized with bio-solids grew faster in the early season and by the end of the season were more mature than plants or crops fertilized with chemical fertilizer, as indicated in Table 4 above. More so, bio-solids application resulted in higher yields as indicated in Table 4 above.

4.0. Conclusion

Bio-synthesized solids from anaerobic digestion treatment of petroleum wastewater contain substantial nutrients: Nitrogen (2,857,000 mg/kg thermophilic, 3,571,500 mg/kg mesophilic), Phosphorus (624 mg/kg thermophilic, 286.20 mg/kg mesophilic), and Potassium (280.65 mg/kg thermophilic, 314 mg/kg mesophilic). These bio-solids serve as effective fertilizers, offering advantages over chemical fertilizers, including longer nutrient retention and soil conditioning benefits. Plants fertilized with bio-solids grow faster and mature earlier, resulting in higher yields.

5.0. Recommendations

It is recommended to encourage the use of bio-synthesized solid fertilizers and educate farmers on their benefits compared to chemical fertilizers. Anaerobic digestion treatment of petroleum wastewater should be prioritized over other methods. The Nigerian Government, Nigerian farmers and the private investors should be informed about the advantages of the biosolids over chemical fertilizers.



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Modelling the Effect of Reactor Temperature on the Pyrolysis of Water Hyacinth (*Eichornia Crassipes*) Biomass to Produce Pyrolytic Bio-oil in a Fixed Bed Reactor

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Abstract

The pyrolysis of water hyacinth was modelled to determine the effect of pyrolysis temperature on pyrolytic bio-oil yield in a fixed-bed reactor. The models were based on a kinetic scheme of superimposed cellulose, hemicellulose, and lignin reactions coupled with the hydrodynamics of the fixed bed reactor, which were implemented using COMSOL Multiphysics (version 5.0) and validated with experimental results based on mean error. The model validation gave a mean error of 0.012675, 0.030320 and 0.011454, respectively, for the prediction of the yield of bio-oil, bio-gas and bio-char, which indicates that the models predicted acceptably the effect of temperature on the pyrolysis product yield. Also, a maximum pyrolytic bio-oil yield of 39.76 wt. % could be obtained from the pyrolysis of water hyacinth at a reaction temperature of 450 °C. The models developed could be useful in the design of reactors for the pyrolysis of water hyacinth to pyrolytic bio-oil in a bio-refinery and as a diagnostic tool for the reactor performance.

Keywords: Water hyacinth; Pyrolysis modeling; Temperature; Pyrolytic Bio-oil; Fixed bed reactor

1.0 Introduction

The use of fossil fuels has increased enormously worldwide in the last few decades, leading to substantial environmental issues, including ozone layer depletion, greenhouse gas emissions and deteriorating air quality occasioned by pollutants such as NO_x, SO_x and fine particulate matter. More so, the fluctuation of fossil fuel prices and the depletion of its resources determine the global economy. The utilization of carbon-neutral and low-emission fuels from renewable resources, such as biomass, is of increasing importance in the gradual replacement of conventional fossil fuels. It is estimated that the global biomass production is approximately 100 billion tons per annum. As a renewable carbonaceous resource, biomass has the potential to produce heat, electricity, fuel, chemicals, and other products (Ahmed et al., 2024; Raman et al., 2025; Elhenawy et al., 2024; Jerzak et al., 2024).

The biomass, water hyacinth, is an invasive species; it has an average annual productivity of 50 dry (ash-free) tonnes per hectare per year, making it one of the most productive plants in the world. It invades freshwater habitats, and it is listed along with some of the worst weeds in the world (Dhal et al., 2011).

Biomass, a renewable energy source, has been considered as an attractive option to fossil fuels. The drive for biomass fuels is driven by the desire to minimize sulfur dioxide and carbon dioxide emissions and the need to eliminate what has previously been considered a waste product. Fresh biomass fixes solar energy in its structure to produce hydrocarbons during photosynthesis. The hydrocarbons are mainly in the form of



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cellulose, hemicellulose, and lignin, can be accepted as energy deposits (Xia et al., 2021; Elhenawy et al., 2024; Jerzak et al., 2024; Gómez-Vásquez, 2025).

Biofuels have a low concentration of carbon and are environment-friendly, as they have negligible content of sulfur, nitrogen, and ash, which results in a lower emission of SO₂, NO_x, and soot on combustion, compared to conventional fossil fuels. Molecular analysis indicates that the CO₂ released during combustion is equivalent to that which was taken up by plants for photosynthesis in their growth, thus balancing the CO₂ cycle (Aboelela et al., 2023; Raman et al., 2025).

The United Nations Climate Panel has set a target to reduce greenhouse gas emissions by 50–80% by 2050. Achieving this requires a shift from fossil fuel dependence to renewable energy sources. Renewable resources harness solar energy either directly or indirectly—through mechanisms such as falling water, wind, plant growth, and photons—as well as tidal forces and geothermal heat. These sources offer vast, underutilised energy potential capable of meeting global energy demands at competitive costs, provided sufficient support is given (Dhyani & Bhaskar, 2018; Duca & Toscano, 2022; Aboelela et al., 2023).

Water hyacinth-derived pyrolytic bio-oil has shown potential in yielding valuable petrochemicals, chemicals, and pharmaceuticals (Wauton & Ogbeide, 2018). Pyrolysis produces three main products—syngas, tar, and char—and the distribution of these products depends on specific operating parameters. Key parameters influencing product yield include temperature, particle size, and inert gas flow rate (Uddin et al., 2018; Fukuda, 2015; Oyebanji et al., 2018; Jerzak et al., 2024). Among these, temperature plays the most significant role in determining biofuel yield from water hyacinth pyrolysis in fixed-bed reactors (Wauton & Ogbeide, 2019).

A sound understanding of the physical and chemical processes governing pyrolysis, supported by appropriate mathematical modelling, is vital for the efficient design of biomass pyrolysis reactors and gasifiers (Borello et al., 2014). This study aims to model the effect of reaction temperature on bio-oil yield from water hyacinth pyrolysis in a fixed-bed reactor.

2.0 Materials and Methods

2.1 Experimental

Proximate analysis of the dry water hyacinth biomass furnished 71.27 wt. % volatile matter, 14.17 wt. % ash and 14.56 wt. % fixed carbon. Component analysis determined the amount of extractive, hemicellulose, cellulose and lignin as 17.50 wt. %, 27.90 wt. %, 26.50 wt. % and 6.10 wt. % respectively; while ultimate analysis gave C 41.47 wt. %, H 5.825 wt. %, N 2.55 wt. %, S 0.10 wt. % and O 37.945 wt. % (Wauton and William-Ebi 2019).



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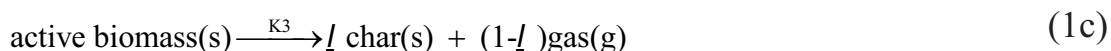
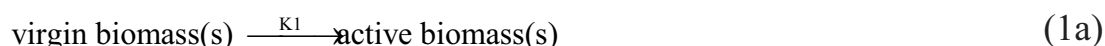
The effect of temperature on product yield was determined by heating up 15 g of the biomass to and maintaining it at 250, 300, 350, 400, 450, 500 and 550°C with a constant heating rate of 50°C/min. The liquid oil was weighed after pyrolysis, and the same goes for the solid bio-char produced, which remains in the reactor tube. The gas produced was determined by material balance. The details of the experiment are available elsewhere (Wauton and Ogbeide 2019).

2.2 Model Formulation

The water hyacinth pyrolysis model consists of the kinetic scheme of superimposed cellulose, hemicellulose, and lignin reactions coupled with the hydrodynamics of the fixed-bed reactor. The description of the sub-models is presented below.

2.2.1 Reaction kinetics models

The reaction mechanism based on superimposed cellulose, hemicellulose, and lignin reactions is presented as (Lathouwers and Bellan 2001; Jones 2011):



The rate of consumption of virgin water hyacinth in the fixed bed reactor is:

$$-R_B = \sum_{i=1}^n R_{Bi} = \sum_{i=1}^n \gamma_i K_{1i} C_B \quad (2)$$

Where R_B = rate of reaction of virgin biomass, kg / m³ s

C_B = concentration of virgin biomass, kg / m³

γ_i = mass fraction of i^{th} component

i = cellulose, hemicellulose and lignin

K_{1i} = rate constant for i^{th} component for virgin biomass components

The rate of formation of the activated biomass components, is R_{AB}

$$R_{AB} = \sum_{i=1}^n R_{ABi} = \sum_{i=1}^n \gamma_i (K_{1i} C_B - K_{3i} C_{AB} - K_{2i} C_{AB}) \quad (3)$$

Where C_{AB} is the concentration of activated biomass, kg / m³

The rate of formation of tar (i.e. bio-oil), R_{TA} is

$$R_{TA} = \sum_{i=1}^n \gamma_i K_{3i} C_{AB} - K_4 C_{TA} \quad (4)$$

Where C_{TA} concentration of tar (or bio-oil), kg / m^3

C_{Bi} concentration of virgin biomass, kg / m^3

The rate of formation of gases and char, R_{CG} is

$$R_{CG} = \sum_{i=1}^n R_{CGi} = \sum_{i=1}^n \gamma_i K_{2i} C_{AB} \quad (5)$$

Assuming that $C_{AB} \cong C_B$ equation (5) becomes

$$R_{CG} = \sum_{i=1}^n \gamma_i K_{2i} C_B \quad (6)$$

The fraction $(1-g\gamma)$ had been determined as $0.35g^{Char/gfuel}$ (Lathouwers and Bellan 2001; Bech et al. 2009), where $g\gamma$ is the gas/ char selectivity, therefore,

$$R_G = 0.65R_{CG} + K_4 C_{TA} \quad (7)$$

and

$$R_C = 0.35R_{CG} \quad (8)$$

Where R_G and R_C are the rates of the formation of gas and char respectively, and

$$R_N = R_B + R_{AB} + R_{TA} + R_G + R_C \quad (9)$$

Where R_N is the overall rate of reaction, $kg. / m^3 s$

2.2.2 Material and momentum balance models for the fixed bed reactor

The material balance is based on the assumptions:

- The variations in the angular direction around the centerline in the reactor are negligible.
- The reactor is isothermal due to the small internal diameter of the reactor.
- Biomass sample is homogeneous.

Based on the above assumptions, the fixed bed pyrolytic reactor for the pyrolysis of water hyacinth to bio-oil can be represented by a 2D-axisymmetric model as illustrated in Figure 1.

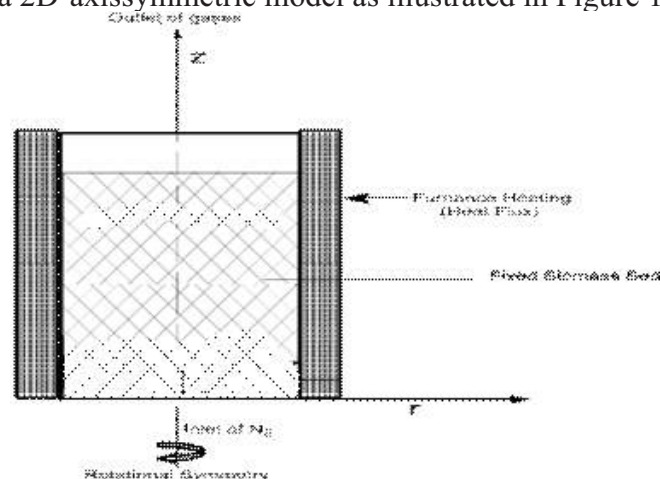


Fig. 1: Geometry for the 2-dimensionally Axisymmetric Model for the Fixed Bed Reactor



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The material balance for species in the fixed bed reactor in Figure 1 is (Tosun 2007; Xia et al., 2021):

$$\frac{\partial C_j}{\partial t} + \nabla \cdot (-D_j \nabla C_i) + u \cdot \nabla C_j = R_j \quad (10)$$

Where C_j is the concentration of specie j , Kg/m^3

D_j = diffusivity of specie j , m^2/s

u = the velocity of flow of fluid into the reactor, m/s

R_j = the rate of reaction of specie j , $Kg/m^3 s$

j = virgin biomass, tar, char and gas

For the flow of fluid through a porous medium, the equation of motion may be replaced by Darcy's equation which is the momentum balance as (Prakash and Karunanithi 2009)

$$u = -\frac{\kappa}{\mu} (\Delta P) \quad (11)$$

Where κ is the permeability of the biomass bed, m^2

u velocity of carrier or inert gas, m/s

μ is the dynamic viscosity of fluid flowing through the biomass bed in the fixed bed reactor, $Pa \cdot s$.

ΔP is the pressure drop across the porous biomass bed, Pa

Initial condition:

$$C_i(r, Z, 0) = C_i 0 \quad (12)$$

Boundary Conditions

$$C_i(r, 0, t) = C_i 0 \quad (13)$$

$$\frac{\partial C_i}{\partial r}(R, Z, t) = \frac{\partial C_i}{\partial r}(0, Z, t) = 0 \quad (14)$$

$$-\frac{D_j \partial C_i}{\partial Z}(r, L, t) = 0 \quad (15)$$

Where $= B, TA, G, C$

2.3 Porosity of Biomass Bed

As the release of volatile substances increase on pyrolysis, the porosity of the biomass increases, which can be predicted (Prakash and Karunanithi, 2008)

$$\varepsilon = \varepsilon_o + \lambda \left(1 - \frac{C_B}{C_{BO}}\right) \quad (16)$$

Where ε is porosity of the biomass,

ε_o is the initial porosity of the biomass,

C_B is the concentration of biomass at time t , Kg / m^3

C_{BO} is the initial concentration of virgin biomass Kg / m^3

λ is a constant,-

2.4 Permeability of Biomass Fixed Bed

The biomass particles in the bed are assumed to be totally spherical, and no volume shrinkage occurs during the pyrolysis. The Kozeny–Carmen equation which is applicable over a wide range of porous materials and flow rates is used to predict the permeability of the biomass bed as (Urumovic and Urumovic Sr. 2014):

$$\kappa = \frac{d_p^2}{180} \frac{\varepsilon^3}{(1-\varepsilon)^2} \quad (17)$$

Where d_p is the biomass particle diameter, m

ε is the porosity of the biomass bed, -

2.5 Product Yield

The yield of products for the pyrolysis of water hyacinth is given as:

$$Y_k = \frac{C_k}{C_{B0}} \quad (18)$$

Where k = tar (bio-oil), gas, and bio-char

C_{B0} = concentration of virgin biomass fed, Kg / m^3

And carbon left behind in the reactor of the char produced unreacted biomass given as:

$$C_R = C_{BO} - C_{TAR} - C_{GAS} \quad (19)$$

Where C_R is the mass of bio-char Kg / m^3

2.6 Method of Solutions

Equation 1 through 19 was implemented in COMSOL Multiphysics (5.0 version). The concise description is addressed below.

2.6.1 Boundary conditions

The reactor is drawn with a 2-dimensional axial symmetry around #1 as in Figure 2; and the boundary

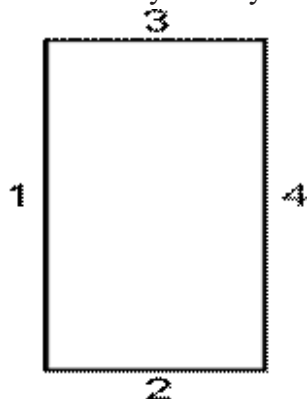


Fig. 2: Boundary Conditions for CFD Simulation conditions were set in the reactor as shown in Table 1.

Table 1: Boundary Conditions

SETTINGS	BOUNDARY			
	1	2	3	4
Boundary type	Axial symmetry	Inlet	Outlet	Wall
B o u n d a r y condition	Axial symmetry	Concentration	Concentration	Insulation/symmetry
Value	$\frac{\partial C_i}{\partial r}(0, Z, t) = 0$ $= B, TA, G, C$	$C_i = C_{i0}$	$-\frac{D_i \partial C_i}{\partial Z}(r, L, t) = 0$	$\frac{\partial C_i}{\partial r}(R, Z, t) = 0$

2.6.2 Meshing

The reactor is represented by a simple geometry as shown in Figure 2; thereafter, a mesh was generated to resolve the physics of water hyacinth pyrolysis in the fixed bed reactor. Mesh 1 was right-clicked, and Physics Controlled Triangular Extra Fine mesh was selected, and Build All was clicked to generate the meshed reactor as shown below in Figure 3. The reactor domain is discretized by a physics-controlled extra-fine triangular mesh to generate 2D meshes as shown in Figure 3. The entire two-dimensional domain is structured with 322 triangular grid elements with an area of 0.006039 m².

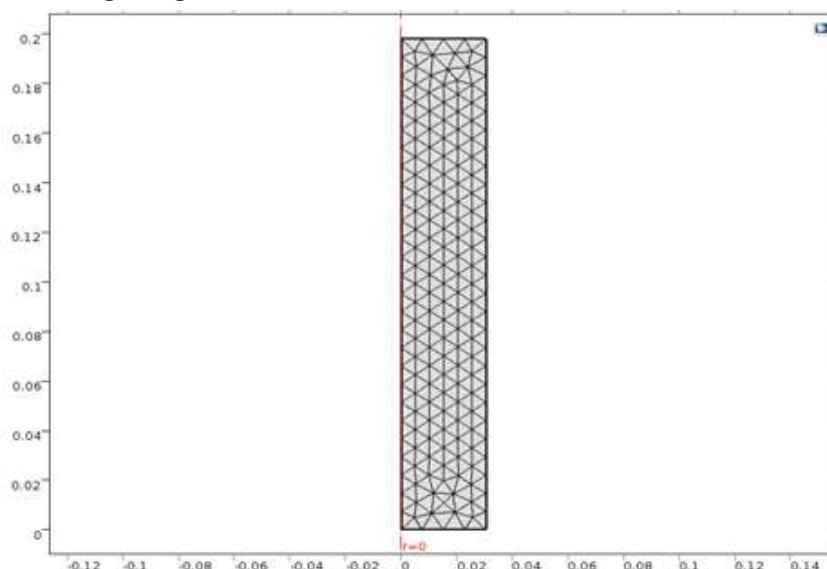


Fig. 3: Meshing of the Fixed Bed Biomass Pyrolytic Reactor

2.6.3 Computing

The *Transport of Diluted Species* (TDS) (Equation 10) and *Darcy's Law* (DL) (Equation 11) were employed to describe the physics of the fixed-bed biomass pyrolysis reactor. TDS represents the mass balance, while DL accounts for the momentum balance within the porous medium. Fluid and matrix properties were

defined using the *Model Wizard*, and key parameters and variables—including the sub-models (Equations 2–9 and 16–19)—were introduced through the *Model Builder* interface.

Simulations were conducted to evaluate the effect of temperature on pyrolysis product yields, within a range of 250–550 °C at 50 °C intervals. The biomass particle size was set at 0.15 mm, with a sweeping gas flow rate of 66.67 cm³/min. A time-dependent simulation was carried out with an initial time of 0 s, a step size of 1 s, and a stop time of 10 s. The thermo-physical parameters used in the CFD simulations are provided in *Appendix 1*, while the kinetic parameters were sourced from Jones (2011) and van de Weerdhof (2010).

2.6.4 Model validation

The results from the model simulation on the effect of pyrolysis temperature on bio-oil yield were validated

$$RSS = \sum_{k=1}^n \left(\frac{y_{ke} - y_{ks}}{y_{ks}} \right)^2 \quad (20)$$

$$MRSS = \frac{RSS}{n} \quad (21)$$

$$MR = \sqrt{MRSS} \quad (22)$$

Where *RSS*, *MRSS* and *MR* are ranked set sampling, median ranked set sampling and mean error; *y_{ke}* and *y_{ks}* are the experimental and simulation composition of pyrolysis products (bio-oil, gas or bio-char), respectively. The mean error is useful in measuring the predictability of the model.

3.0 Results and Discussion

3.1 Model Results

The effect of temperature on pyrolysis product yields is illustrated in Figures 4–6. Overall, the COMSOL simulation results align well with the experimental data, with only slight deviations. In Figure 4, the model predicts a bio-oil yield rising from 14.60 wt.% at 250 °C to a peak of 39.76 wt.% at 450 °C, then falling to 29.38 wt.% at 550 °C. Experimentally, the yield follows a similar trend, increasing from 15 wt.% at 250 °C to 41 wt.% at 450 °C, and then dropping to 30 wt.% at 550 °C. This decline beyond 450 °C is attributed to secondary cracking reactions that convert bio-oil to gas (Chaurasia & Babu, 2011). The optimal bio-oil yield occurs at 450 °C, consistent with the established pyrolysis range for liquid fuels (426.85–526.85 °C) (Papadikis et al., 2009; Elhenawy et al., 2024), and in line with previous findings (Oyebanji et al., 2018; Bridgwater, 2012).

Figure 5 shows that gas yield increases with temperature. Experimentally, it rises from 25 wt.% at 250 °C to 42 wt.% at 550 °C. The model similarly predicts an increase from 27 wt.% to 43 wt.% over the same range, confirming that higher temperatures promote gas formation due to secondary reactions.

Figure 6 demonstrates a steady decline in bio-char yield with increasing temperature. Experimental results show a decrease from 60 wt.% at 250 °C to 28 wt.% at 550 °C, while the model predicts a similar drop from 58.26 wt.% to 27.85 wt.%. This trend confirms that bio-char formation is favoured at lower temperatures, as supported by literature (Chaurasia & Babu, 2011; Uddin et al., 2018; Xia et al., 2021).

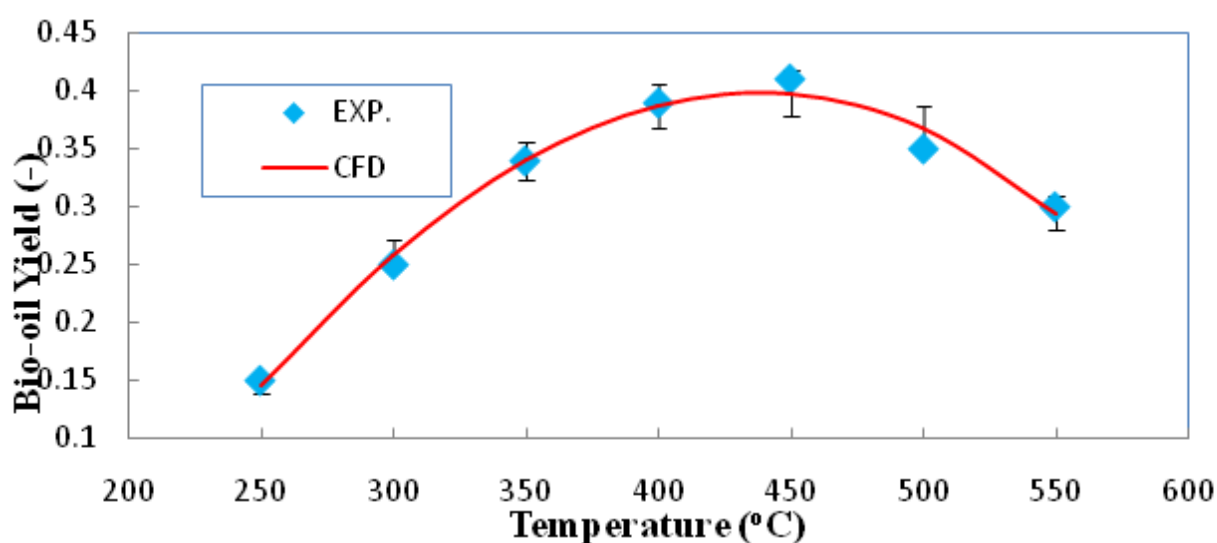


Fig. 4: Effect of Reactor Temperature on Bio-Oil Yield

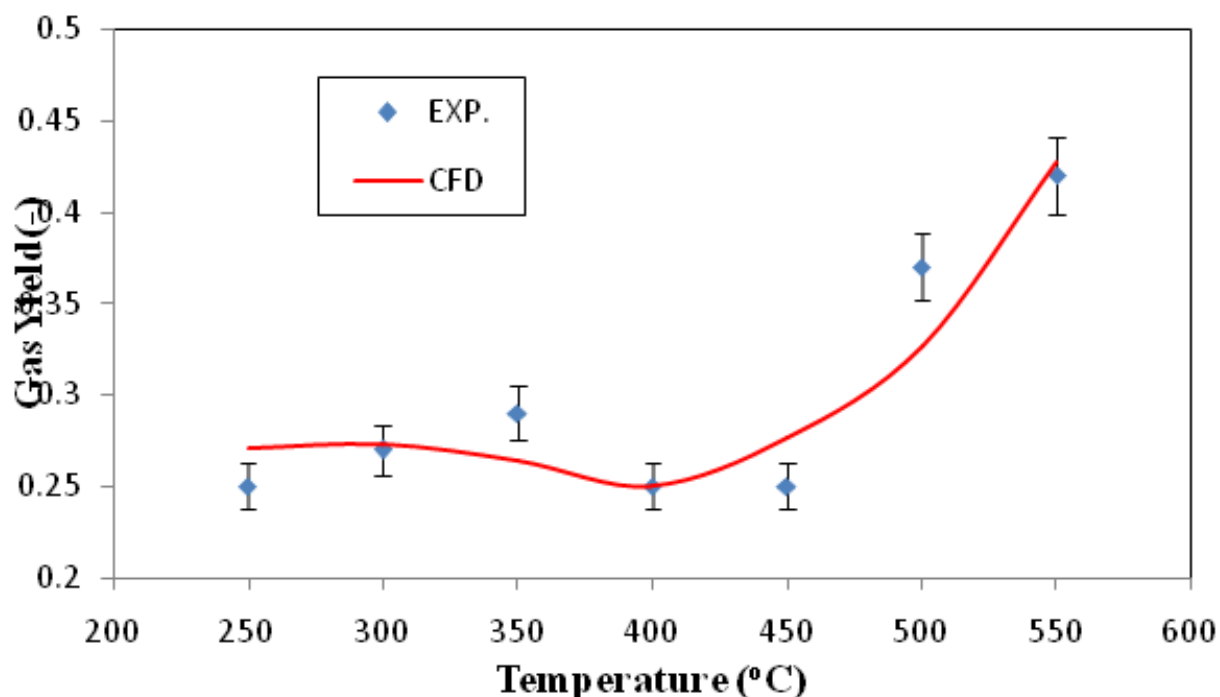


Fig. 5: Effect of Reactor Temperature on Gas Yield

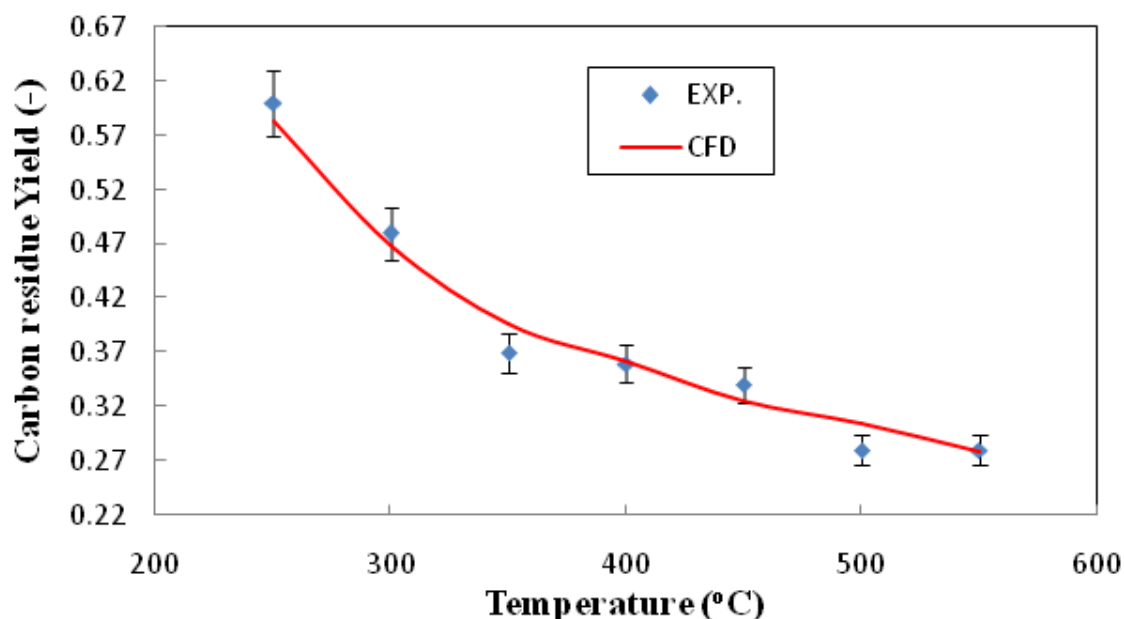


Fig. 6: The Effect of Reactor Temperature on Carbon residue Yield

3.2 Model Validation

Table 2 shows the accuracy of the predicted product yield on the pyrolysis of water hyacinth to bio-oil in a fixed-bed reactor based on the mean error. The prediction of the bio-char and bio-gas yield furnishes the lowest and highest deviations of 0.011454 and 0.030320, respectively. The highest mean error for the gas could be attributed to the fact that in the experimental work used for the model validation, the pyrolytic bio-oil and bio-char yield were measured, and the gas yield was obtained by material balance as a result of experimental system limitations, hence any error made in the measurement of the pyrolytic bio-oil and bio-char compared to that of the gas yield.

Table 2: Accuracy of the Predicted Product Yield

Pyrolysis Parameter	Mean Error		
	Bio-oil	Gas	Carbon Residue
Temperature	0.012675	0.030320	0.011454
Particle size	0.006571	0.018475	0.005687
Inert gas flow rate	0.000089	0.006526	0.006616
Average Error	0.004255	0.012282	0.006023



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Also, the error in the prediction of the model on bio-oil yield is higher than that of bio-char; there is the possibility that a very small fraction of condensable gases could pass through the condenser without condensation. However, the mean error range of 0.011454 to 0.030320 is very low; therefore, the models predicted acceptably the effect of temperature on product yield in the pyrolysis of water hyacinth in the fixed bed reactor. The predictability or error of the present model is comparable to that of date palm waste gasification products prediction in a downdraft gasifier, which ranged from 0.039651 to 0.270876 (Bassyouni *et al.*, 2014).

4.0 Conclusion

Modelling the effect of temperature on the pyrolysis of water hyacinth (*Eichhornia crassipes*) to bio-oil in a fixed bed reactor was carried out, and it was concluded as follows:

- The model validation shows a mean error of 0.012675, 0.030320 and 0.011454, respectively, for the prediction of the yield of bio-oil, bio-gas and bio-char which indicates that the models predicted acceptably the effect of temperature on pyrolysis product yield of water hyacinth.
- Maximum pyrolytic bio-oil yield of 39.76 wt. % could be obtained from the pyrolysis of water hyacinth at a reaction temperature of 450 °C; bio-gas yield increases with temperature, and that of the bio-char decreases with temperature from the model prediction.
- The models developed could be used in the design of a bio-refinery for the production of biofuel from water hyacinth.



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Appendix 1: Thermo-Physical Values Adopted in the CFD Simulation

Property	Symbol	Value	Reference
Diffusion coefficient of Biomass	B	$m^2 s^{-1}$	Efendiev,2013
Diffusion coefficient of char	C	$m^2 s^{-1}$	Efendiev,2013
Diffusion coefficient of bio-oil	TAR	$m^2 s^{-1}$	Lathouwers and Bellan,2001
Diffusion coefficient of gas	G	$m^2 s^{-1}$	Lathouwers and Bellan, 2001
Diffusion coefficient nitrogen	N_2	$m^2 s^{-1}$	Lathouwers and Bellan, 2001
Density of biomass	B	$kg m^{-3}$	Determined
Density of char	C	$kg m^{-3}$	Determined
Density () of Nitrogen	N_2	$kg m^{-3}$	Iyagba,2012
Density () of Gas	GAS	$kg m^{-3}$	Iyagba,2012
Density () of Tar	TAR	$kg m^{-3}$	Iyagba,2012
Dynamic viscosity of Nitrogen	N_2	$Pa s$	Lathouwers and Bellan, 2001
Dynamic viscosity of Gas	GAS	$Pa s$	Lathouwers and Bellan, 2001
Dynamic viscosity of Tar	TAR	$Pa s$	Lathouwers and Bellan, 2001
Initial Porosity of biomass at:	ϕ		Determined
2 mm		0.78	
1.7 mm		0.74	
1.4 mm		0.71	
1 mm		0.70	
0.6 mm		0.61	
0.3 mm		0.48	
0.15 mm		0.41	
Char Formation Ratio for Reaction	g	0.65	Bech <i>et al.</i> , 2009
Porosity constant	λ	0.3	Babu and Chaurasia,2004
Mass fraction of cellulose	Y1	0.265	Determined
Mass fraction of hemi-cellulose	Y2	0.279	Determined
Mass fraction of lignin	Y3	0.061	Determined
Average molecular mass of gases		30 kg/kmol	Lathouwers and Bellan, 2001
Average molecular mass of tar		100 kg/kmol	Lathouwers and Bellan, 2001
Average molecular mass of N_2		28.013 kg/kmol	Lathouwers and Bellan, 2001



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Compositional Model for Predicting the Physical and Mechanical Properties of A Natural Fiber Reinforced Polymer Composite

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Abstract

*Polymeric composite substances which are based completely on virgin polymer resins are not completely biodegradable and are structurally so bulky for industrial use or application, hence polymer composites which are biodegradable with enhanced or improved mechanical and physical properties fabricated using natural fibres (biomaterials) such as okro (*Hibiscus esculentus*) plantain (*Musa paradisiaca*) and okoho (*Cissus Populnea*) and a blend of high density polyethylene (HDPE) polymer resins is much desirable and a better alternative to the use of pure polymer resins for industrial and household applications. The work consist of fabricating a polymer composite specimen using the mentioned natural fibres and then testing for the physical and mechanical properties such as thickness swelling (%) water absorption capacity (%) and density (kg/m^3) and then tensile strength, tensile modulus (MPa), flexural strength (MPa) flexural modulus (GPa) elongation at break (%) The fabricated polymer composite specimens exhibited good qualities of high tensile strength of 44.13MPa, 58.85MP and 36.80MPa for *Hibiscus esculentus*, *Cissus Populnea* and *Musa paradisiaca* respectively with corresponding densities of 0.65kg/m^3 , 0.70kg/m^3 and 0.82kg/m^3 . The scenario show that *Cissus Populnea* fibre reinforced composite had the highest tensile strength, lower water absorption capacity and lower density.*

Keywords: Hydrophilic fibre, hydrophobic polymer, fibre reinforcement, mercerization, polymer composites

INTRODUCTION

The thermosets and thermoplastic materials can be reinforced and made into polymer composite structures. Thermosets were the first to be introduced as a matrix to be reinforced with natural fibres (Bledzki et al., 2008). Recently developments shifted to thermoplastic matrix composites, this is because thermoplastics are more easily molded in manufacturing technologies (e.g. injection moulding, extraction, etc.) than reinforced thermosets (Ander, 2006). Another reason for thermoplastics being used as matrix is that they often need the additional strength or additional stiffness gained from reinforcement (Gassan, 1999) (Bledzki et al 2007) compared some common type of thermoplastics with different, properties used as matrix in natural fibre reinforced composites. They concluded that polyethene (HDPE) was suitable to be the matrix in natural fibre reinforced composites because they had lower characteristic temperatures and higher mould shrinkage, although their mechanical properties were relatively low. PP and PE are alkyl and hydrogen groups. PP has been studied as a matrix in fibre reinforced composites by many researchers because of its low cost and good thermal stability (Bo Masden and Hans, 2003). other thermoplastics such as polyester amide (PEA), poly (3-hydrobuty rate - co- b hydrovalerate) PHBV polylactic acid [PLA] polyphenylene sulphide (PPS) polyetherether ketone (PEEK) polycarbonate [PC] polyamide 6(PA-6) polybutylene terephthalate has better mechanical properties than PP and PE but also more costly were chosen as matrix for fabricating composite reinforced with natural fibres (water loving characteristics)



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hence the hydrophobic (water hating) matrix have mould shrinkage which is the amount of shrinking (%) when a polymer is cooled down (Ander, 2001). Mould shrinkage occurs in all thermoplastic materials due to thermal and other contractions in the molecules. Crystalline polymers exhibit the worst problems [shrinkage [1-4%] for nylon, HDPE, pp. etc. while amorphous polymers (Polystyrene, etc.) have less mould shrinkage (Alakali, 2009). By introducing natural fibres into the polymer matrix, the mould shrinkage of composites is all reduced. HDPE and LLDPE have greater stiffness or strength than LDPE]. HDPE also has good chemical resistance and excellent stiffness from room temperature to the boiling point of water (100 °C). The mechanical properties are influenced by the individual mechanical properties of both polymer matrix and fibre reinforcement.

The bonding strength between fibre and polymer matrix in the composite is considered a major factor in order to get a superior fibre reinforcement in composite properties. Because of the pendant hydroxyl and polar group in the fibre, this leads to extremely high moisture absorption, resulting in weak interfacial bonding between the fibre and the hydrophobic polymer matrix. To develop a composite with good mechanical properties, chemical modification of the natural fibre (a process called mercerization) is carried out to reduce the hydrophilic behaviour of the fibre, increase the cellulose content (hence the mechanical properties) and then reduce the moisture absorption capability (Hashim et al, 2012). The different surface chemical treatment of natural fibres includes, but, is not limited to the following.

I. Alkaline treatment

Alkaline treatment, also known as mercerization, is one of the most used chemical treatments for natural fibres when used to reinforce thermoplastics and thermosets (Ikezue, 2016). Addition of aqueous sodium hydroxides (NaOH) to natural fibre promotes the ionization of the hydroxyl group to the alkoxide: $\text{Fibre-OH} + \text{NaOH} \rightarrow \text{Fibre-O-Na} + \text{H}_2\text{O}$

This increases the cellulose and hemicellulose content of the fibre thereby improving the physical and mechanical properties of the fabricated composite.

ii. Silane Treatment

Silane is a chemical compound with the chemical formula SiH_4 . Silane coupling agent may reduce the number of cellulose hydroxyl groups in the fibre-matrix interface. In the presence of moisture, a hydrolysable alkoxy group leads to the formation of silanol. The silanol then reacts with the hydroxyl group of the fibre, forming stable covalent bonds to the cell wall that are chemisorbed onto the fibre surface. This increases the interfacial strength of the fibre.

iii. Acrylation Treatment.

Acrylic acid ($\text{CH}_2=\text{CHCOOH}$) is also used in graft polymerization to modify fibre surface (Okoye, 2023). The reaction is initiated by free radicals of the cellulose molecule.

iv. Permanganate Treatment

Permanganate is a compound that contains the permanganate group, MnO_4^- .

The permanganate treatment leads to the formation of cellulose radical through MnO_4^- ion formation. Most treatments are done through potassium permanganate (KMnO_4) solution in acetone.

This decreases the hydrophilic tendency of the fibre.

MATERIALS AND METHOD OF RESEARCH

The three natural fibres, okro (*Hibiscus esculentus*), plantain (*Musa paradisiaca*) and okoho (*Cissus Populnea*) were sourced and extracted from a farm land in Amechi, Enugu South Local Government Area, Enugu state located at 6.4° North of latitude, 9.52° East of longitude and 197m or 646.33ft of elevation



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above sea level.

The thermoplastic polymers ie, HDPE, used in the work were supplied by Centre for Composite Research and Development (CCRD) JUNENG Nigeria Ltd. The other materials include sundry chemicals-methanol, glacial acetic acid, triethoxyvinyl silane coupling agent, benzoyl chloride, methylethyl ketone, NaoH pellets, sulphuric acid, acetic anhydride, benzene solution, toluene solution, Ca(OH)₂ pellets, peroxide (catalyst), mould release agents, Accelerator (helps in solidification and curing), metal cutter, metal hammer, filling machine (composite cutter) digital weight balance, plastic drum, masking tape, Hounsfield Digital Tensometer, Buck 530 Fourier Transform infra spectroscopic analyser.

EXTRACTION OF THE FIBRES

The okro stem fibres were retted in water for 12 days in a mud tank, the plantain pseudo stem fibres were mechanically extracted, while the okoho bast fibre was retted in water for 21 days in a mud tank. Each of these fibres was dried in air until a constant weight and then subjected to hot KOH treatment and also dried to obtain the single fibre.

THE MOULDING PROCESS

The ground blend from the compound process was gradually poured into specially made moulds. The surface of the moulds was coated with oleic acid to avoid adhesion of the mixture and for easy removal of the polymer composites. The mixture was then spread equally on the surface of the moulds and allowed to stand for 24 hours at ambient temperatures.

The mechanical - Tensile strength, Tensile modulus, flexural strength, flexural modulus and elongation at break were determined using the hounsfield digital tensometer according to ASTM 190-03, and the results were presented in the Tables 1.0 for *Cissus Populnea*, 3.0 for *Hibiscus esculentus*, and 5.0 for *Musa paradisiaca* fibre. The water absorption capacity and thickness swelling were done according to ASTM D570, the composite samples were immersed in distilled water for 24 hrs at ambient condition and then dried in an oven at 50 °C for 24 hours. They were stored in a desiccator, and the moisture uptake and thickness swelling were determined and presented in Table 2.0.

The density was measured using a precision balance (Mettler Toledo model XP 5035, CCRD Nsukka) as seen in Table 2.0.

RESULTS AND DISCUSSION

The mechanical properties as well as the physical properties of virgin high-density polyethylene (HDPE) are shown in Table 4.0, which shows the density (g/cm³), water absorption capacity (%), and the flexural modulus (GPa). The tensile strength and the mould shrinkage (%). The physical properties data for the treated and untreated natural fibres of the three plants are presented in Tables 4 and 2. It is observed that there is tremendous improvement of the physical properties, i.e. thickness swelling (%), water absorption capacity (%) and density (Kg/m³). Also the data on the Tensile Strength (MPa), flexural modulus (GPa) and Elongation at break (%) for the fabricated polymer composites from the three natural fibres are presented in table 1.0 (*Cissus Populnea* fibre), Table 3.0 (*Hibiscus esculentus* fiber) and Table 5.0 (*Musa paradisiaca* fibre) these data on the three respective Table 1, 3 and 5 were compared with those of the virgin polymer resin Table 4.0 it was observed that there were improvements on the determined mechanical properties. The

$$y(x) = a_0 + a_1x_1 + a_2x_2 + a_3x_1x_2 + a_4x_1^2 + a_5x_2^2 + a_6x_2^2x_1$$

$y(x)$ is the physical/mechanical properties of individual fibre.

x_1 = fibre length x_2 = fibre volume fraction

Table 1: Effect of process variables on the Mechanical Properties of Composites Produced from Treated and Untreated *Cissus Populnea* fibre



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Sample	Tensile Strength (Mpa)	Tensile Modulus (Mpa)	Flexural Strength (Mpa)	Flexural Modulus (Gpa)	Elongation@ Break (%)
1	35.53±51 ^r	36.81±52 ^{b-e}	20.60±51 ^{de}	159.47±35 ^a	4.35±56 ^j
2	39±00 ^{lm}	36.03±05 ^{b-g}	21.17±06 ^{c-e}	142.23±23 ^a	5.04±05 ^l
3	43.6±86 ^{lm}	27.50±17.32 ⁱ	20.56±50 ^{de}	158.04±05 ^a	4.52±02 ^j
4	38.99±84 ^{lm}	36.23±23 ^{b-f}	21.20±26 ^{c-e}	156.10±10 ^a	5.20±10 ^{hi}
5	53.91±16 ^{ef}	35.13±05 ^{i-h}	20.48±46 ^{de}	145.20±26 ^a	6.03±05 ^{fg}
6	53.62±03 ^f	36.73±63 ^{b-e}	22.03±05 ^{c-e}	130.20±26 ^{ab}	4.02±01 ^{jk}
7	37.78±58 ^{no}	30.66±76 ^{g-i}	25.20±26 ^{b-e}	150.40±60 ^a	8.27±23 ^b
8	58.04±91 ^a	37.06±05 ^{b-e}	21.03±05 ^{c-e}	155.26±20 ^a	9.00±00 ^a
9	50.72±32 ^g	40.00±05 ^{abc}	25.73±55 ^{a-d}	159.10±09 ^a	3.13±05 ^l
10	42.45±55 ^j	40.83±66 ^{ab}	20.43±51 ^{de}	155.07±05 ^a	4.10±00 ^{jk}
11	39.18±94 ^{lm}	38.06±05 ^{bcd}	21.13±05 ^{c-e}	156.26±37 ^a	4.07±05 ^{jk}
12	31.12±64 ^q	36.16±20 ^{b-f}	20.36±55 ^{de}	160.533±45 ^a	5.33±28 ^{hi}
13	56±85 ^{bc}	40.40±51 ^{abc}	22.16±11 ^{c-e}	158.20±49 ^a	6.20±62 ^{ef}
14	56.12±64 ^{bc}	41.23±23 ^{ab}	23.73±64 ^{c-e}	158.43±49 ^a	3.20±34 ^l
15	55.34±33 ^{cd}	45.36±55 ^a	21.13±11 ^{c-e}	161.37±54 ^a	4.07±05 ^{jk}
16	37.84±64 ^{no}	44.03±05 ^a	20.50±00 ^{de}	160.80±51 ^a	5.33±57 ^{hi}
17	56.13±11 ^{bc}	40.00±00 ^{abc}	21.33±57 ^{c-e}	155.70±61 ^a	4.10±00 ^{jk}
18	45.63±40 ^h	40.84±75 ^{ab}	30.20±25 ^{ab}	155.06±05 ^a	5.60±05 ^{gh}
19	38.1±01 ^{no}	38.33±29 ^{bcd}	31.20±26 ^a	148.33±28 ^a	6.03±05 ^{fg}
20	56.24±99 ^b	31.18±23 ^{f-j}	27.00±00 ^{abc}	145.40±51 ^a	6.53±05 ^{de}
21	30.59±08 ^q	36.78±57 ^{b-e}	20.60±51 ^{de}	159.47±35 ^a	4.35±56 ^j
22	30.9±52 ^{qh}	30.67±58 ^{g-i}	20.53±57 ^{de}	153.33±57 ^a	6.80±17 ^{cd}
23	54.61±5.0 ^{de}	40.76±66 ^{ab}	21.86±16.34 ^{c-e}	160.37±55 ^a	6.30±43 ^{ef}
24	55.4±00 ^{bcd}	40.76±66 ^{ab}	30.90±72 ^{ab}	155.53±45 ^a	6.03±05 ⁱ
25	40.81±01 ^k	33.03±05 ^{d-h}	27.03±05 ^{abc}	105.53±78.40 ^b	7.13±05 ⁱ
26	53.16±10 ^f	32.00±00 ^{e-l}	26.06±05 ^{a-d}	154.10±10 ^a	3.20±26 ⁱ
27	41.25±01 ^k	32.40±5.1 ^{e-l}	27.06±05 ^{abc}	154.16±15 ^a	5.40±34 ^{hi}
28	54.55±50 ^{de}	30.02±02 ^{b-i}	22.50±00 ^{c-e}	140.50±60 ^a	4.50±00 ^j
29	54.65±38 ^{de}	30.02±02 ^{hi}	21.10±00 ^{c-e}	140.87±57 ^a	6.26±28 ^{ef}
30	31.35±04 ^q	30.10±00 ^{hi}	22.03±05 ^{c-e}	155.20±17 ^a	7.06±05 ^c
31	39.35±21 ^{lm}	36.20±26 ^{b-f}	21.20±26 ^{c-e}	160.53±45 ^a	3.76±6 ^k
32	58.37±11 ^a	35.20±26 ^{c-h}	8.03±10.45 ^f	162.86±77 ^a	4.16±28 ^{jk}
33	56.1±09 ^{dc}	32.20±26 ^{c-h}	22.36±55 ^{c-e}	158.03±05 ^a	5.10±10 ⁱ
34	44.2±11 ^j	36.70±60 ^{b-e}	26.10±10 ^{a-d}	155.10±10 ^a	3.13±05 ^l
35	39.5±43 ^l	40.13±15 ^{abc}	20.43±51 ^{de}	143.10±00 ^a	8.16±20 ^h
36	38.52±45 ^{mn}	36.66±57 ^{b-e}	22.03±05 ^{c-e}	130.20±26 ^{ab}	4.35±56 ^j
37	39.23±11 ^{lm}	35.08±06 ^{c-h}	25.03±05 ^{b-e}	105.36±78.17 ^b	6.06±05 ^{efg}
38	37.33±31 ^o	36.00±00 ^{d-g}	19.00±00 ^e	160.67±58 ^a	5.04±06 ⁱ
39	37.68±27 ^{no}	40.04±05 ^{abc}	25.70±61 ^{a-d}	159.00±00 ^a	3.00±00 ^l
40	37.3±20 ^o	40.83±66 ^{ab}	20.10±00 ^{de}	155.07±05 ^a	4.10±00 ^{jk}



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Tensile Strength (Mpa) of *Cissus Populnea* fibre reinforced composite
Tensile Modulus (Mpa) of *Cissus Populnea* fibre reinforced composite
Flexural Strength (Mpa) of *Cissus Populnea* fibre reinforced composite
Flexural Modulus (Gpa) of *Cissus Populnea* fibre reinforced composite
Elongation @ Break (%) of *Cissus Populnea* fibre reinforced composite

Table 2: Physical properties of composites produced from treated and untreated fibres of the three plants

S/N	Sample	Thickness Swelling (%)	Water Absorption Capacity (%)	Density (kg/m ³)
1.	Polymer resin	0.00 ^f	0.00 ^f	... ^f ±0.10
2.	Composite produced with untreated CP	3.30 ^a ±0.21	1.83 ^c ±0.06	0.76 ^b ±0.25
3.	Composite produced with CP fibre treated with KOH	2.43 ^{bc} ±0.21	1.83 ^c ±0.06	0.76 ^b ±0.25
4.	Composite produced with CP fibre with Acetic Anhydride	2.70 ^b ±0.26	2.17 ^b ±0.21	0.74 ^c ±0.15
5.	Composite produced with CP fibre treated with Nitric Acid	3.20 ^a ±0.20	2.33 ^b ±0.21	0.71 ^d ±0.020
6.	Composite produced with untreated HE fibre	2.17 ^c ±0.15	1.77 ^c ±0.25	0.68 ^d ±0.23
7.	Composite produced with HE fibre treated with KOH	1.37 ^{de} ±0.32	1.30 ^d ±0.10	0.65 ^d ±0.10
8.	Composite produced with HE fibre treated with Acetic Anhydride	1.63 ^d ±0.21	1.23 ^d ±0.21	0.64 ^e ±0.20
9.	Composite produced with HE fibre treated with Nitric Acid	2.20 ^c ±0.020	1.63 ^c ±0.15	0.66 ^d ±0.25
10.	Composite produced with untreated MP fibre	1.57 ^{de} ±0.49	0.80 ^e ±0.20	0.63 ^e ±0.10
11.	Composite produced with MP fibre treated with KOH	1.17 ^e ±0.15	0.30 ^f ±0.10	0.82 ^f ±0.15
12.	Composite produced with MP fibre treated with Acetic Anhydride	1.50 ^{de} ±0.10	0.30 ^f ±0.10	0.80 ^f ±0.24
13.	Composite produced with MP fibre treated with Nitric Acid	1.70 ^d ±0.10	0.73 ^e ±0.32	0.78 ^f ±0.20

CP=*Cissus Populnea*, HE=*Hibiscus esculentus*, MP=*Musa paradisiaca*

Table 3: Effect of process variables on the Mechanical Properties of Composites Produced from Treated and Untreated *Hibiscus esculentus* fibre

Sample	Tensile Strength (Mpa)	Tensile Modulus (Mpa)	Flexural strength (Mpa)	Flexural modulus (Mpa)	Elongation @ break (%)
1	33.08±.80 ^{cd}	48.20±.17 ^{cd}	25.16±.05 ^{im}	150.40±.51 ⁱ	5.40±.51 ^{ijkl}
2	39.68±.50 ^{ab}	46.70±.60 ^{e-h}	25.90±.34 ^{ijkl}	155.53±.45 ^{fg}	5.70±.34 ^{h-l}
3	31.87±.00 ^{cd}	42.21±.25 ⁿ	26.11±.02 ^{ijk}	156.10±.00 ^{ef}	6.10±.01 ^{g-l}
4	34.03±.02 ^{cd}	44.33±.20 ^m	27.75±.65 ^{fg}	160.20±.26 ^d	6.45±.56 ^{e-j}
5	42.61±.01 ^a	45.67±.58 ^{h-l}	28.16±.05 ^{fgh}	160.90±.72 ^{cd}	6.48±.41 ^{e-j}
6	42.61±.01 ^a	48.17±.06 ^{cd}	30.10±.00 ^e	175.36±.63 ^a	7.80±.17 ^{a-f}
7	40.65±.48 ^{ab}	53.86±.2.8 ^a	28.40±.51 ^{fg}	165.70±.60 ^b	7.5±.00 ^{a-g}
8	31.77±.00 ^{de}	56.20±.2 ^b	25.04±.05 ^{mn}	160.17±.06 ^d	8.07±.05 ^{abc}
9	26±.00 ^{fg}	58.03±.05 ^a	28.09±.02 ^{fgh}	161.47±1.17 ^{cd}	8.08±.07 ^{a-e}
10	42.16±.00 ^{ab}	45.04±.05 ^{u-m}	26.20±.26 ^{ujk}	162.43±.67 ^c	9.03±.02 ^a
11	32.53±.37 ^{cd}	40.51±.00 ^{op}	26.36±.23 ^{ijk}	155.20±.00 ^{fgh}	9.05±.00 ^a
12	40.7±.17 ^{ab}	45.70±.25 ^{h-l}	26.20±.26 ^{ijk}	156.10±.00 ^{ef}	8.16±.28 ^{a-d}
13	42.07±.06 ^{ab}	45.25±.26 ^{i-m}	26.45±.56 ^{ij}	155.10±.10 ^{fgh}	8.41±.36 ^{abc}
14	40.82±.02 ^{ab}	46.20±.26 ^{f-j}	26.43±.49 ^{ij}	145.16±.28 ^j	7.40±.34 ^{a-g}
15	31.24±.64 ^c	46.20±.26 ^{d-g}	26.66±.57 ^l	150.36±.55 ⁱ	7.50±.00 ^{a-g}
16	42.55±.04 ^a	47.21±.29 ^{d-g}	20.11±.02 ^q	150.16±.28 ^j	7.00±.00 ^{c-j}
17	13.11±17.32 ^h	40.44±.000 ^{op}	20.26±.21 ^q	158.06±.05 ^e	6.50±.00 ^{d-j}
18	44.19±.00 ^a	44.67±.28 ^{v-m}	24.38±.33 ^{no}	156.57±.80 ^{ef}	6.1±.28 ^{f-j}
19	32.82±.71 ^{cd}	41.53±2.57 ^{no}	24.06±.05 ^{op}	155.86±.32 ^{fg}	7.54±.03 ^{a-g}
20	34.01±.01 ^{cd}	40.66±.05 ^p	25.03±.05 ^{mn}	150.83±.28 ⁱ	7.54±.03 ^{a-g}
21	30.97±.84 ^{ef}	47.73±.63 ^{kde}	30.36±.55 ^e	145.10±.00 ^j	6.26±.28 ^{f-j}
22	30.43±.75 ^{def}	48.16±.28 ^{cd}	30.07±.64 ^e	145.17±.28 ^j	7.00±.00 ^{c-j}
23	41.22±.29 ^{ab}	49.20±.17 ^{cb}	32.06±.05 ^c	156.33±.57 ^{ef}	4.51±3.43 ^{kl}
24	32.15±.99 ^{cd}	49.1±.22 ^{cb}	31.16±1.25 ^d	156.67±.58 ^{ef}	7.25±.61 ^{b-h}
25	37.01±.91 ^{bc}	49.50±.00 ^b	35.00±.00 ^b	157.00±.50 ^{ef}	7.70±.00 ^{a-g}
26	34.24±.21 ^{cd}	48.23±.32 ^{cd}	36.17±.28 ^a	140.48±.50 ^k	4.53±3.45 ^{kl}
27	31.46±.40 ^{de}	48.40±.34 ^{cbd}	35.00±.00 ^b	140.96±.83 ^k	6.54±.55 ^{d-j}
28	25.18±.30 ^{fg}	46.00±.00 ^{g-k}	30.38±.24 ^e	140.83±.76 ^k	6.39±.33 ^{f-j}
29	32.2±.6 ^{cd}	45.71±.60 ^{h-l}	30.51±.02 ^e	150.85±.56 ^l	7.11±.02 ^{b-i}

Tensile Strength (Mpa) of *Musa paradisiaca* fibre reinforced composite

Tensile Modulus (Mpa) of *Musa paradisiaca* fibre reinforced composite

Flexural Strength (Mpa) of *Musa paradisiaca* fibre reinforced composite

Flexural modulus (Gpa) of *Musa paradisiaca* fibre reinforced composite

Elongation @ Break (%) of *Musa paradisiaca* fibre reinforced composite

Table 4: Properties of PE polymers

Thermal and Mechanical Properties	LDPE	PE HDPE	LLDPE
Density (g/cm ³)	0.910-0.925	0.935-0.1	0.918-0 0.940
W _{24h} (%) [*]	<0.015	<0.01-0.20	
Tg(°C) ^{**}	-20-125	-20-110	-120
Tm(°C) ^{***}	105-16	120-140	
Tp(°C) ^{****}	150-230	150-290	
Mold shrink(%)	1.5-5.0	1.5-5.0	
Specific heat (kJ/kg °C)	1.901-1.989	1.566-2.281	
Tensile strength (MPa)	10-12	14.5-38.0	15-32
Youngs modulus (GPa)	0.055-0.380	0.413-1.490	
Flexural modulus (GPa)		0.41-1.07	
Ultimate tensile strain(%)	90-800	12-1000	

^{*}W_{24h}: Water absorption

^{**}Tg: Glass transition temperature

^{***}Tm: Melt point

^{****}Tp: Process temperature

Table 5: Effect of process variables on the Mechanical Properties of Composites Produced from Treated and Untreated *Musa paradisiaca* fibre



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Sample	Tensile Strength (Mpa)	Tensile Modulus (Mpa)	Flexural Strength (Mpa)	Flexural Modulus (Gpa)	Elongation @ Break (%)
1	25.36±55 ^{op}	45.13±05 ^{lj}	21.20±00 ^{d-n}	160.83±05 ^f	5.40±51 ^{j-l}
2	34.61±01 ^{d-g}	45.36±23 ^{hi}	21.55±39 ^{c-h}	155.50±00 ^{kl}	5.70±34 ^{h-k}
3	35.17±28 ^{cde}	46.20±26 ^{gh}	20.63±32 ^{e-h}	155.03±05 ^l	6.10±01 ^{g-k}
4	26.51±00 ^{mn}	46.13±98 ^{gh}	23.33±29 ^{a-f}	155.67±58 ^{kl}	6.45±56 ^{e-j}
5	20.42±01 ^s	46.20±52 ^{gh}	24.55±00 ^{a-d}	156.33±57 ^{jk}	6.48±41 ^{e-j}
6	20.81±00 ^s	46.80±00 ^g	20.42±03 ^{c-h}	156.83±76 ^{hij}	7.80±17 ^{a-f}
7	33.63±03 ^{hi}	45.10±00 ^{ij}	21.44±03 ^{c-h}	157.67±58 ^h	7.50±00 ^{a-g}
8	26.22±0 ^{lmn}	46.13±51 ^{gh}	22.48±01 ^{a-g}	159.17±28 ^g	8.07±05 ^{a-e}
9	35.13±00 ^{c-f}	45.00±00 ^{ijk}	20.44±00 ^{f-h}	160.83±29 ^f	8.08±07 ^{a-e}
10	25.73±57 ^{hop}	44.34±57 ^{jk}	21.45±01 ^{c-h}	160.70±75 ^f	9.03±02 ^a
11	33.53±40 ^l	44.67±28 ^{ijk}	25.05±05 ^{ab}	154.13±63 ^m	9.05±00 ^b
12	26±00 ^{mno}	45.36±31 ^{hi}	24.00±00 ^{a-e}	155.63±77 ^{kl}	8.16±28 ^{a-d}
13	25.24±22 ^{op}	48.17±28 ^f	24.57±06 ^{a-d}	156.133±98 ^{jk}	8.41±36 ^{a-c}
14	33.53±40 ^l	49.54±03 ^e	25.33±57 ^a	156.76±55 ^{hij}	7.40±34 ^{a-g}
15	26.67±28 ⁿ	55.92±88 ^{bcd}	25.37±54 ^a	156.34±58 ^{jk}	7.50±00 ^{a-g}
16	24.33±49 ^q	55.33±29 ^d	24.71±61 ^{abc}	160.70±75 ^f	7.00±00 ^{c-j}
17	34.34±56 ^{ghi}	56.54±45 ^b	25.01±00 ^{ab}	165.40±10 ^{fg}	6.50±005 ^{d-j}
18	34.7±17 ^{d-g}	56.20±53 ^{bc}	20.74±56 ^{e-h}	166.05±52 ^d	6.16±28 ^{f-j}
19	25.84±.58 ^{m-p}	55.43±.50 ^{cd}	21.67±.28 ^{b-h}	167.75±.30 ^c	7.54±.03 ^{a-g}
20	27.5±.00 ^l	58.78±.57 ^a	20±.55 ^{e-h}	148.40±.34 ^p	5.70±.25 ^{h-k}
21	25.82±.64 ^{m-p}	44.90±.81 ^{ijk}	19.00±.00 ^{gh}	165.33±.57 ^{de}	6.26±.28 ^{f-j}
22	27.49±.44 ^l	46.33±.28 ^g	19.67±.28 ^{gh}	164.86±.80 ^e	7.00±.00 ^{c-j}
23	26.34±.29 ^{m-n}	44.70±.51 ^{hi}	21.10±.77 ^{d-h}	170.60±.34 ^b	451±.3.43 ^{kl}
24	20.83±.62 ^s	45.40±.51 ^{hi}	21.28±.55 ^{c-h}	175.18±.16 ^a	7.25±.61 ^{b-h}
25	34.38±.54 ^{e-h}	44.86±.70 ^{ijk}	19.70±.61 ^{gh}	170.79±.44 ^b	7.70±.00 ^{a-g}
26	35.4±.60 ^{cd}	46.57±.55 ^g	20.41±.50 ^{f-h}	165.00±.00 ^e	4.53±.3.45 ^{kl}
27	20.59±.45 ^s	40.40±.60 ⁿ	21.03±.05 ^{e-h}	160.18±.27 ^f	6.54±.55 ^{d-j}
28	31.03±.89 ^j	44.13±.11 ^k	20.34±.56 ^{f-h}	160.41±.60 ^f	6.39±.33 ^{f-j}
29	34.05±.05 ^{ghi}	40.61±.01 ^m	20.33±.57 ^{f-h}	170.80±.61 ^b	7.11±.02 ^{b-j}
30	23.11±.84 ^r	40.61±.01 ^m	19.43±.02 ^{gh}	170.85±.56 ^b	7.75±.56 ^{a-g}
31	35.2±.27 ^{cd}	44.43±.05 ^{ijk}	20.34±.57 ^{f-h}	157.36±.63 ^{hi}	4.51±.01 ^{kl}
32	27.6±.55 ^l	44.53±.55 ^{ijk}	20.47±.45 ^{e-h}	156.50±.50 ^{ijk}	4.57±.0.6 ^{KL}
33	36.48±.49 ^a	45.37±.54 ^{hi}	21.44±.53 ^{c-h}	156.10±.1.00 ^{jk}	5.46±.40 ^{j-k}
34	28.56±.38 ^k	46.35±.56 ^g	19.88±.11 ^{f-h}	158.60±.55 ^g	6.75±.21 ^{d-j}
35	35.54±.42 ^{bc}	44.53±.54 ^{ijk}	18.57±.97 ^h	149.47±.55 ^o	6.73±.25 ^{d-j}
36	27.44±.48 ^l	45.34±.58 ^{hi}	19.03±.02 ^{gh}	150.54±.58 ⁿ	8.48±.45 ^{a-c}
37	25.13±.22 ^p	46.80±.17 ^g	19.20±.26 ^{gh}	150.86±.72 ⁿ	8.71±.25 ^b
38	26.51±.5 ^{mn}	46.83±.14 ^g	21.77±.82 ^{b-h}	148.19±.07 ^p	8.73±.55 ^{ab}
39	25.84±.03 ^{m-p}	48.00±.00 ^f	22.22±.32 ^{a-g}	149.47±.45 ^o	4.00±.86 ^l
40	36.17±1.20	42.66±.28 ^l	14.58±10.92 ^l	147.33±.58 ^q	5.53±.50 ^{i-l}



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Tensile Strength (Mpa) of *Musa paradisiaca* fibre reinforced composite
Tensile Modulus (Mpa) of *Musa paradisiaca* fibre reinforced composite
Flexural Strength (Mpa) of *Musa paradisiaca* fibre reinforced composite
Flexural modulus (Gpa) of *Musa paradisiaca* fibre reinforced composite
Elongation @ Break (%) of *Musa paradisiaca* fibre reinforced composite

CONCLUSION

From the data on the mechanical properties, it was observed that adding fibre to a polymer matrix influenced the properties by improving them, i.e. Tensile Strength, Tensile modulus, flexural strength, flexural modulus and elongation at break. It also lowered the water absorption capacity and the thickness swelling, as well as the mould shrinkage. Among the three natural fibres, the *Cissus Populnea* fibre reinforced polymer composite had the highest mechanical properties improvement. Also, the water absorption capacity, thickness swelling properties of the fabricated polymer composites showed that the composite with *Hibiscus esculentus* fibre had the least (better) property. The chemical treatments of the three natural fibres helped in increasing the mechanical properties of the produced polymer composites and reducing the moisture uptake or water absorption capacity as well as the thickness swelling of the composites by increasing the cellulose and hemicelluloses content of each of the fibres. These two components of the individual fibres are responsible for the structural strength and mechanical properties.

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Performance Evaluation of Adsorption of Antibiotics from Wastewater Using Polyaniline-*Luffa Cylindrica* Composite (PLCC) Adsorbent

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Abstract

Polyaniline-Luffa cylindrical fibre composite (PLCC) was synthesised, and batch operation was employed to test the synthesised adsorbent for the adsorption of levofloxacin from an aqueous medium. The performance of PLCC was x-rayed and the process optimized using response surface methodology (RSM). PLCC before and after adsorption was characterized using scanning electron microscopy (SEM), X-ray diffraction (XRD), and Fourier transform infrared (FTIR) spectrometry. The relationship between the equilibrium concentration (Ce), energy involvement of levofloxacin in the bulk solution and the amount of levofloxacin (qe) adsorbed from the solution at different temperatures was ascertained using the adsorption isotherms and adsorption kinetics. The outcome demonstrated the adsorbent's excellent adsorption capacity and great affinity for removing levofloxacin. One factor at a time analysis was used to examine the effects of pH, time, initial concentration, temperature, and adsorbent dosage, and equilibrium conditions. At equilibrium, adsorbent dosage of 0.03 to 0.05g, initial concentration of 50mg/L, 30°C and pH 4 gave the best adsorption of levofloxacin, giving percentage removal of 94.8%, 97.9% and 98.9% at 0.03, 0.04 and 0.05g, respectively. Response surface methodology (RSM) optimization utilizing analysis of variance (ANOVA), was used to validate the results. With an adjusted R² value of 0.9937 and a coefficient of determination (R²) of 0.9965, the model's fitness was demonstrated. It was found that the levofloxacin uptake fitted the Freundlich isotherm and pseudo-second order (PSO) kinetics. The results showed the great potential of PLCC in removing levofloxacin from aqueous solutions.

Introduction

Even with water being one of the most plentiful natural resources on Earth, only around 1% of it is fit for human use (Sultana et al., 2021). Water makes up around 3/4 of the Earth's surface, and 70% of that fresh water is used for agriculture, demonstrating the importance of water to the global economy (Ahmed et al., 2022). Human civilization depends critically on a steady supply of fresh, clean water (Brinza et al., 2022), despite its constant contamination. The alarming rise in dangerous contaminants in the water bodies is attributed to industrialization, enlargement of energy-related facilities, pharmaceutical, and mining industries, as well as environmental disasters occasioned by climate change (Ethaib et al., 2020), among others.

A good number of pharmaceuticals contain antibiotics (Mohammed et al., 2023). This is because of their wide utilization in treating a variety of bacterial infectious disorders in both humans and animals (Rashtbari et al., 2022). Through a series of human-induced actions, including effluent streams discharge from hospitals, pharmaceutical companies, and veterinary clinics, the impacts of excessive chemical use get into water bodies, including surface and ground water, without treatment (Kiranjeet and Gulshan 2021).

Membrane filtration, biological treatments, electrocoagulation, extraction, and advanced oxidation processes are some of the methods used to remove pharmaceuticals from bulk wastewater (Nadi et al., 2023; Negarestani et al., 2024). However, adsorption is the most efficient, cost-effective and



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environmentally friendly method for removing various impurities from wastewater sources (Ali et al., 2021). Because of its exceptional adsorption capabilities, high surface area, high electrical conductivity, outstanding chemical stability, high selectivity, reusability, sustainability, and ease of synthesis, polyaniline, a conductive polymer, has drawn a lot of interest as an adsorbent material. Similarly, it has been discovered that *Luffa cylindrica* is made up of a fibrous morphology that is typified by wide, porous, interlocking fibres, which indicate adsorption capabilities (Ali et al., 2024; Mehrdad et al., 2021).

2.0. Materials and Methods

2.1. Adsorbate Preparation

Five grams of powdered levofloxacin (Agabaxin) was added to 1000mL of distilled water to create a representative pharmaceutical wastewater sample. After 30 minutes of stirring, the solution was allowed to settle for 24 hours. The non-dissolved particles were subsequently eliminated via filtering.

2.2 Preparation of Polyaniline

Mansour et al. (2011) reported that polyaniline (PAN) was made in the following manner: After dissolving 5.0g of aniline (or 5mL of aniline in liquid form) in 250mL of HCL(1N), the mixture was cooled with an ice bath below 5°C. After 30minutes of vigorous stirring, 250mL of pre-cooled (NH₄)₂S₂O₈ (0.3M) in HCL solution (1N) was gradually added to the monomer (aniline) solution. The reaction vessel was cooled in an ice bath during the oxidation process since the reaction is exothermic. The reaction mixture was agitated for two hours at low temperature (0–5°C) after full oxidation, and then left undisturbed overnight at room temperature. After filtering the precipitated polymer (dark blue powder), it was washed with diluted HCL solution and then rinsed with distilled water until it lost its hue. Aligomers and non-polymeric contaminants were eliminated by washing with methanol and distilled water. The polymer was then ground into powder in a mortar, dried in an oven at 50–60°C, and kept for further processing.

2.2.1 Preparation of Polyaniline – *Luffa Cylindrica* Fibre Composite

The polymer was treated with a 0.5M NaOH solution for two hours in order to make polyaniline soluble in formic acid for coating and composite production. After that, it was cleaned with purified water and dried at 60°C in an oven. 50mL of formic acid was used to dissolve 0.50g of base-treated PANI, Emeraldine base (EB). After that, the polymer solution was filtered to get rid of any particles that couldn't dissolve. To create the polyaniline-luffa fibre composite, 5g of luffa fibre and 50mL of EB were combined in a 100 cm³ beaker with formic acid. The mixture was swirled for two hours at room temperature and then left for another two hours without stirring. The PANI/luffa fibre composite was heated in an oven to around 60°C in order to allow the surplus solvent to evaporate. This procedure was documented by Mansour et al. (2011).

2.3 Adsorbent characterization

To ascertain the different characteristics of polyaniline, polyaniline-luffa composite, and the sludge that was produced following the adsorption process, the adsorbent was evaluated using Fourier transform infrared (FTIR) spectroscopy (FTIR, Perkin Elmer BX2), X-ray diffraction (XRD 7000 Shimadzu

diffractometer), and scanning electron microscopy (SEM-JEOL JSM-6060, Netherlands). These characteristics aid in identifying the adsorbent's functional group, crystallinity, and surface shape.

3.0 Results and Discussion

3.1 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR analysis was used to determine the chemical functional group of polyaniline, polyaniline-luffa composite, and sludge. The outcome is displayed in Figures 1a-c. Understanding the chemical properties of the resulting polyaniline and polyaniline-luffa composite and the mechanism of adsorption depends on the chemical functional groups. Figure 1b the FTIR spectrum showed distinctive peaks of the luffa and polyaniline components, including possible C-N stretches between 1100–1300 cm^{-1} , which indicate amine groups, and C=C stretching in aromatic rings about 1600 cm^{-1} , a revelation of polyaniline structure. Peaks in the upper ranges of 3200–3500 cm^{-1} indicate -NH or -OH groups, which could be a result of interactions or hydrogen bonds between polyaniline and the luffa matrix. Changes in functional group peaks, particularly those connected to -OH, -NH, C=C, and C-N stretches, in Fig.1c, indicate effective adsorption.

These variations suggest that the functional groups in the composite interacted with medicinal chemicals to successfully capture pollutants. The residue FTIR examination indicates good reusability and validates the

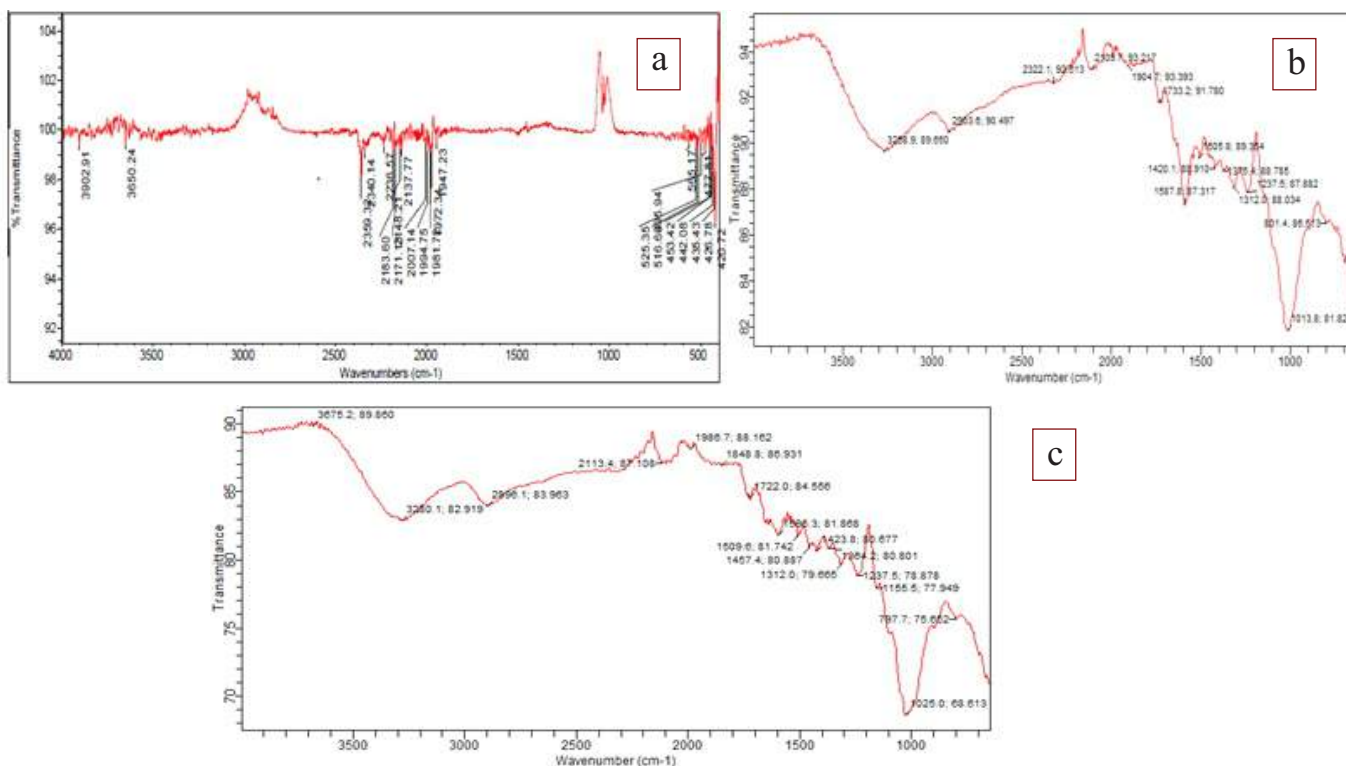


Fig. 1 FTIR for Polyaniline before adsorption (a), Polyaniline-luffa composite before adsorption (b), Slurry obtained after Adsorption (c)

3.2 X-Ray Diffraction (XRD) Results

XRD analysis was used to examine the crystalline nature and structure of the polyaniline-*Luffa cylindrica* composite (PLCC) and the residues following adsorption. The pertinent information is provided by the peaks' position and magnitude. The XRD pattern of PLCC displayed two significant peaks with 2θ at 14 and 23, according to the result (Fig. 2a). The existence of the carbonaceous *Luffa cylindrica* is demonstrated by the composite formation, which displayed a crystalline character of a combined effect of graphite, silicon oxide, magnetite, etc. A disintegration of these peaks was seen in Fig. 2b, indicating that the component had been absorbed onto the PLCC surface.

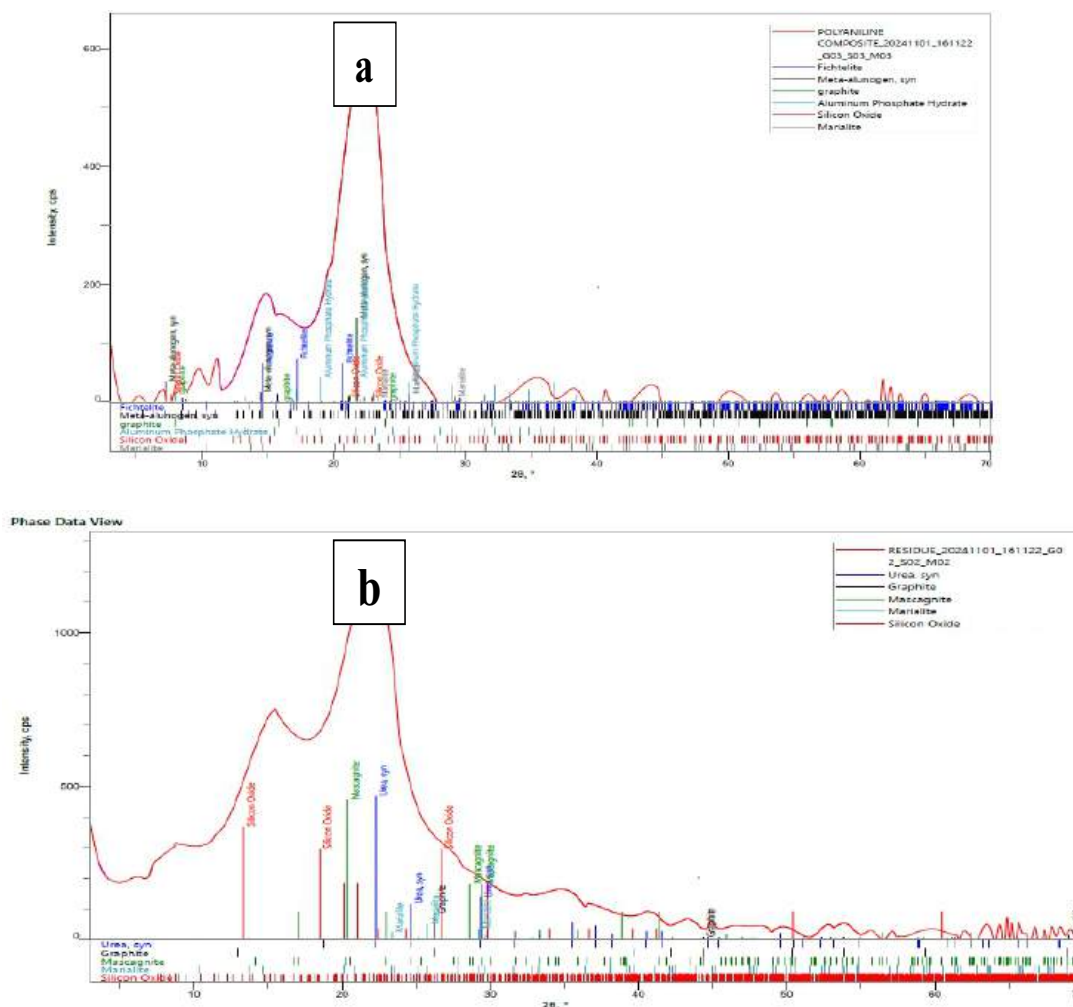


Fig. 2 XRD for the polyaniline-luffa composite (a);Residue after adsorption (b)

3.3 Scanning Electron Microscopy (SEM)

The surface morphology of the polyaniline-luffa fibre composite before adsorption and the residues following adsorption were assessed using scanning electron microscopy (SEM). Figure 3 displays the SEM micrographs of both samples. As seen in Fig. 3a, the sample was rough and uneven, with holes that increased the surface area available for the adsorption of levofloxacin (Sharma et al., 2019).



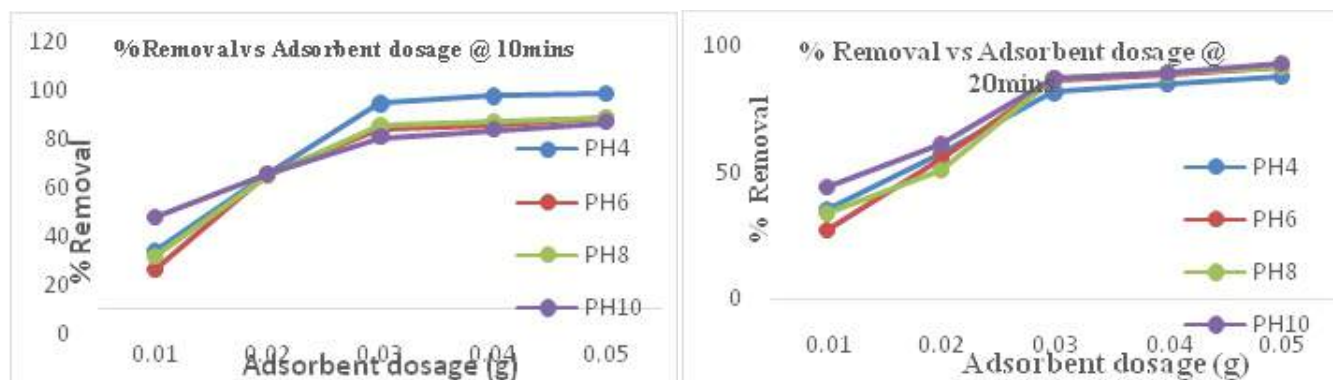
Fig. 3: SEM result for the PLCC (a)Residue after adsorption (b).

3.4 Process Operational Variable Optimization

The equilibrium conditions of the operational variables were investigated using one factor at a time (OFAT) laboratory analysis.

3.4.1 Effect of adsorbent dosage

To investigate the impact of various parameters using PAN-luffa fibre composite on the percentage removal of levofloxacin, a dosage range of 0.01g to 0.05g was used on an initial concentration range of 50 to 150 mg/L, a contact time range of 10 to 30 minutes, a pH range of 4 to 10, and temperatures between 30 and 40 °C. The highest % removal of levofloxacin was observed at 0.05g, as shown by the result in Fig. 4a below, with an initial concentration of 50 mg/L, a pH 4 and a temperature of 30 °C. There is no doubt that increasing the adsorbent dosage causes the percentage removal of levofloxacin to increase sharply at first, reaching an adsorbent dosage of 0.03g and 94.8% removal. Subsequently, the percentage removal increased narrowly to 98.9% at an adsorbent dosage of 0.05g for a 50 mg/L initial concentration, 10minutes contact time, and 30 °C. For all contact times (10, 20, and 30 minutes), the worst-case situation was observed at pH 6 and 0.01g adsorbent dosage, yielding 26.6, 27.6, and 29.6%, respectively. This suggests that greater adsorption results from an increase in the number of accessible active sites and the adsorbent's surface area when the dosage of the adsorbent rises (Okolo et al., 2021).



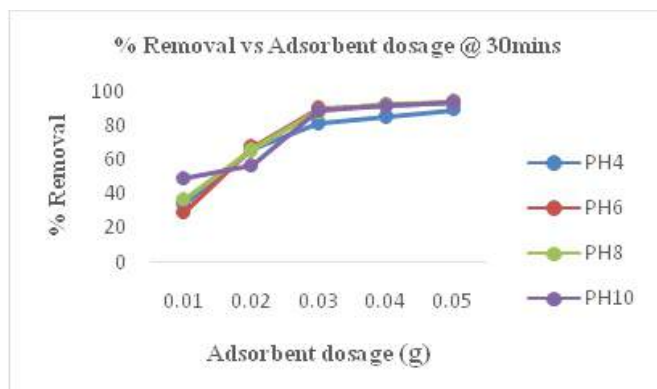
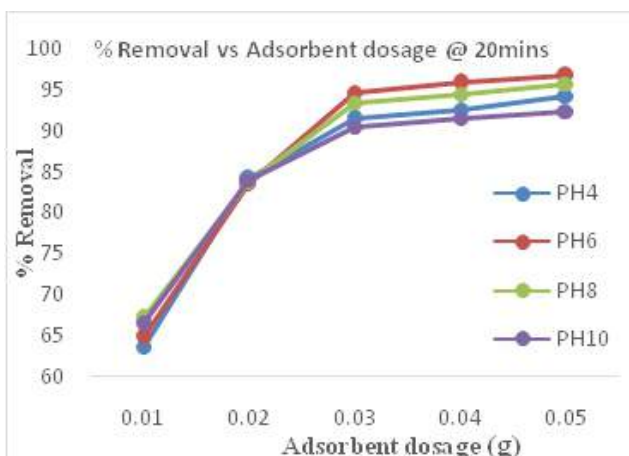
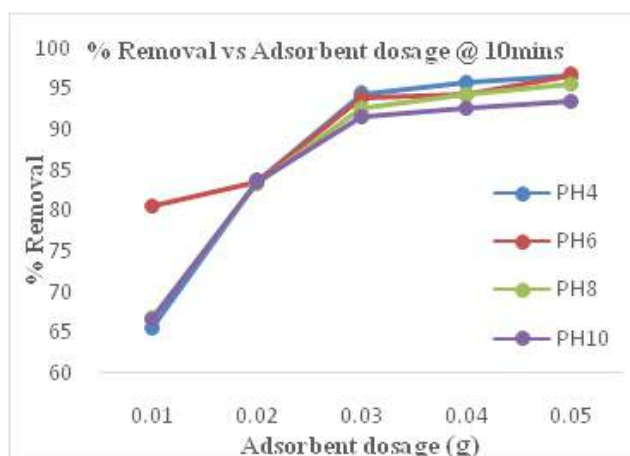


Fig. 4a. Effect of adsorbent dosage and solution pH on the percentage removal of Levofloxacin by PAN-luffa adsorbent fibre (initial adsorbent conc. of 50mg/L, contact time: 10min, 20min, 30min and 30°C).

The highest % clearance of levofloxacin was observed at 0.05g, as shown by the result in Fig. 4b below, which showed an initial concentration of 100 mg/L and a temperature of 30°C. There is no doubt that increasing the adsorbent dosage causes the percentage removal of levofloxacin to increase sharply at first, reaching an adsorbent dosage of 0.03g with a percentage of 93.9%. Subsequently, the percentage removal increased narrowly, reaching 96.6% at an adsorbent dosage of 0.05g, pH 4, initial concentration of 100 mg/L, 10 minutes of contact time, and 30°C. For all contact times (10, 20, 30 minutes), the worst-case situation was observed at 0.01g adsorbent dosage, yielding 65.6, 63.6, and 64.6%, respectively. Due to a higher initial concentration, the findings clearly showed more levofloxacin adsorption even with 0.01g of adsorbent. This suggests that greater adsorption results from an increase in the number of accessible active sites and the adsorbent's surface area when the dosage of the adsorbent rises (Okolo et al., 2021).



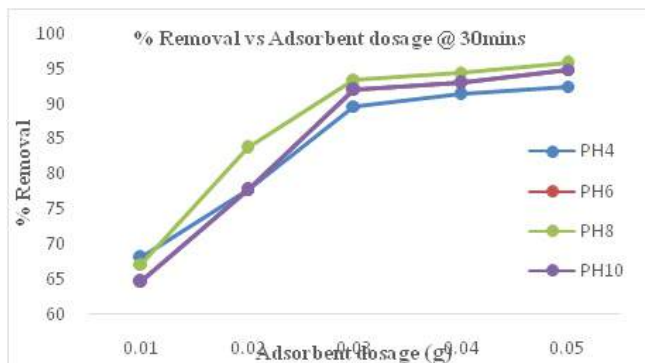


Fig. 4b: Effect of adsorbent dosage and pH on the percentage removal of Levofloxacin by PAN-luffa adsorbent fibre (initial adsorbent conc. of 100mg/L, contact time: 10min, 20min, 30min and 30 °C).

Similarly, 0.05g of the adsorbent was used to achieve the greatest percentage removal of levofloxacin in Fig. 4c, with an initial concentration of 150 mg/L and a temperature of 30 °C. There is no doubt that increasing the adsorbent dosage causes the percentage removal of levofloxacin to increase sharply at first, reaching an adsorbent dosage of 0.03 and pH 6, yielding 95.1% removal. Subsequently, the percentage removal increases narrowly, reaching 97.6% at an adsorbent dosage of 0.05g for the initial concentration of 150 mg/L, pH 6, 10 minutes of contact time, and 30 °C. For all contact times (10, 20, 30 minutes), the worst-case situation was observed at 0.01g adsorbent dosage, yielding 63.4, 73.8, and 35.4%, respectively. Due to a higher initial concentration, the results showed more levofloxacin adsorption. This suggests that greater adsorption results from an increase in the number of accessible active sites and the adsorbent's surface area when the dosage of the adsorbent rises (Okolo et al., 2021).

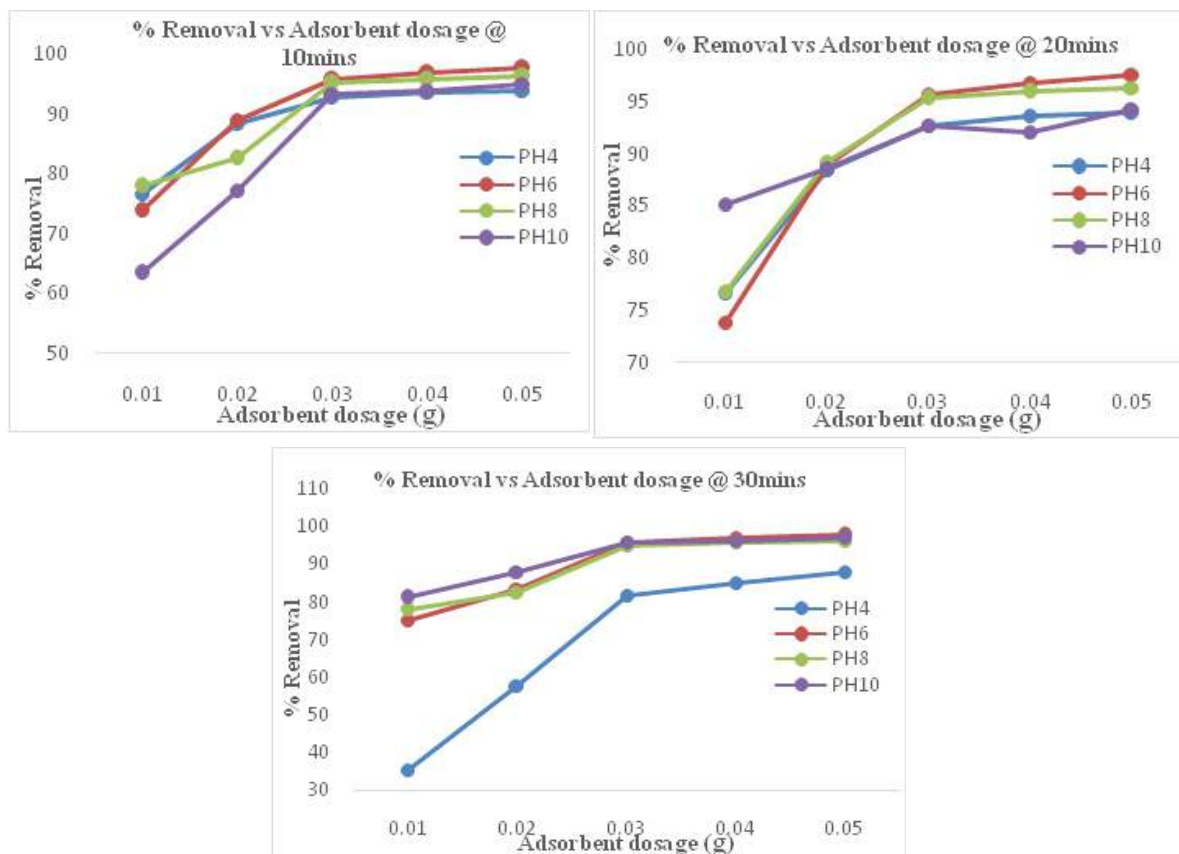


Fig. 4c: Effect of adsorbent dosage and pH on the percentage removal of Levofloxacin by PAN-luffa fibre adsorbent (initial adsorbent conc. of 150mg/L, contact time: 10min, 20min, 30min and 30 °C).

When the temperature rose to 40°C, similar patterns were observed. This was evident from the results in Fig. 5a–c, which showed initial concentrations of 50, 100, and 150 mg/L at 40°C. At 0.05g, the highest percentage of levofloxacin was also eliminated. It is evident that when the adsorbent dosage is increased, the percentage removal of levofloxacin increases sharply first to an adsorbent dosage of 0.03 g and then narrowly increases to 94.5, 97.5, and 97.7% at an adsorbent dosage of 0.05g and pH of 8 and 10, initial concentration of 50, 100, and 150 mg/L, respectively, at 40°C. Except for the starting concentration of 50 mg/L, all adsorbent doses demonstrated a notable adsorption capability at initial concentrations of 100 and 150 mg/L, resulting in a percentage removal of levofloxacin of greater than 60%. This further demonstrated the impact of the initial adsorbate concentration and the adsorbent dosage. The latter raises the concentration of the adsorbate, resulting in enhanced adsorption, whilst the former increases the number of accessible active sites and the adsorbent's surface area (Okolo et al., 2021).

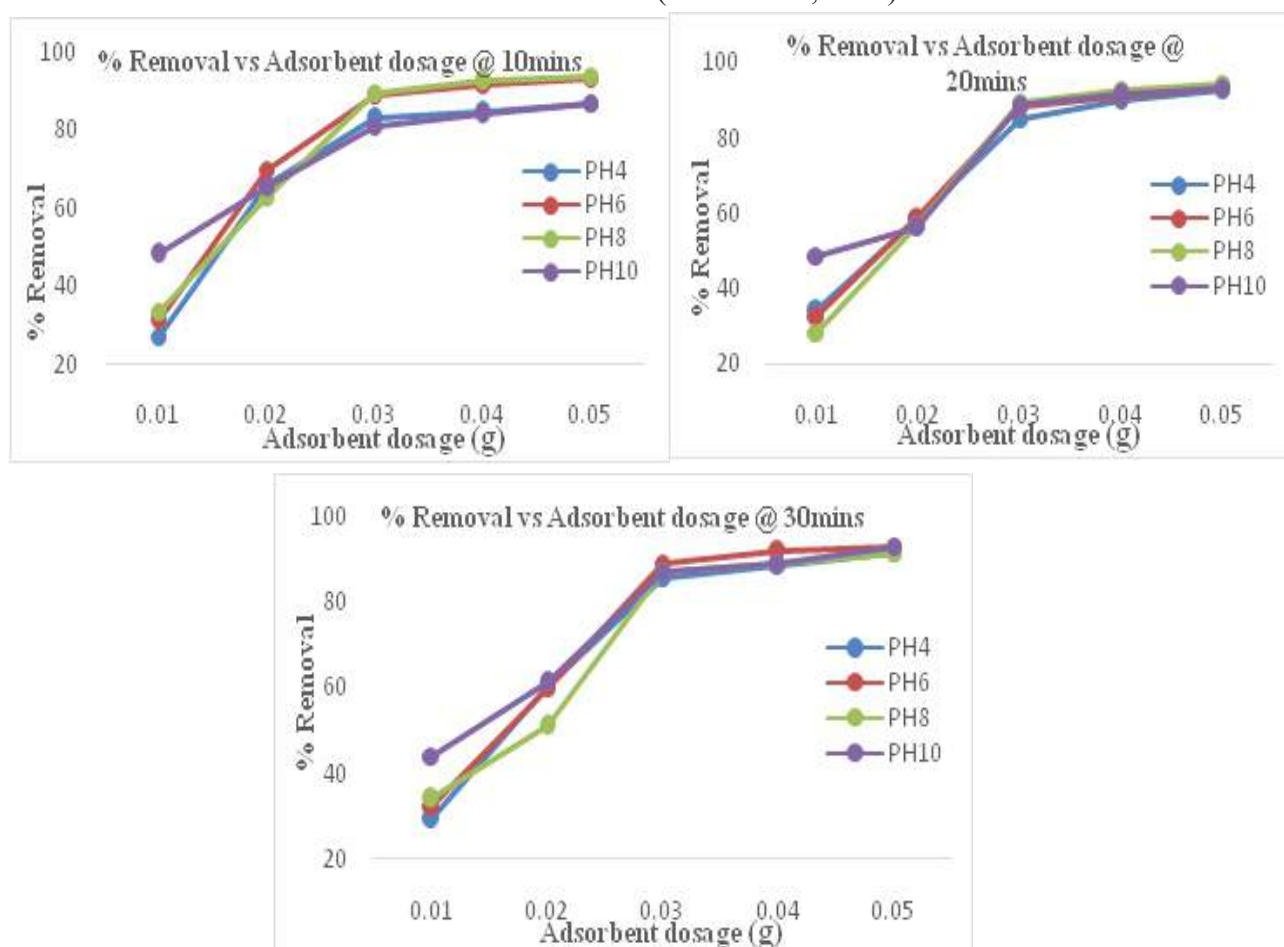


Fig. 5a: Effect of adsorbent dosage on the percentage removal of Levofloxacin by PAN-luffa fibre adsorbent (initial adsorbent conc. of 50mg/L, contact time: 10min, 20min and 30min, temp. 40 °C).

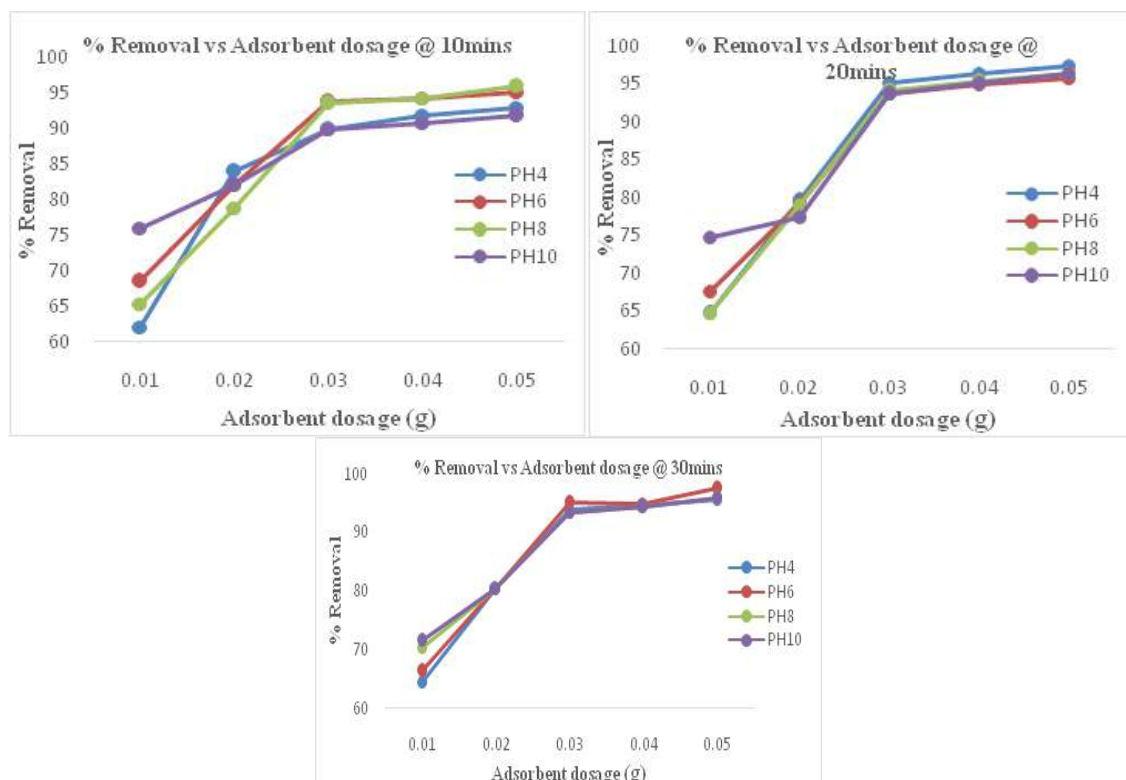


Fig. 5b: Effect of adsorbent dosage and pH on the percentage removal of Levofloxacin by PAN-luffa fibre adsorbent (initial adsorbent conc. of 100mg/L, contact time: 10min, 20min and 30min, temp. 40 °C)

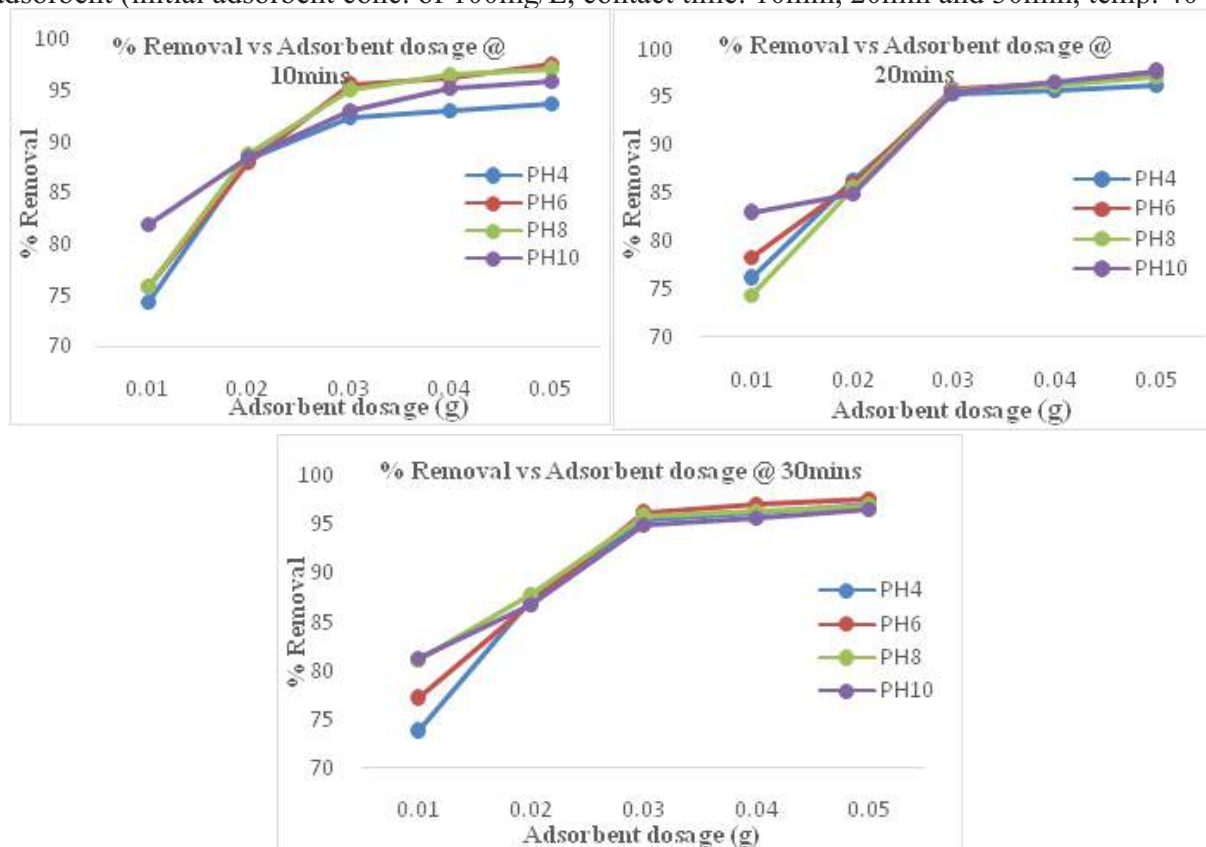


Fig. 5c: Effect of adsorbent dosage on the percentage removal of Levofloxacin by PAN-luffa fibre adsorbent (initial adsorbent conc. of 150mg/L, contact time: 10min, 20min and 30min, temp. 40 °C).

3.4.3 Adsorption isotherms

The link between the amount of levofloxacin (q_e) adsorbed from the solution and the equilibrium concentration (C_e) of levofloxacin in bulk solution was ascertained using the adsorption isotherms. As shown below, three two-parameter adsorption isotherms were examined for the purposes of this study, and the linear regression result was used to identify the model that best fit the data. Table 1 displays the regression coefficient, maximum adsorption, and related constants for the three distinct isotherm models under investigation, while Fig. 6a displays the Langmuir adsorption isotherms at temperatures of 303K, and 313K.

A high adsorption capacity of the PLCC is indicated by the Langmuir monolayer adsorption capacity (q_m), which ranged from 54.054 to 109.89 mg/g; the value of K_L , which ranged from 0.0126 to 0.7371 L/mg, was relatively high, indicating high surface energy in the process and consequently high bonding between levofloxacin atoms and the PLCC. The table showed that the Langmuir isotherm model had the highest correlation coefficient ($R^2 = 0.9916$) at 313K, indicating that the best fitting of experimental data in the equation was achieved at this temperature (Jonas et al., 2018). The Freundlich isotherm (Fig. 6b), which has a maximum coefficient of determination (R^2) of 0.9987 at 313K, comes next and really matched the experimental results. Furthermore, since the results met the heterogeneity criteria ($1 < n < 10$), the n , which ranges from 2.21 to 4.56, demonstrates the heterogeneous surface nature of the adsorbent. Additionally, a high uptake of the levofloxacin atoms from the bulk medium was indicated by the k_f range of 2.29 to 4.12. In contrast, a study by Jonas et al. (2018) reported that the k_f value was 0.358 mg/g, indicating a limited absorption of its adsorbate to the adsorbent under investigation.

In contrast, the Temkin isotherm (Fig. 6c) reaches its maximum R^2 value (0.9925) at 313K and then (0.9746) at 303K. The adsorption of levofloxacin ions was caused by the linear decrease in the heat of adsorption of all the ions in the layer due to increased surface coverage, which suggests that the experimental data fit the Temkin isotherm well. The table showed that the optimal R^2 values were recorded at a temperature of 313K. In summary, the adsorption model was found to be well-suited to the three adsorption model equations that were being examined. The Freundlich isotherm model, however, provided the best fit for the isotherm.

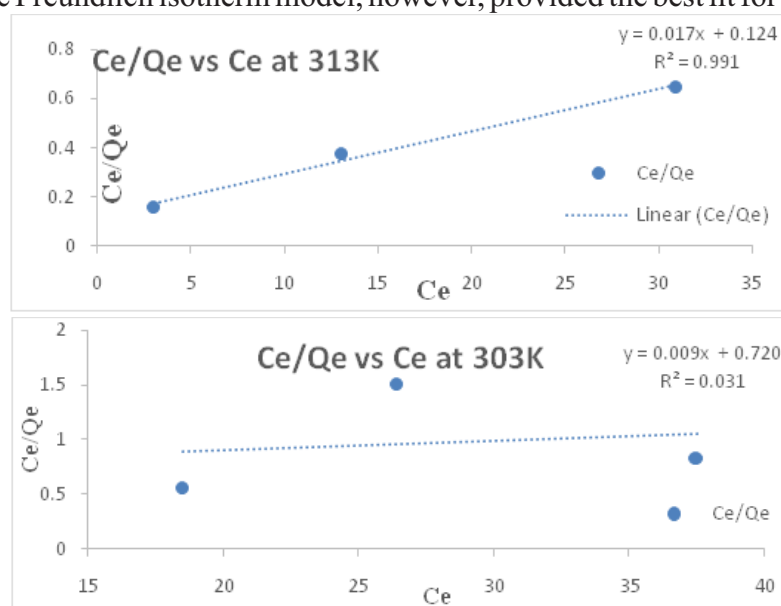


Fig. 6a: Langmuir adsorption model isotherm

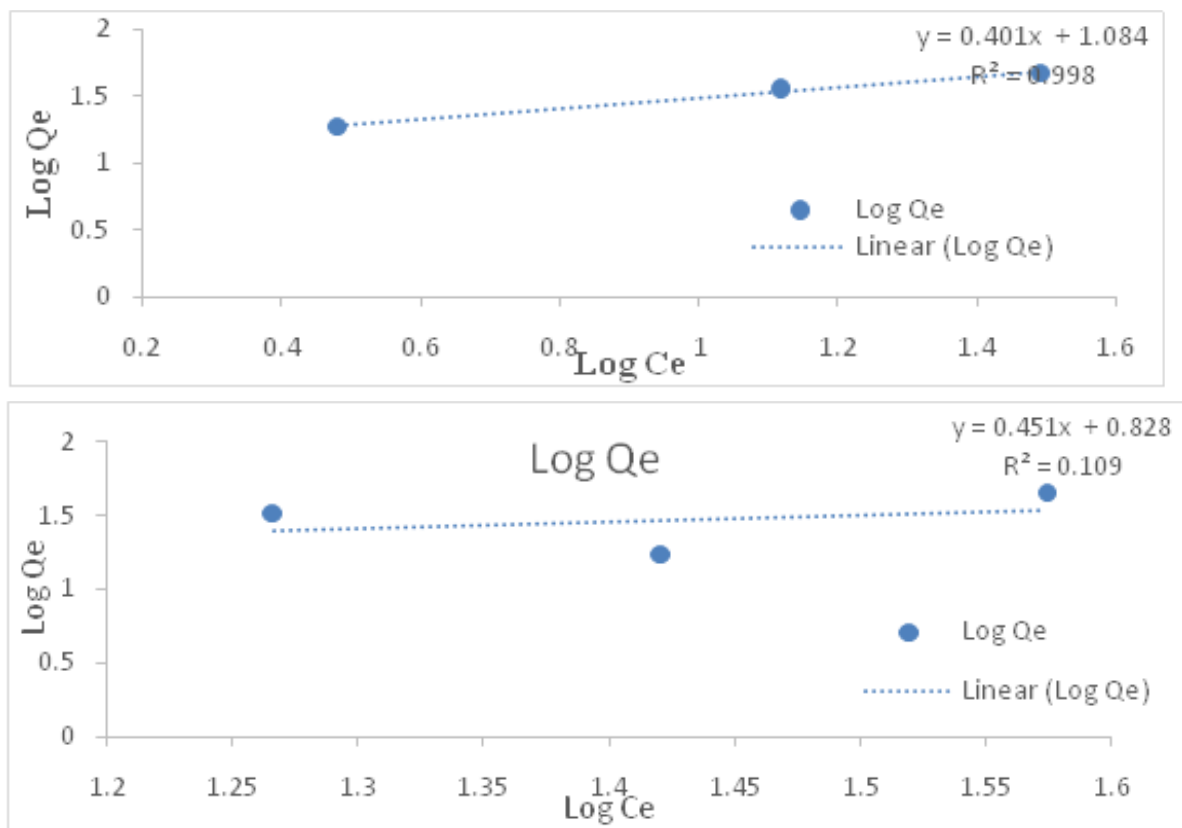


Fig. 6b: Freundlich adsorption model isotherm

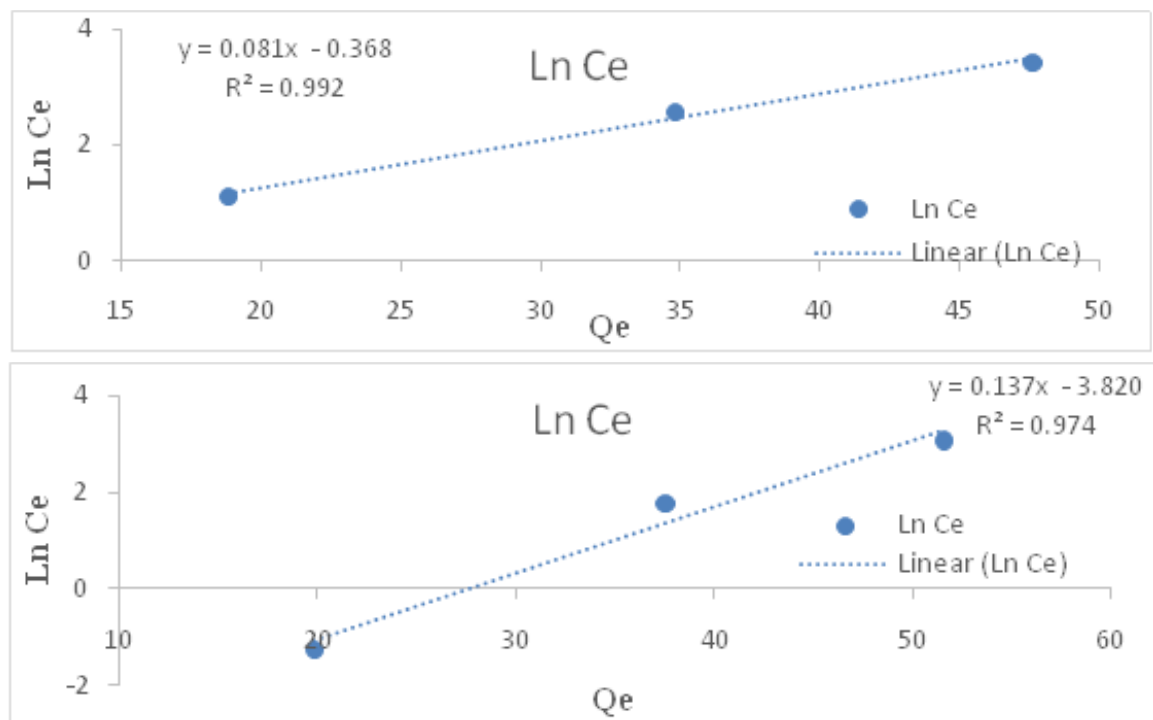


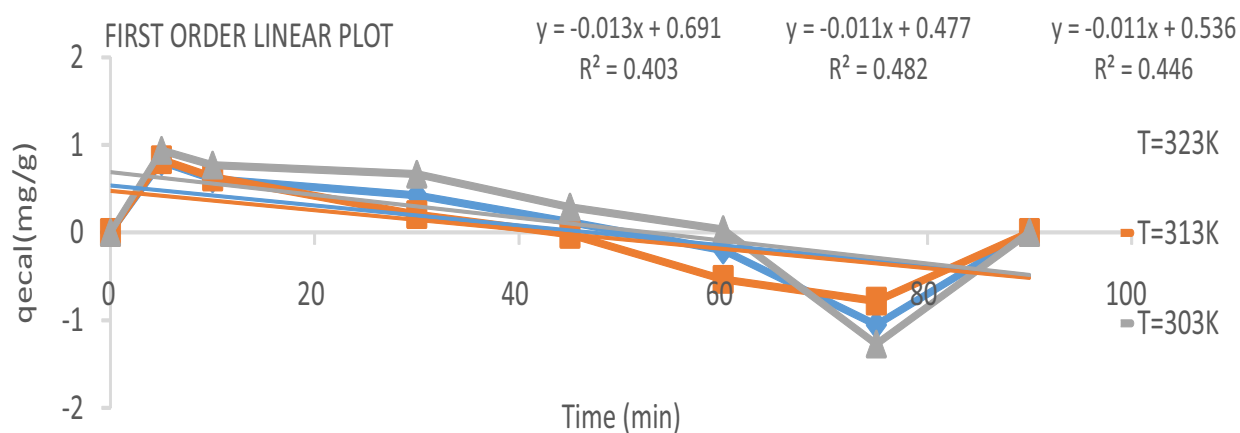
Fig. 6c: Temkin adsorption model isotherm plot

Table 1 Calculated Isotherm Parameters for the Adsorption of Levofloxacin on PLCC

Isotherm model	Temperature(K)	
	303	313
Langmuir		
Q_m	109.89	58.14
K_L	0.0126	0.138
R_L	0.3454	0.0461
R²	0.0319	0.9916
Freundlich		
N_f	2.216312	2.488181
K_f	2.29011	2.958256
R²	0.1099	0.9987
Temkin		
B	21733	30550
KT	6.10E+110	94.50997
R²	0.1992	0.9925

3.4.4 Adsorption Kinetic Modelling

Three kinetic model templates, the Elovich, pseudo-first, and second-order kinetic models, were used to conduct the levofloxacin kinetic adsorption model. At a temperature of 313 K, it was evident from the results (Figs. 4.7a–4.7c) that the kinetic models fit the second-order kinetic model (Fig. 4.7c) better than the others. This is demonstrated by the (R^2) value of 0.9988, which was found to be greater than the rest and closer to unity when compared to the pseudo-first order (Fig. 4.7b) and the Elovich (Fig. 4.7a). According to Mukul et al. (2021), a kinetic model with the best fit could be defined using adsorption capacity (q_e). As a result, when compared to the q_e determined for the Elovich and pseudo-first order kinetic models, the experimental q_e of 18.79 mg/g is closer to the q_e determined at 313K for the pseudo-second order kinetic model.



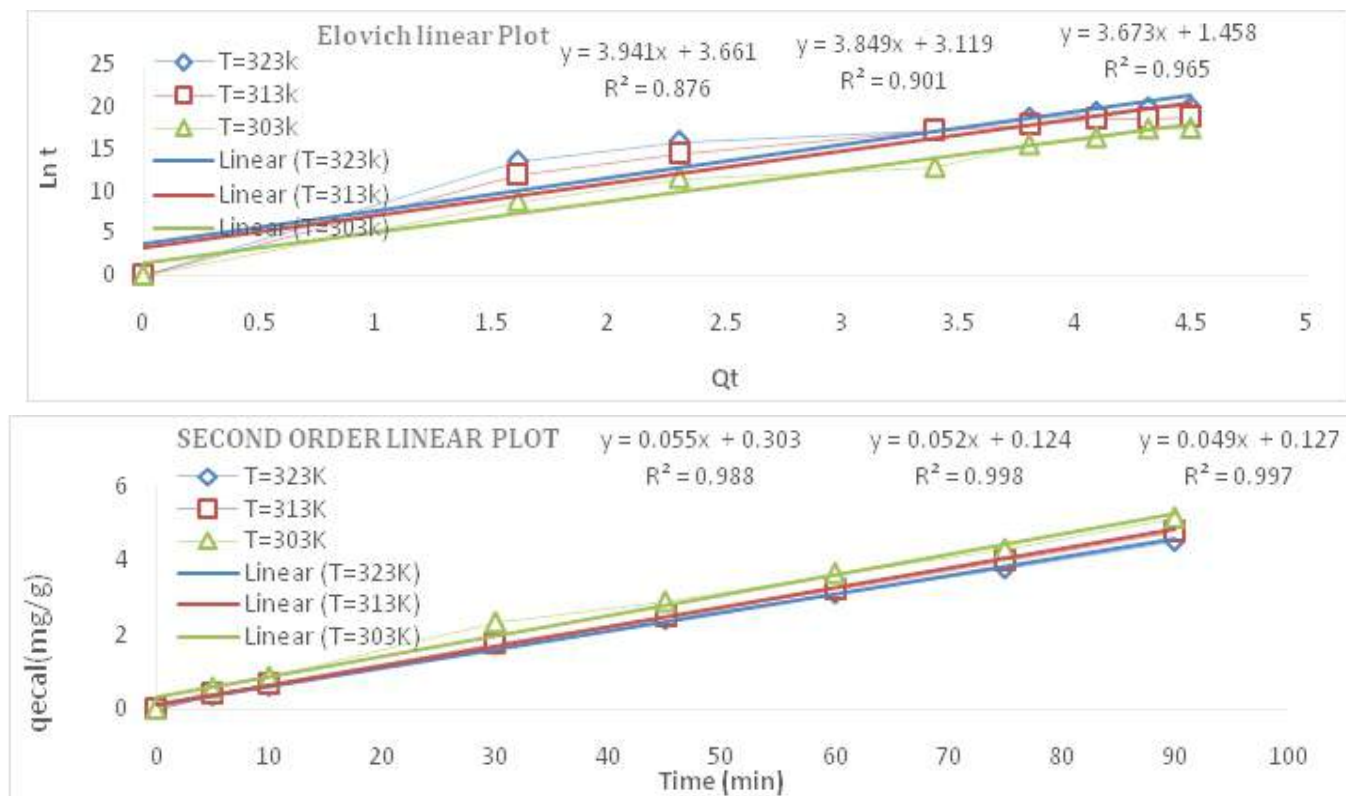


Fig. 7: First-order kinetic adsorption model plot (a), Second-order kinetic adsorption model plot (b), Elovich kinetic adsorption model plot (c).

Table 2 Kinetic parameters for the adsorption of levofloxacin on PLCC

Kinetic model	Temperature (K)	
	313	303
Pseudo first order		
R^2	0.4824	0.4469
$K_1(\text{min}^{-1})$	0.0111	0.0114
$q_e(\text{mg/g})$	1.6112	1.7105
Pseudo second order		
R^2	0.9988	0.9885
$K_2(\text{min}^{-1})$	0.007319	0.004436
$q_e(\text{mg/g})$	19.157	20.202
Elovich		
R^2	0.9013	0.9651
$\beta(\text{g/mg})$	0.259808	0.272235
$\alpha(\text{mg/gmin})$	0.584223	0.404965



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Conclusion

This study investigated the use of polyaniline-*Luffa cylindrica* fibre composite (PLCC) for the treatment of simulated pharmaceutical wastewater. Levofloxacin was removed using a recently updated adsorbent called polyaniline-*Luffa cylindrica* fibre composite. The outcome demonstrated the adsorbent's excellent adsorption capacity and great affinity for removing levofloxacin. One factor at a time analysis was used to examine the effects of pH, time, initial concentration, temperature, and adsorbent dosage, and equilibrium conditions were obtained. FTIR was used to characterize the adsorbent and validate that levofloxacin was adsorbed onto the polyaniline-*Luffa cylindrica* fibre composite surface. The process was observed to be best fitted into the Freundlich isotherm and pseudo-second order kinetics due to their highest coefficient of determination, R^2 .

Using polyaniline-*Luffa cylindrica* fibre composite, at various dosages and pH and varying initial levofloxacin concentrations, indicated a sharp rise in adsorption capacity up to 0.03g and a marginal increase thereafter to the highest removal efficiency. The highest removal efficiency of 98.9% was recorded at an adsorbent dosage of 0.05g, pH 4, initial concentration of 50mg/L, after 10minutes shaking and 30 °C. This demonstrated the great potential of PLCC in the removal of levofloxacin from aqueous solution.



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Kinetics and Thermodynamics of Methylene Blue Adsorption onto Surface Modified Ikpobia Clay

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Abstract

The need for water preservation, restoration, and treatment has become very pertinent to address the United Nations Sustainable Development Goal. In this study, the kinetics and thermodynamics of methylene blue adsorption from aqueous solution using surface-modified Ikpobia clay were evaluated. The clay samples were characterized for pH, surface functional groups, crystallinity, micrograph and textural properties. A batch adsorption experiment was carried out by varying the solution pH, adsorbent dosage, temperature and contact time. The refined clay (RC) pH was slightly acidic (6.84). The surface functional groups and crystallinity suggested the presence of O–H, C=O, Si–O/Al–O, Al–OH and Si–O–Al/Si–O–Si. The textural properties suggested a surface area of 235.50 m²/g. Maximum adsorption solution pH, adsorbent dosage, contact time and temperature were 6.48, 100 mg, 878 min and 24 °C, respectively. The pseudo-second-order model best described the adsorption kinetic data due to its least sum of square error (SSE), highest regression coefficient ($R^2 \rightarrow 1$) and better adapted calculated adsorption capacity (q_{tc}) to the experimental data (q_{tc}). This suggested the possibility of strong chemical bonding in the adsorption. The thermodynamics study suggested the feasibility of adsorption and the spontaneity of Ikpobia clay. RC exhibited the best performance (12.38 mg/g). This study has placed Ikpobia clay as a low-cost alternative adsorbent for effective cationic dye removal from wastewater.

Keywords: Adsorbent, elimination, refined clay, methylene blue, adsorption.

1. Introduction

The rapid development of industries and population growth have increased the demand for clean water resources for domestic and agricultural use (Carlsen and Bruggemann, 2022). The situation is becoming worse as industrial sectors continue to discharge toxic, hazardous, and persistent water pollutants into water bodies, which has elevated water scarcity to become a greater challenge that nearly all countries encounter to a certain degree (Ewis et al., 2022). A majority of wastewater comes from extensive use of organic dyes and other pollutants in the paper, pharmacy, rubber and textile industries (Francis and Zaini, 2023; Kumar *et al.*, 2020). The release of wastewater into natural water bodies can cause dramatic effects by changing colour, pH or oxygen concentration, which may result in serious health and environmental issues.

Dyes and pigments are extensively employed in industries such as leather tanning, printing, and the manufacturing of textiles, paper, rubber, plastics, food, and cosmetics. Globally, over 700,000 tons of these substances are produced annually, and between 2% and 15% is lost in the effluent during dyeing processes (Kaushal and Mahajan, 2022). Even dye concentrations below 1 ppm can visibly alter water quality due to



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noticeable colouration (Li *et al.*, 2022). The need to invest in water preservation, restoration and treatment has become very pertinent to address the United Nations Sustainable Development Goal number 6 (SDG 6) (Carlsen and Bruggemann, 2022).

Methylene blue is a common synthetic dye with a $C_{16}H_{18}ClN_3S$ molecular formula. It creates colour in textiles and is often used as an antidote for poisoning and methemoglobinemia treatment in medical science (Yilmaz *et al.*, 2021). Methylene blue dye molecule is characterized by non-biodegradable but stable heterocyclic aromatic compounds, which end up in water bodies as a result of a lack of pollution control, awareness and enforcement, thereby contaminating the water bodies by restricting sunlight penetration, reducing dissolved oxygen and hindering aerobic activities, and restricting photosynthesis. These not only make the water inadequate for drinking, but also result in increased heart rate, hypertension, vomiting, anaemia, convulsion and bone damage when humans are exposed to it excessively (Francis *et al.*, 2023; Alipour *et al.*, 2021).

Dye in wastewater remediation involves physical, chemical and biological processes. These processes include flocculation, precipitation, membrane separation, coagulation, adsorption, ozonation, photodegradation, electrochemical destruction, irradiation and aerobic or anaerobic treatment (Francis *et al.*, 2023; Kumar *et al.*, 2020). These dye removal methods have limitations, are costly and often ineffective. However, adsorption is considered superior in water treatment due to its convenience, ease of operation, low cost, environmentally friendly technology and simple design (Francis and Zaini, 2024; Negarestani *et al.*, 2023).

Clay minerals such as kaolinite, bentonite, illite, halloysite, montmorillonite, sepiolite, and smectite have been studied successfully and found to have a strong affinity for methylene blue adsorption due to their abundant availability, cost-effectiveness, surface properties, excellent textural characteristics, and chemical and physical stability (Hamad *et al.*, 2024). Other studies have also highlighted that the presence of SiO_2 , Fe_2O_3 , and Al_2O_3 , which can develop positive and negative charges on the surface of clay minerals at neutral pH, as suitable ingredients for both cations and anions adsorption (Hamad *et al.*, 2024). Additionally, its high porosity and availability of anion exchange sites are also beneficial for the adsorption of methylene blue (Gunathilake *et al.*, 2023). Adsorption capacity of pollutants onto clay minerals has also been enhanced by their surface modification. However, acid-modified clay minerals have demonstrated slow adsorption of cation materials in aqueous solution due to their competition for the H_3O^+ and other ions in the solution because of their acid value (Abu *et al.*, 2024; Munvuyi *et al.*, 2022).

This study pioneered the surface modification of Ikpobia clay thermally and by oxalic acid impregnation, and characterization using pH, Fourier transform infrared (FTIR), x-ray diffraction (XRD), scanning electron microscope/electron dispersive x-ray (SEM/EDX), Brunauer-Emmett-Teller (BET) surface area, and the kinetics and thermodynamics of methylene blue adsorption.

2. Materials and Methods



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2.1 Materials

A clay sample was collected from Ikpobia quarry, Okpella, Edo State, Nigeria. All solutions were prepared using distilled water from the Chemical Engineering Department, Edo State University, Iyamho, Nigeria. All the chemical reagents used in this study were of analytical grade; Oxalic acid (99%, Merck, Germany), hydrochloric acid (37% Fisher scientific Waltham, USA), sodium hydroxide pellets (97% LOBA CHEMIE PVT LTD, Mumbai, India), calcium chloride (94% UniClean, America) and methylene blue (98%, Merck, Germany).

2.2 Pretreatment and Surface Modification of the Clay Sample

A clay sample (10 kg) in its crude state was collected from Ikpobia quarry in Okpella, Etsako West Local Government Area of Edo State, Nigeria. A 5 kg sample of clay was crushed and ground. A 500 g of the ground sample was soaked in 250 mL of distilled water for 24 h. The mixture after 24 h at room temperature was stirred for 3 h on a magnetic stirrer at 600 rpm, and left to sediment and age for 4 days to allow for the removal of quartz impurities. Meanwhile, the clay-water mixture was decanted daily and replaced with fresh distilled water until the mixture became less milky. The colloid clay and quartz impurities were separated, filtered using Whatman filter paper, dried in an oven at 105 °C for 180 min and stored in a desiccator. The dried clay sample was ground to and designated as refined clay (RC). A 20 g of RC was collected and calcined at 300 °C (being the optimum adsorption response temperature from the design of experiment) for 3 h, left to cool at room temperature and designated as calcined clay (CC). Another 20 g of RC was collected and impregnated with oxalic acid in the ratio of 1:1 (being the optimum adsorption response blend ratio from the design of experiment) for 24 h and calcined at 300 °C for 3 h. The sample was left to cool, washed with distilled water until a pH of 7, dried in an oven at 105 °C for 180 min and designated as activated clay (AC) (Alexander *et al.*, 2018). The pretreated and surface-modified clay samples (RC, CC and AC) were all stored in a desiccator before to characterization and adsorption study.

2.3 Characterization of Clay Samples

The AOAC 2007 method was adopted to determine the pH of RC, CC and AC. It reflected their surface characteristics as either acidic or alkaline. One gram of the sample was soaked in 20 mL of distilled water, stirred with a glass rod and left undisturbed for 60 min. The pH of the supernatant was measured with a pH meter. The surface functional groups of the clay samples in the wavenumber range of 4,000–600 cm⁻¹ were determined using a FTIR spectrometer (Thermo Scientific Nicolet ISI 10, USA). 50 mg of each sample and 120 mg of KBr were mixed, triturated and compacted into a disk form with a hydraulic press, dried at 80 °C for 16 h for analysis. The crystallinity of the clay samples was determined using an X-ray diffractometer (XRD) with monochromatic Cu-K α radiation (BRUKER Corporation, Germany). The samples were mounted as an evaporated hexane film in a vertical arrangement, and a 45 kV and 40 mA voltage and current, respectively, were applied. A continuous mode spectrum was obtained over a 2 θ range of 0 to 70° and a scan rate of 2°/min. The micrograph and elemental composition of the samples were carried out in a vacuum



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environment using the Karl Zeiss Company, Germany type scanning electron microscope $125\ \mu\text{m}$ dispersive X-ray spectroscopy (SEM/EDX) techniques. The clay samples were coated with Au, dispersed onto sticky C or Al tapes, which were supported on metallic disks, and images of the sample surfaces were captured at specific magnifications. Meanwhile, for the EDX, the X-ray beam influenced the electrons in the inner shell of the atom of the samples. The quantity of energy lost in the process was unique to each element; hence, this different energy was used to denote the element from which it emanated. Each fluorescence energies that was unique to the elements in the samples were found. The clay samples' textural characteristics were determined using the Thermo Scientific (USA) surface area analyzer according to the Brunauer-Emmett-Teller (BET) method. The clay samples were outgassed overnight at varying increased pressure, $250 \pm 1\ ^\circ\text{C}$ and exposed at 77 K to nitrogen gas.

2.4 Batch Adsorption of Methylene Blue

The batch adsorption experiment was carried out by varying solution pH, adsorbent dosage, temperature and contact time. For pH effect, 50 mg of RC, CC and AC each was brought into contact with 10 mg/L of 50 mL methylene blue solution at a pH of 2, temperature of $24\ ^\circ\text{C}$ and for 72 h. The pH was also varied at 4, 6.5, 9 and 11. This contact time was presumed to be long enough for equilibrium to be achieved (Francis and Zaini, 2023). Meanwhile, the solution pH was adjusted using 0.1 M HCl and NaOH solution. For the dosage effect, 10 mg of RC, CC and AC were contacted with 10 mg/L of 50 mL methylene blue solution at a pH of 6.48 for 72 h and $24\ ^\circ\text{C}$. The dosage was also varied at 25, 50, 75 and 100 mg. For the contact time effect, 50 mg RC, CC and AC each were contacted with 10 mg/L of 50 mL methylene blue solution at predetermined time intervals from 0 to 2138 min at a pH of 6.48 and a temperature of $24\ ^\circ\text{C}$. For the temperature effect, 50 mg of RC, CC and AC each was contacted with 10 mg/L of 50 mL methylene blue solution at varying temperatures of 24, 35, 45, 55, 65 and $75\ ^\circ\text{C}$ at a pH of 6.48 and for 72 h. The residual concentration of the suspension, which was withdrawn from the mixture, was measured using an E. Track Instruments England Standard (model N6000) double beam ultraviolet-visible (UV-Vis) spectrophotometer by measuring its absorbance at a wavelength of 700 nm.

The adsorption capacity, q_t (mg/g) was calculated from a mass balance equation,

$$q_t = \left(\frac{C_o - C_t}{m} \right) \times V \quad (1)$$

where C_o and C_t (mg/L) are the concentration of methylene blue at initial time and time t , respectively, V (L) is the volume of the solution and m (g) is the mass of the adsorbent (Francis *et al.*, 2023).

Pseudo kinetics and intraparticle diffusion models were adopted to evaluate the adsorption kinetics data. They showed the process of adsorption and the mechanism of adsorption. The pseudo-first-order, pseudo-second-order and intraparticle diffusion nonlinear models are given in Equations (2), (3) and (4), respectively.



$$q_t = q_e(1 - e^{-K_f t}) \quad (2)$$

$$q_t = \frac{K_s q_e^2 t}{1 + K_s q_e t} \quad (3)$$

$$q_t = K_{id} t^{0.5} + C \quad (4)$$

where q_t (mg/g) and q_e (mg/g) are the adsorption capacity at time, t (min) and at equilibrium, the constants, K_f (min⁻¹), K_s (g/mg.min) and K_{id} (mg/g.min^{0.5}) are the rate coefficients of pseudo-first-order, pseudo-second-order and intraparticle diffusion, respectively and C is the boundary layer thickness. Excel Solver was used to determine the unknown variables in the models, the regression coefficient (R^2) and the sum of squared error (SSE).

The thermodynamic data of enthalpy (ΔH° , kJ/mol), entropy (ΔS° , kJ/mol. K) and Gibbs free energy (ΔG° , kJ/mol) were determined from Equations (5)–(7),

$$K^\circ = K_D \frac{m}{V} \quad (5)$$

$$\Delta G^\circ = -RT \ln K^\circ \quad (6)$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (7)$$

Where K_D (L/g) is the partition coefficient, K° is the standard thermodynamic equilibrium constant, m (g) is the mass of the adsorbent, and V (L) is the volume of the solution (Zhou *et al.*, 2024). T (K) is the absolute temperature and R is the gas constant (8.314 J/mol. K)

3. Results and Discussion

3.1. Characteristics of Clay Samples

The results of the pH of RC, CC and AC were 6.84, 6.56 and 5.15, respectively. RC and CC were slightly acidic, and AC was moderately acidic. This could be attributed to either the minimal presence or absence of soluble salts with basic attributes, such as silicates, bicarbonates and carbonates (Munvuyi *et al.*, 2022). Meanwhile, the moderate acid pH of AC (5.15) could slow adsorption of cation materials in aqueous solution due to its competition for the H_3O^+ and other ions in the solution (Munvuyi *et al.*, 2022).

The FTIR spectra of RC, CC and AC in the wave number range of 4000- 500 cm⁻¹, which revealed the functional groups, mineral identification fingerprint and molecular water distinction from hydroxyl constituent, are presented in Figure 1. The adsorbent samples all exhibited bands located at 3690, 1640, 998, 909 and 790 cm⁻¹. However, the bands exhibited by AC and CC in the region of 685 and 678 cm⁻¹ were not present in RC. However, the band exhibited at 3690 cm⁻¹ reflected a characteristic O–H stretching

vibration, typical of hydroxyl groups in kaolinite (Munvuyi *et al.*, 2022; Bentahar, 2017). The band at 1640 cm^{-1} revealed the H–O–H bending vibration of water molecules. The Si–O stretching vibration, which is characteristic of silicate mineral, was found in the band at 998 cm^{-1} . The band at 909 cm^{-1} corresponded to the Al–OH bending vibration, which was typical of clay minerals. The band at 790 cm^{-1} was characteristic of Si–O–Al or Si–O–Si bending vibrations in clay. The bands at 685 and 678 cm^{-1} were attributed to Si–O or Al–O vibrations (El Kerdoudi *et al.*, 2023; Munvuyi *et al.*, 2022; Alexander *et al.*, 2018)

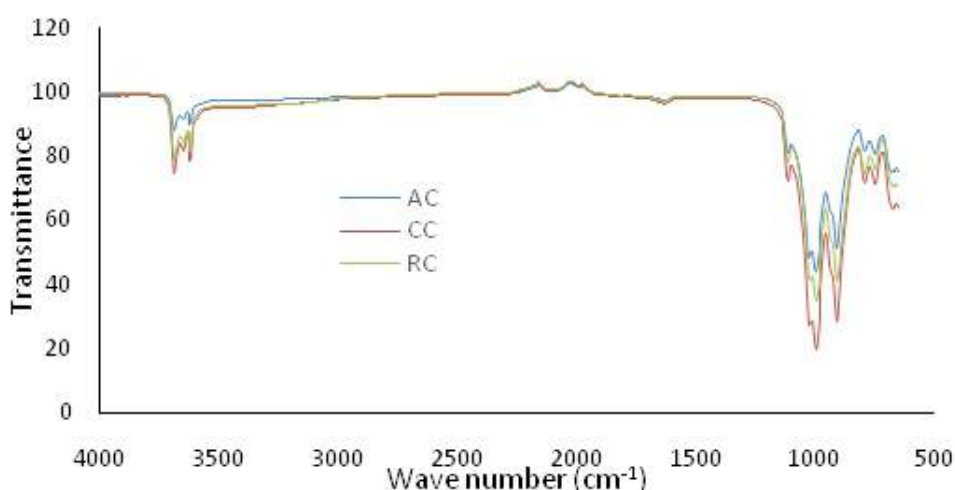


Fig. 1. FTIR spectra of RC, CC and AC

The RC, CC and AC XRD spectra, which describe their mineral compositions, are presented in Figure 2. The 2θ values are highest in AC than in RC and CC, suggesting greater lattice parameter phase values in AC than in RC and CC. The XRD patterns of RC, CC and AC showed peaks at $2\theta = 10^\circ$, 14° , 29° and 31° which revealed the presence of illite, kaolinite, siderite and quartz minerals (Muwawaet *et al.*, 2024; El Kerdoudi *et al.*, 2023; Munvuyi *et al.*, 2022). However, AC revealed an additional peak at $2\theta = 53.5^\circ$, which reflected the presence of a new phase after oxalic acid modification. The XRD results showed that calcination at 300 $^\circ\text{C}$ did not degrade the mineralogical phases of the RC, thereby suggesting high chemical stability of the RC mineral mixtures (García *et al.*, 2020)

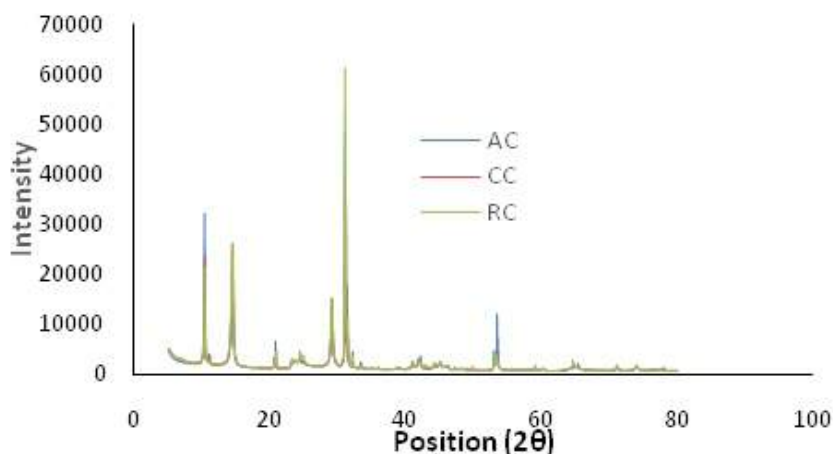


Fig. 2. XRD spectra of RC, CC and AC

The RC, CC and AC textural properties are presented in Table 1. AC showed the largest BET surface area, total pore volume, micropore volume and mesoporosity of 313.70 m²/g, 0.158 cm³/g, 0.043 cm³/g and 72.78%, respectively, suggesting the effect of acid modification. These increased textural properties could increase the monolayer adsorption capacity of AC over RC and CC. Meanwhile, the decreased BET surface area of RC and CC could be a result of particle aggregation and less developed pore structure. Based on the definition of IUPAC, all the clay adsorbent samples are mesoporous with pore diameters in the range of 2-50 nm, suggesting the possibilities of ions and macromolecules penetration (Mistar *et al.*, 2020; Alexander *et al.*, 2018)

Table 1. Surface Textural Properties of AC, CC and RC Materials

Parameters	AC	Sample CC	RC
BET surface area (m ² g ⁻¹)	313.70	213.80	235.50
Total pore volume (cm ³ g ⁻¹)	0.158	0.129	0.132
Micropore volume (cm ³ g ⁻¹)	0.043	0.040	0.038
Pore diameter (nm)	2.100	2.138	2.128
Mesoporosity (%)	72.78	68.99	71.21

The RC, CC and AC SEM micrographs, which describe their surface texture and morphology, are presented in Figure 3. All the images showed a similar morphological multiphase structure of flake-like sharps and flake-aggregate. A similar result was reported by Garcia *et al.* (2020). This multiphase structure suggested that the clay samples would be good candidates for adsorption (El Kerdoudi *et al.*, 2023).

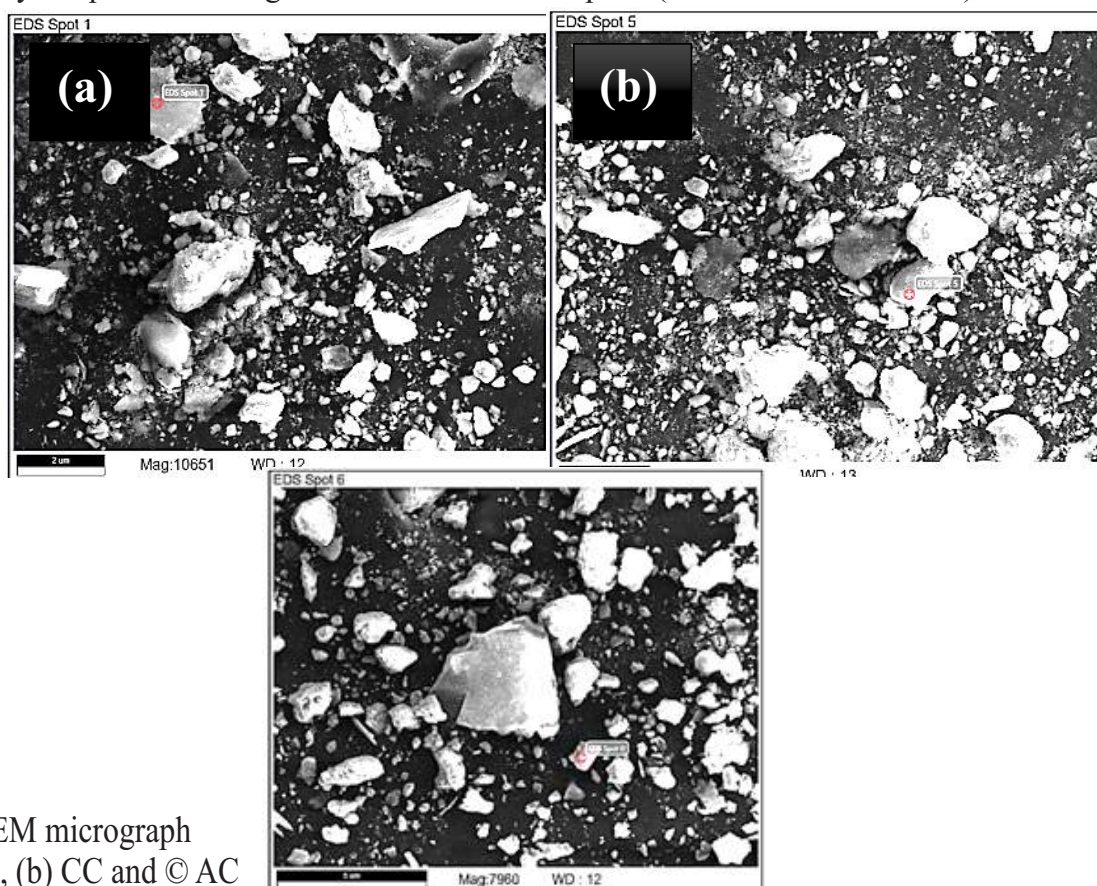


Fig. 3. SEM micrograph of (a) RC, (b) CC and (c) AC

3.2 Batch Adsorption of Methylene Blue

The effect of solution pH (Figure 4a), adsorbent dosage and temperature of methylene blue adsorption are presented in Figure 4. The solution pH was varied by dropwise addition of 0.1 M HCl or NaOH. The adsorption capacity of RC, CC and AC showed increasing adsorption capacities in the pH range of 2 to 6.48, from 9.25 mg/g to 9.62 mg/g for RC, 9.18 mg/g to 9.60 mg/g for CC, and 7.07 mg/g to 9.42 mg/g for AC. Above 6.48, the adsorption capacity decreased slowly to 9.38 mg/g for RC, 7.82 mg/g for CC and 8.37 mg/g for AC. These outcomes in adsorption capacities could be attributed to the fact that at low pH values, the surface of adsorbents was bound by hydrogen ions (H^+), which reduced the dye cationic ions' contact with the adsorbents' active adsorption sites. Meanwhile, at moderate pH, the H^+ concentration decreased, thereby allowing for a good contact between the adsorbent active adsorption sites and the dye cationic ions (Ouaddari *et al.*, 2024). At higher pH, the excess of OH^- ion around the cationic dye slowed the retention of methylene blue by the active anionic sites of the adsorbents as a result of the forces of electrostatic attraction (Ouaddari *et al.*, 2024). For all adsorbents, maximum adsorption was reached at the dye solution pH, suggesting unfavourable adsorption outside the solution pH. However, RC had the maximum adsorption capacity of 9.62 mg/g.

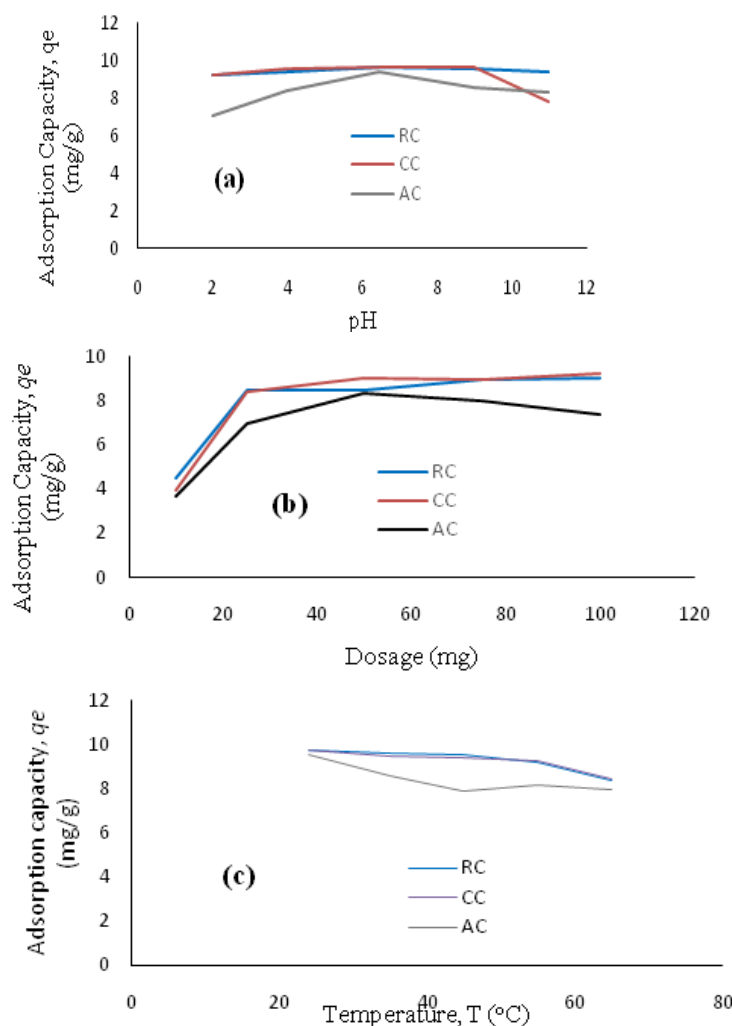


Fig. 4 Effects of (a) solution pH (b) adsorbent dosage (c) temperature on methylene blue adsorption by RC, CC and AC ($C_o = 10$ mg/L; $T = 24^\circ\text{C}$; Dosage = 50 mg; pH = 6.48; $t = 72$ h).

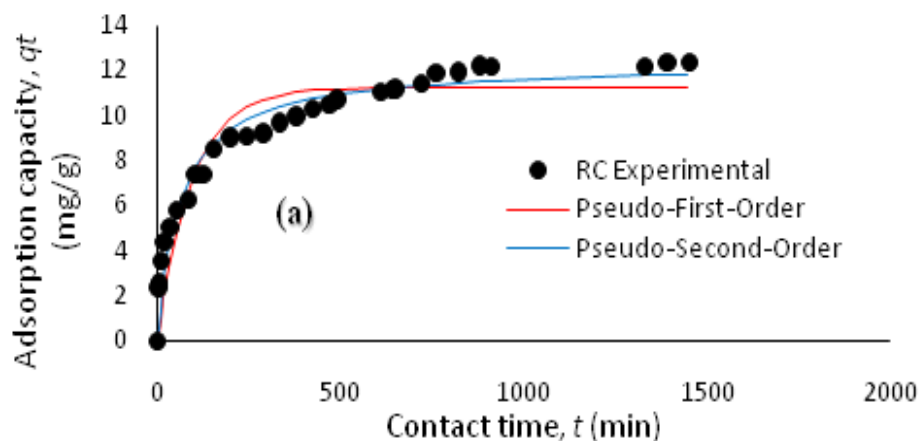


The effect of adsorbent dosage (Figure 4b) demonstrated increasing adsorption capacities of RC, CC and AC under varying adsorbent dosages from 10 to 100 mg. For RC, CC and AC, the adsorption capacities increased from 4.49 to 9.05 mg/g, 3.95 to 9.25 mg/g, and 3.67 to 8.37 mg/g. Meanwhile, AC demonstrated an intermediate adsorption saturation at 50 mg, followed by a decreasing adsorption capacity. The availability of active adsorption sites and improved mass transfer phenomenon were responsible for the increasing adsorption capacities at the beginning up until 100 mg (El-Sharkaway *et al.*, 2020). Meanwhile, for AC, the decreasing adsorption capacity after saturation could be attributed to adsorbent-adsorbate electrostatic repulsion, active adsorption sites blocking and adsorbate diffusion resistance (Ouaddari *et al.*, 2024; Francis and Zaini, 2023). The maximum adsorption capacity of RC and CC was at 100 mg dosage, and AC was at 50 mg dosage.

The temperature effect on adsorption (Figure 4c) suggested that for all adsorbents (RC, CC and AC), increasing the adsorbate solution temperature from 24 – 65 °C, RC, CC and AC demonstrated similar adsorption behaviour of decreasing adsorption capacities from 9.76 mg/g to 8.37 mg/g for RC, 9.73 mg/g to 8.44 mg/g for CC and 9.56 mg/g to 7.96 mg/g for AC. This suggested that the process was exothermic and that increasing temperature weakened the adsorbent-adsorbate attractive force as well as adsorbate molecule collision (Hamad *et al.*, 2024; Francis *et al.*, 2021). For all adsorbents, maximum adsorption capacity was obtained at 24°C

3.2.1 Kinetics of dye adsorption

The adsorption kinetics of methylene blue onto RC, CC and AC are presented in Figure 5. Their adsorption behaviours were similar, with equilibrium attained in 1488 min. Adsorption rate was fastest in the first 123 min, 83 min and 33 min for RC, CC and AC, respectively, due to the large active adsorption vacant sites of the adsorbents. Going further, the adsorption rate slowed until equilibrium was attained due to reduced vacant adsorption sites and formation of adsorbent-adsorbate repulsive forces (Rehman *et al.*, 2021). At equilibrium, there was a complete occupancy of the available active adsorption sites. The maximum adsorption capacity of RC, CC and AC was 12.38 mg/g, 10.07 mg/g and 8.10 mg/g, respectively.



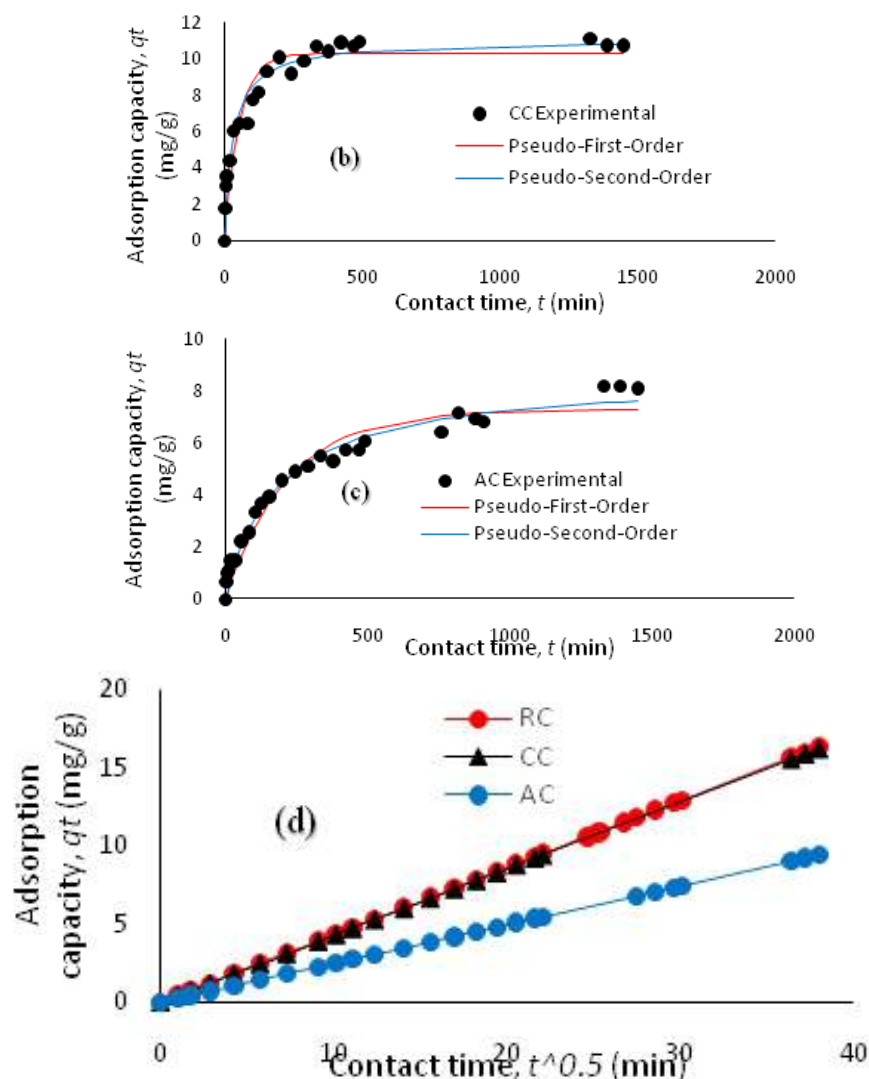


Fig. 5 Fittings of kinetics data of (a) RC (b) CC and (c) AC into pseudo-first-order and pseudo-second-order models, and (d) intraparticle diffusion model ($C_o = 10$ mg/L; $T = 24^\circ\text{C}$; dosage = 50 mg; pH = 6.48).

The results of the kinetic models are presented in Table 2. The adsorption kinetics of all the adsorbents were best presented by the pseudo-second-order kinetics model with the least sum of square error (SSE), the highest regression coefficient (R^2) and better adapted calculated adsorption capacity ($q_{t,exp}$) to the experimental data ($q_{t,cal}$). This suggested the possibility of strong chemical bonding in adsorption (Hamad *et al.*, 2024). However, the positive kinetic constant variables (k_f and k_s) were validations of the reliability of the models and indications that the process was governed by kinetics (Hamad *et al.*, 2024; Kebede *et al.*, 2022).

The intraparticle diffusion model was also adapted to determine the adsorption mechanism (Figure 5c). The profile showed two distinct straight lines, which suggested two-step adsorption mechanism of surface adsorption and intraparticle diffusion (Mohamed *et al.*, 2023). The linear form of the profile through the origin suggested that the intraparticle diffusion was a likely rate-determining mechanism (Francis and Zaini, 2023).

Table 2. Variables of kinetic models.

Parameters	RC	CC	AC
$q_{t,exp}$ (mg/g)	12.38	10.75	8.10
Pseudo-first order			
$q_{t,cal}$ (mg/g)	11.25	10.34	7.31
K_f (min ⁻¹)	0.0105	0.0185	0.0046
SSE	42.28	25.21	8.760
R ²	0.931	0.938	0.964
Pseudo-second order			
$q_{t,cal}$ (mg/g)	12.32	11.05	8.61
K_s (g/mg.min)	0.0013	0.0030	0.0006
SSE	22.85	13.60	4.448
R ²	0.959	0.958	0.980
Intraparticle diffusion			
K_{id} (g/mg.min ^{0.5})	0.431	0.426	0.246
C	0	0	0
SSE	138.2	217.9	13.01
R ²	0.884	0.679	0.959



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The thermodynamic parameters are presented in Table 3. The negative values of ΔG° in Table 5 suggested adsorption feasibility and spontaneity. Increasing temperature resulted in increased ΔG° values of RC and AC, which suggested that the adsorption of methylene blue onto RC and AC was less efficient and spontaneous at higher temperature. Meanwhile, for CC, the ΔG° values decreased at higher temperature, suggesting increased spontaneity of adsorption at higher temperatures. The positive ΔS° values suggested increased irregular randomness on the adsorbent-adsorbate interface (Rehman *et al.*, 2021; Asokogene *et al.*, 2020). The enthalpy, ΔH° values of RC and AC were negative, suggesting an exothermic adsorption process. However, for CC, ΔH° was positive, indicating an endothermic adsorption process. All ΔS° values were less than 1 ($\Delta S^\circ < 1$), suggesting that the adsorption process was reversible (Asokogene *et al.*, 2020).

Table 3. Thermodynamics data of methylene blue adsorption onto adsorbents.

Adsorbent	C_o (mg/L)	Temperature (K)	$\ln K^\circ$	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol.K)
RC	10	297	4.50	-11.10	-3.65	0.017
		308	2.75	-7.05		
		318	2.64	-6.98		
		328	3.81	-10.38		
		338	3.71	-10.43		
CC	10	297	4.32	-10.67	11.21	0.065
		308	2.54	-6.50		
		318	2.44	-6.46		
		328	4.22	-11.51		
		338	4.13	-11.60		
AC	10	297	3.44	-8.50	-11.58	0.019
		308	1.66	-4.25		
		318	1.23	-3.24		
		328	1.90	-5.17		
		338	2.56	-7.21		

3.3 Comparison with Previous Works

The adsorption kinetic and thermodynamic data of RC, CC and AC, and their comparisons with previous works are presented in Tables 4 and 5, respectively. In Table 4, RC, CC and AC had rate constants (K_s) with the least magnitude compared to other adsorbents for methylene blue adsorption. This suggested that the adsorbents demonstrated a slower rate constant compared to other adsorbents. All adsorbents in Table 5 showed negative ΔG° at different temperatures. The exothermic adsorption process by RC and AC was also demonstrated by GO/CS granules (Luong *et al.*, 2024) and rGO (Arias *et al.*, 2020). However, all the other adsorbents demonstrated an endothermic adsorption process as CC with positive ΔG°

Table 4. Pseudo-second-order kinetic data of methylene blue adsorption by various adsorbents

Adsorbent	C_o (mg/L)	pH	Q_m (mg/g)	K_s (g/mg.mi n)	References
RC	10	6.48	12.38	0.0013	This study
CC	10	6.48	10.75	0.0030	This study
AC	10	6.48	8.10	0.0006	This study
Pakistani clay	100	-	107.18	-	Rehman <i>et al.</i> , 2021
Moroccan natural clay (TMG)	50 100	6.43	48.00 81.18	0.025 0.010	Mohamed <i>et al.</i> , 2023
Bentonite clay (NaOH)	200	7	22.131	-	Hamad <i>et al.</i> , 2024
Kaolinite (H ₂ SO ₄)	20	-	3.40	-	Sagita <i>et al.</i> , 2021
Malaysian kaolinite (HCl)	20 -70	6	1.35- 1.37	-	Sandollah <i>et al.</i> , 2020
Clay composite/TiO ₂	200	8	6.3	-	Aljar <i>et al.</i> , 2021
DS	10	4.8	5.53	0.0028	Francis and Zaini, 2023
Sludge derived biochar	50 100 150 200	- - - -	1.32 1.78 1.89 1.95	-0.6377 0.4642 1.3631 1.8838	Roslan <i>et al.</i> , 2022

Table 5. Thermodynamic parameters of methylene blue adsorption onto various adsorbents.

Adsorbent	Temp. (K)	C_o (mg/L)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol)	References
RC	297	10	-11.10	-3.65	0.017	This study
	308		-7.05			
	318		-6.98			
	328		-10.38			
	338		-10.43			
CC	297	10	-10.67	11.21	0.065	This study
	308		-6.50			
	318		-6.46			
	328		-11.51			
	338		-11.60			
AC	297	10	-8.50	-11.58	0.019	This study
	308		-4.25			
	318		-3.24			
	328		-5.17			
	338		-7.21			
SGO	302	8	-6.08	17.5	0.080	Francis and Zaini, 2024
	323		-9.38			
	343		-9.94			
	363		-11.31			



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GO/CS	303	20	-9.887	-64.609	-0.1971	Luong <i>et al.</i> , 2024
Granules	308		-8.902			
	313		-7.916			
	318		-6.931			
	323		-5.945			
	333		-3.974			
rGO	293	100	-22.51	-2.20	0.069	Arias <i>et al.</i> , 2020
	313		-25.84		$\times 10^{-5}$	
	333		-27.58			
Coarse neem	303	15	-3.79	13.7	0.06	Asokogene <i>et al.</i> , (2019)
leave/chitosan	313		-5.69			
aggregates	323		-5.91			
	333		-5.81			
	343		-6.63			

4. Conclusion

The adsorption of methylene blue onto Ikpobia clay (RC, CC and AC) was studied. The effects of solution pH, adsorbent dosage, temperature and contact time were studied to establish the performance of RC, CC and AC. These parameters significantly affected the adsorption kinetics and thermodynamics of methylene blue. The pseudo-second-order model best described the adsorption kinetic data. The thermodynamic study suggested the feasibility and spontaneity of the adsorption of Ikpobia clay. RC exhibited the best performance. This study has positioned Ikpobia clay in its natural form (RC) as an alternative for effective wastewater purification technology.

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Catalytic Co-Pyrolysis of Plastic Waste and Oil Palm Fiber for the Production of Bio-Oil Using SBA-15 as Catalyst

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Abstract

Nigeria has not maximally exploited its biomass and waste resources as an option for providing bio-oil. Consequently, there is an urgent need to explore processes that can simultaneously and sustainably transform two or more feed-stocks into value-added products. In this study, catalytic co-pyrolysis (CCP) of a plastic mixture and oil palm fibre (OPF) was carried out for the production of bio-oil in a fixed-bed reactor. The effect of experimental parameters such as temperature and feedstock mixing ratios on the product yield and composition of the oil product was investigated. The oil yield was determined by calculation, and the composition was determined by Gas Chromatography-Mass Spectrometry. The effect of varying the co-pyrolysis temperature from 450 to 600 °C showed that a maximum oil yield of 53.8 % was attained at 550 °C while elevated temperatures favoured the formation of alcohol and ester compounds. A plastic mixture-OPF ratio of 1:1 produced a bio-oil with the maximum concentration of hydrocarbons. The results indicate the viability of bio-oil as a fuel substitute and chemical feed-stock. These findings further indicate that CCP is a promising method with the potential to provide a sustainable energy solution while also offering opportunities for waste valorisation.

Keywords: SBA-15 catalyst, Biomass, Catalytic Co-Pyrolysis, Oil Palm Fiber, Waste Management

1. Introduction

Access to reliable, sustainable, and affordable energy is vital for Nigeria's socio-economic development, impacting education, health, and industry. Despite global efforts to promote renewable energy sources like biomass, over 90 million Nigerians lack electricity and rely on traditional biomass fuels, which adversely affect health and the environment "(International Energy Agency, 2021). The potential of biomass as a clean energy source is underutilized in Nigeria due to infrastructure challenges and inefficiencies (Abogunrin-Olafisoye et al., 2024).

Nigeria's large agricultural sector, particularly palm oil production, generates significant biomass waste, such as oil palm fibre (OPF), alongside increasing plastic waste (Radhakrishnan et al., 2023). Co-pyrolysis, a process that simultaneously heats biomass and plastic waste to produce bio-oil (Cupertino et al., 2024), offers a promising solution for managing these resources. This method can enhance the yield and quality of bio-oil, address plastic waste disposal, and utilize OPF energy, thus advancing both waste management and renewable energy production (A. W. Gin et al., 2021).

Previous studies have established the efficacy of pyrolysis for converting various organic materials into bio-oils (Duan et al., 2019; Radhakrishnan et al., 2023). However, there is limited research focusing on the catalytic co-pyrolysis (CCP) of OPF and plastic waste, particularly in the context of varying operational



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temperatures and feedstock mixing ratios (Adelodun et al., 2020). Understanding how both experimental parameter affects the CCP process is crucial for optimizing the yield and composition of the resultant bio-oil. For example, elevated temperatures have been shown to influence the formation of different chemical compounds in bio-oil, such as alcohols and esters, which are valuable as both fuels and chemical feedstocks (Oyewo & Awosika, 2025). This study aimed to fill this gap by investigating the impact of temperature on the CCP of these materials in a fixed-bed reactor setup.

The primary objective of this research was to determine how varying temperatures and feedstock mixing ratios affect both the yield and composition of bio-oil produced from the CCP of OPF and plastic in the presence of SBA-15 catalyst. SBA-15 possess a highly organised hexagonal mesoporous structure that permits the diffusion of the large pyrolysis intermediate products (W. A. Gin & Salami, 2024) into the inner pore of the catalyst. By evaluating the oil yield and its chemical composition, this study seeks to identify the best CCP experimental parameters for bio-oil production using oil palm fibre (OPF) and plastic as feedstocks. The findings are expected to highlight the viability of CCP as a sustainable solution for waste management and renewable energy generation.

2. Materials and Methods

2.1 Raw Materials

In this study, OPF and a mixture of high-density polyethylene (HDPE) and polypropylene (PP) plastics were used as feedstock. OPF was sourced from an oil palm plantation in Wukari, Nigeria, and subsequently dried, ground, and sieved to a particle size of 0.50 mm to 2.0 mm. To maintain consistency in the moisture levels and avoid contamination, both materials were stored in airtight containers until required for the experiments.

2.2. Co-Pyrolysis Experiment Apparatus

Co-pyrolysis experiments were conducted using a fixed-bed reactor system equipped with a nitrogen gas supply, furnace, temperature controller, and wax trap. The reactor was securely clamped into the furnace, and the setup included a thermocouple for temperature measurement and a nitrogen inlet to create an oxygen-free environment. During the experiment, the produced organic vapours were condensed into liquid bio-oil using a test tube ice-box condenser. The wax trap, positioned beneath the reactor with the aid of a lab jack, collected the solid residues. A schematic of the experimental setup is shown in Figure 1.

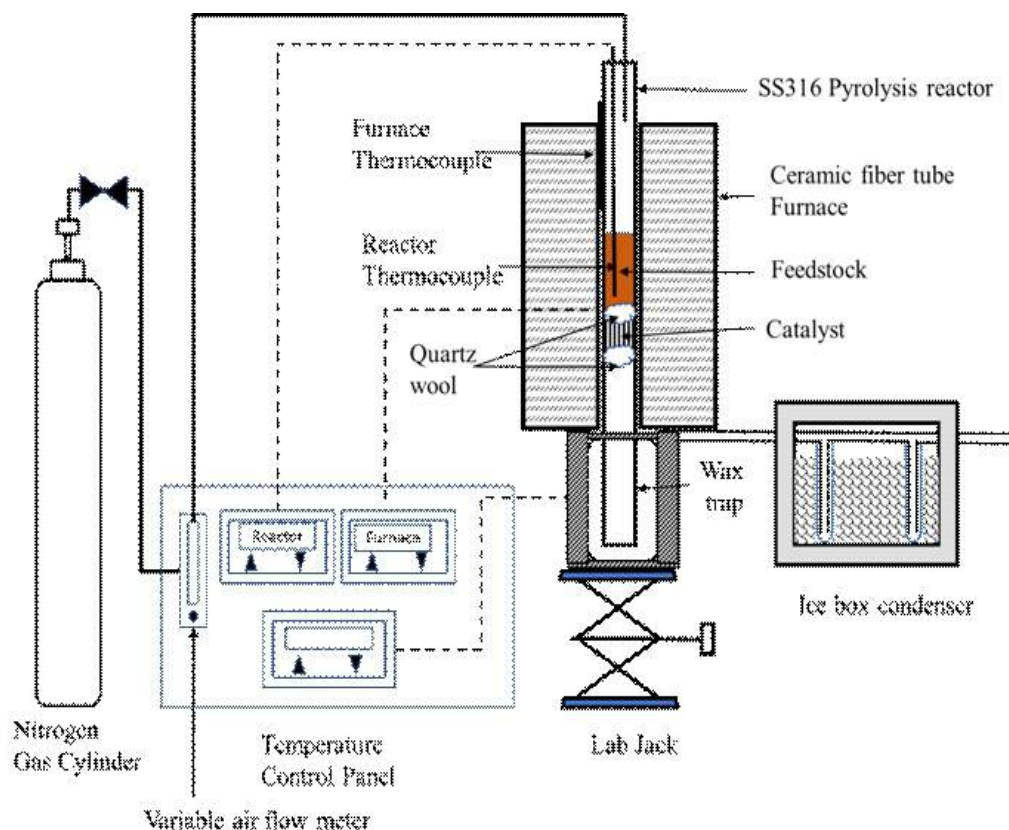


Fig. 1. Schematic Diagram of the Fixed Bed Reactor Used for CCP

2.3. Catalytic Co-Pyrolysis Procedure

In each co-pyrolysis run, 0.32 g of SBA-15 catalyst was placed on a wire mesh overlaid with quartz wool to prevent direct contact with the feedstock. A mixture of the plastic and OPF (1.6 g) was introduced into the reactor (Figure 1), which was then purged with 99.9% nitrogen gas at a flow rate of 250 cm³/min for 15 min to establish an inert atmosphere. The yields of pyrolytic oil and char were measured, with the oil collected in two stages: first, at the wax trap, heated to 170°C, and then in an ice bath at -5°C. The procedure outline above is that of the authors.

2.4 Determination of Oil Yield and Composition

After each CCP process, the mass percentage yields of the liquid and char products were computed using Equation 1 (Kar, 2011):

$$M_{Yield} = \frac{100x_1}{x_2}$$

Where M_{Yield} is the percentage mass product yield, x_2 is the initial mass of the feedstock.

The reactor and associated equipment were cleaned with acetone between runs to remove residues and prepare for subsequent experiments. The bio-oil was analyzed using Gas Chromatography-Mass Spectrometry (GC-MS) with a capillary column (Elite-5MS) and helium as the carrier gas. The GC



conditions included an initial temperature of 50°C, ramped at 5°C/min to 280°C, and maintained at 280°C for 20 minutes. Mass spectra were obtained with 70 eV ionization energy and compared to the NIST library for compound identification (Ye et al., 2008).

2.5 Effect of Experimental Parameters

The effect of two selected experimental parameters such as temperature and mixing ratio, on the co-pyrolysis process was investigated.

2.5.1 Effect of temperature

To determine the effect of temperature on both the product yield and composition, the co-pyrolysis was conducted within a temperature range of 450–650°C for 45 min. Upon completion, the reactor was cooled to room temperature by using a fan.

2.5.2 Effect of mixing ratio on catalytic co-pyrolysis

To determine the effect of mixing ratio on both the oil yield and composition, the mixing ratio of plastic mixture and OPF was varied from 3:1 to 1:3. The CCP was conducted at the best temperature.

3. Result and Discussion

3.1 Characterization of SBA-15 Catalyst and Feedstock

Detailed characterisation of the SBA-15 catalyst and feedstocks used in this study is reported in previous investigations carried out by Gin and Salami (2024) and Gin et al. (2022), respectively.

3.1. Effect of Temperature on Product Yield and Oil Composition

Temperature is an important operational parameter in the co-pyrolysis process as it determines both the yield and composition quality of the final product. **Figure 2** illustrates the yields of oil, char, and gas obtained during the catalytic co-pyrolytic conversion of OPF and plastic waste at varying temperatures

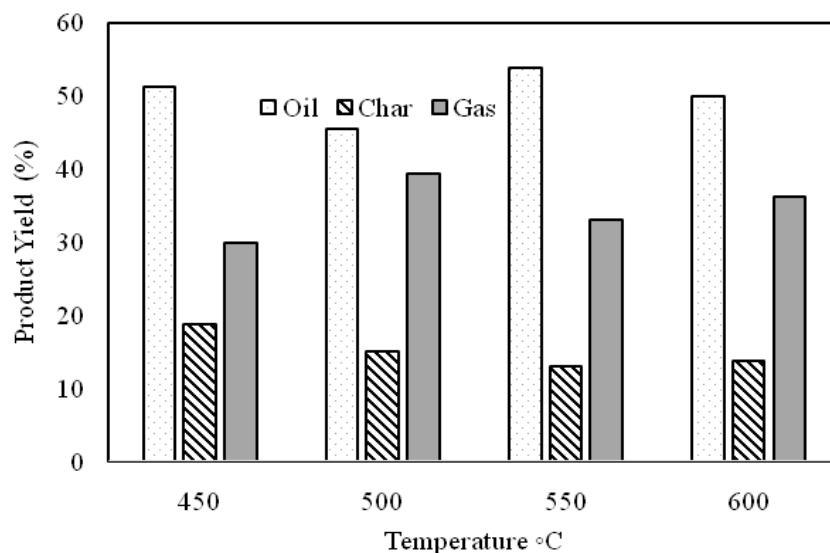


Fig.: Effect of Temperature on Product Yield

Figure 2 shows that the highest yields of oil (53.8%), char (18.8%), and gas (39.4%) were achieved at 550°C, 450°C, and 500°C, respectively. This variability indicates a synergistic effect of temperature on the product yields, with 550°C emerging as the optimal temperature for oil production. The observed decrease in char yield from 18.8% at 450°C to 13.1% at 550°C suggests that higher temperatures facilitate the breakdown of the plastic-biomass mixture –(Park et al., 2018), leading to increased production of volatile compounds like oil and gas. This trend supports the endothermic nature of the co-pyrolysis process, where elevated temperatures enhance the degradation of feedstocks into valuable products. The findings align with previous studies that identified an optimal temperature range for maximizing bio-oil yield between 500 °C and 600 °C (Inayat et al., 2022). This information highlights the efficiency of high-temperature co-pyrolysis in converting waste materials into high-yield bio-oil.

Temperature not only affects the yield of the pyrolytic products but also their composition. **Figure 3** presents the impact of various temperatures on the composition of the bio-oil produced.

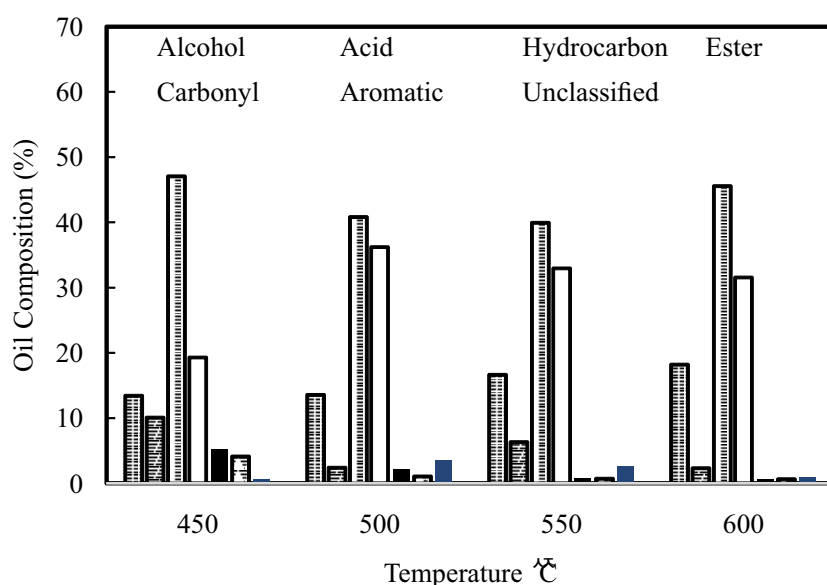


Fig.: Effect of Temperature on Composition of Bio-Oil

Figure 3 indicates an increase in alcohol compounds with temperature, likely due to decarboxylation and repolymerization of sugars derived from cellulose and hemicellulose in OPF (Abel Williams Gin et al., 2023). This increase is beneficial, as alcohols can be used in fuel applications and chemical synthesis. The peak in acid yield at 450°C (10.1%) and its decline to 2.34% at 600°C suggest that higher temperatures promote esterification reactions between alcohols and acids, leading to the formation of esters. The rise in ester compounds from 19.31% to 36.21% at higher temperatures enhances the bio-oil's potential for use in biodiesel production. Additionally, the decrease in hydrocarbon yield from 47.07% to 39.96% and the decline in aromatic compounds from 4.14% to 0.66% with increasing temperature indicate a shift in the composition towards more desirable fuel components while reducing less favourable by-products. These changes reflect the efficiency of temperature optimization in enhancing the quality of bio-oil for various applications.

The ability to optimize temperature for higher yields of oil and desirable bio-oil components, such as hydrocarbons and esters, makes co-pyrolysis an attractive method for converting waste into renewable energy. High temperatures that maximize oil and gas yields also reduce the production of char, which can improve waste management and resource utilization. The enhanced quality of bio-oil, characterized by increased alcohol and ester content, provides a viable alternative to diesel and other fossil fuels. Furthermore, the reduction in undesirable compounds like carbonyls and aromatics at elevated temperatures improves the combustion performance and environmental impact of the bio-oil. Optimizing pyrolysis conditions to enhance the production of high-value bio-oil components not only increases economic value but also contributes to environmental conservation by reducing reliance on fossil fuels and minimizing waste.

3.2 Effect of Mixing Ratio on Product Yield and Oil Composition

The study of the mixing ratio on product yield and composition is important in order to ascertain the existence of synergistic or antagonistic effects during the CCP process. Figure 4 presents the effect of mixing ratio on product yield for SBA-15 catalysed co-pyrolysis of plastic mixture and OPF. The oil yield increased from 39.9 % to 54.4 % with decreased OPF in the blend (3:1 to 1:3), whereas the char yield increased from 6.3 % to 18.8 % with increased OPF in the blend. The gas yield ranged between 33.1 % and 39.9 % and no definite trend was observed for the gas yield as the plastic mixture: biomass ratio was varied due to a synergistic effect.

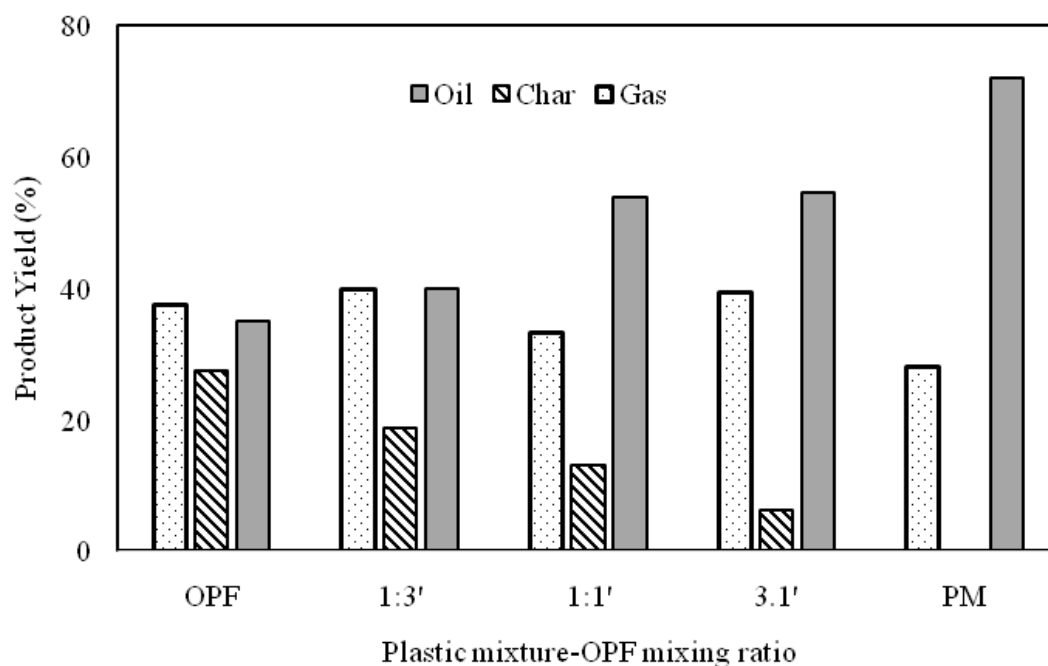


Fig..Effect of Mixing Ratio on Product Yield SBA-15 Catalysed Co-Pyrolysis of Plastic Mixture and OPF At 550 °C (Wax Trap 200 °C, N₂ Flow = 250 cm³/min, Pressure 2 Bar)

In terms of synergistic effect, at the plastic mixture-biomass mixing ratio of 3:1 and 1:3, the increase in gas yield led to a decrease in both the oil and char yield. However, maximum improvement in the gas yield was at the plastic mixture-OPF mixing ratio of 3:1 since the experimental yield of the gas was much higher than the theoretical yield. It may be concluded that the addition of plastic mixtures to OPF in the presence of SBA-15 improved the gas yields. Likewise, Lee et al. (2014b) found that the CCP of *L. japonica* and polypropylene over Al-SBA-15 increased the gas yield and decreased the oil yield. At the plastic mixture-biomass mixing ratio of 1:1, the decrease in the yield of char led to only a slight improvement in the yields of the oil and gas, since the experimental value of oil and gas were 0.6 and 0.9 % respectively, higher than the theoretical value. Dyer et al. (2021) studied the ZSM-5 catalysed co-pyrolysis of sawdust and HDPE at different mixing ratios from 1:2 to 2:1 using a fixed bed reactor. It was found out that an increase in the biomass/plastic ratio led to an increase in char yield along with a decrease in gas and liquid yield.

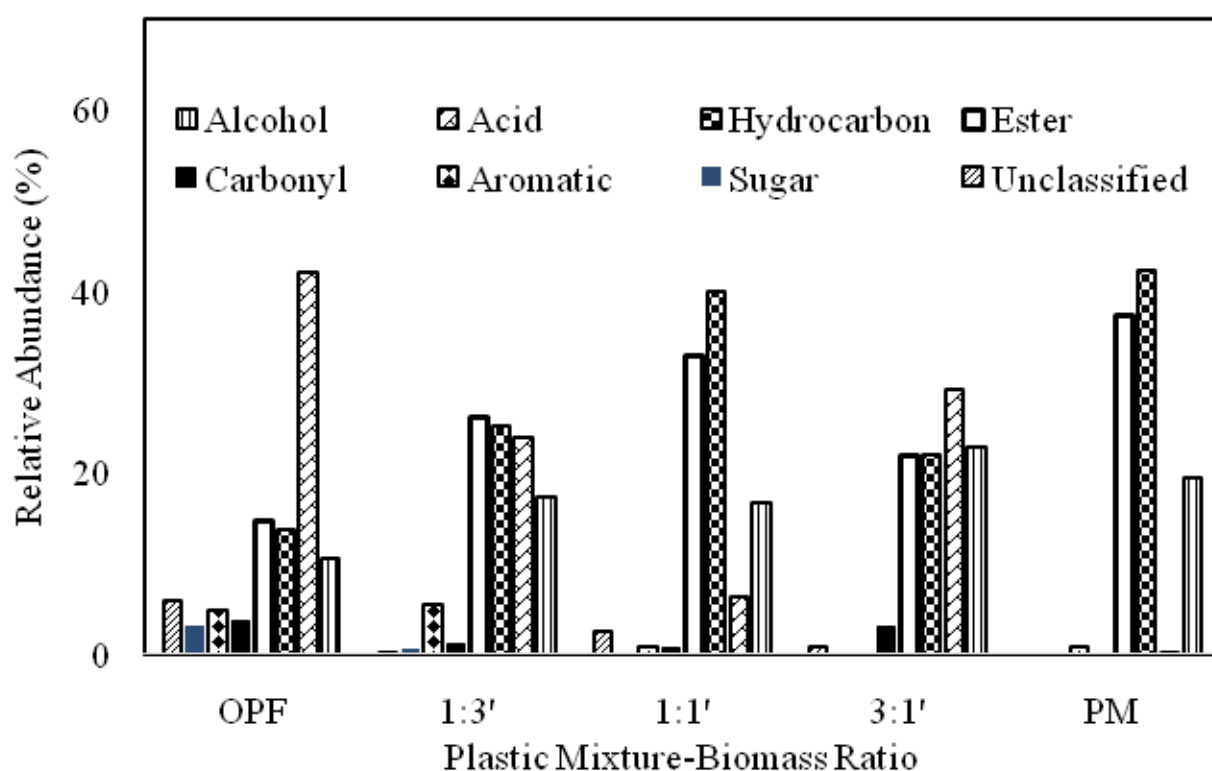


Fig. 5 Effect of Mixing Ratio on Composition Of SBA-15 Catalysed Co-Pyrolysis of Plastic Mixture (PM) and OPF at 550 °C (wax trap 200 °C, N₂ flow = 250 cm³/min, pressure 2 bar)

Figure 5 presents the effect of mixing ratio on composition for the SBA-15 catalysed co-pyrolysis of plastic mixture and OPF. The alcohol compounds in the oil were highest (22.88 %) when a higher amount of plastic mixture in the blend (3:1) was used. The amount reduced to 16.66 % with an equal mass of the plastic mixture and OPF (1:1), and thereafter the amount increased to 17.29 % with a higher amount of OPF in the blend. The acid compounds in the oil were highest (29.2 %) when a higher amount of plastic mixture in the blend (3:1) was used. The amount reduced to 6.34 % with an equal mass of the plastic mixture and OPF (1:1), and thereafter the amount increased to 23.92 % with a higher amount of OPF in the blend.



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The hydrocarbon compounds in the oil were highest (39.96 %) when an equal mass of the plastic mixture and OPF (1:1) was used. The amount reduced to 21.9 % with a higher amount of plastic mixture in the blend, whereas the amount reduced to 25.09 % with a higher amount of OPF in the blend. The ester compounds in the oil were highest (32.96 %) when an equal mass of the plastic mixture and OPF (1:1) was used. The amount reduced to 22.08 % with a higher amount of plastic mixture in the blend, whereas the amount reduced to 26.14 % with a higher amount of OPF in the blend. The lowest carbonyl content of 0.74 % was obtained when an equal amount of the plastic mixture and OPF was used. The amount significantly increased to 3.03 % with a higher amount of plastic mixture in the blend, whereas a slight increase to 1.1 % was obtained with a higher OPF in the blend. The aromatic content significantly increased from zero to 5.5 % as the OPF content increased from 25 % to 75 % in the blend.

Conclusion

The impact of temperature and feedstock mixing ratio on the catalytic co-pyrolysis of oil palm fibre and plastic waste in the presence of SBA-15 has been studied. Results showed temperature-dependent effects on product distribution and composition, with optimal bio-oil yields at 550°C. Higher temperatures increased oil and gas yields while reducing char production. The plastic mixture- OPF feedstock ratio of 1:1 produced a bio-oil with the highest composition of hydrocarbons (39.96 %). This study highlights the potential of plastic waste and oil palm fibre as a chemical feedstock for bio-oil production.

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High Sorptive Performance of Chemically Modified *Vigna Subterranea* Husks for Remediation of Oil Contaminated Water Surfaces

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Abstract

The central point of this study is the use of rawvigna subterraneahusks (RVSH) and esterified vigna subterranea husks (EVSH) for the treatment of water surfaces spilt with crude oil. Sorbents from agricultural products have been adopted in recent times due to their exceptional qualities, such as low cost, biodegradability, availability, and, most importantly, their friendliness with the environment. The characterizations of the studied sorbents were achieved by BET, SEM, FTIR and TGA procedures. The investigation was conducted by batch methodology at optimum conditions of temperature, pH, initial concentration, and time. The Langmuir model provided the best fit for both sorbents, exhibiting higher regression coefficients and lower chi-square values compared to other models, with maximum monolayer removal capacities of 3.79 and 4.97 g/g attained for RVSH and EVSH, respectively, as revealed by equilibrium isotherm analysis. The kinetic data revealed a strong fit to the pseudo-second-order model, with sorption equilibrium achieved at 70 and 60 min for RVSH and EVSH, respectively. The modified sample demonstrated improved regenerability and reusability using n-hexane, maintaining effectiveness over multiple sorption-desorption cycles. Significantly, the sorbents successfully removed oil from both simulated and actual contaminated water samples, highlighting their applicability in real-world oil spill mitigation strategies.

Keywords: Contamination, Remediation, Sorption, Oil spill, Esterification

1. Introduction

Environmental pollution associated with oil spills is a major problem in oil-producing areas. Oil spills are due to pipeline vandalism, equipment failures, transportation of crude oil, etc (Behnood et al., 2013). Oil spills can contaminate water, resulting in foul odours and unpleasant taste.

Considering the adverse effects, effective decontamination as well as clean-up is necessary. Methods commonly applied to remove oil in water make use of oil booms, dispersants, skimmers, sorbents, etc. (Liu et al., 2016). The preferred sorption technique was utilized in the treatment process.



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Among sorbent materials, synthetic products such as polyurethanes and polypropylenes stand out due to their hydrophobic and oleophilic properties, making them highly effective for sorption. Lately, organic natural sorbents, including agro-wastes, are becoming increasingly popular due to their advantages over inorganic and synthetic sorbents, including lower cost, accessibility and biodegradability (Ogbu et al., 2022).

The study is aimed at developing sorbents for oil-spilt water surfaces from agro wastes (*Vigna subterranean* husks)

2. Experimental

2.1. Sorbents (RVSH & EVSH) Preparation

The *vigna subterranean husks* were cleansed with purified water, dried in the sun and in the oven for 70 min at 65 °C and then ground into tiny particles. The ground sample was then made to pass through a sieve of 500 µm and labelled *rawvigna subterranea husks* (RVSH) (Eze et al., 2019). Also, the raw sample was treated with oleic acid in n-hexane that contained a few drops of concentrated H₂SO₄ as a catalyst and then set up in a reflux system for 4 hours at 65 °C. The fatty acid-grafted sorbent formed after the reaction was cleansed by n-hexane and dried in an oven to produce esterified *vigna subterranea husks* (EVSH) (Banerjee et al., 2006).

2.2. Sorbent Characterization

The sorbents were characterized using Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), as well as Brunauer-Emmett-Teller (BET) surface area analysis. FTIR is used to identify the functional groups responsible for the binding of oil molecules; SEM to examine surface morphologies of the sorbents; TGA to study thermal stabilities of sorbents, and BET to determine the surface areas and pore properties of the sorbents

2.3. Sorbate Characterization

Characterization of the crude oil from an oil location was achieved using standard ASTM methods to determine water content, carbon residue, total acid value, total base value, density, °API gravity, total sulfur, pour point, flash point and refractive index.

2.4. Sorption by Batch Experiment

The batch sorption technique was used to perform all sorption experiments in the simulated and real oil-spilt water, as described by Ogbu et al. (2022). The sorption was performed to assess the influence of pH (3–11), oil concentration (8–12 g/L), mass of sorbent (0.1–0.5 g), interaction time (20–90 minutes) and heat level (303–323K). The oil percentage sorption and the sorption capacity (*q_e*) of the sorbent for oil from the solution were estimated from the equations given below



$$\text{Sorption}(\%) = 100[C_o - C_e]/C_o \quad (1)$$

$$(g/g) = v[C_o - C_e]/m \quad (2)$$

Where C_o (g/L) is the oil initial concentration in solution, C_e (g/L) is the oil concentration at equilibrium, v (L) stands for the volume of oil-water concoction and m (g) is the mass of the sorbent applied.

2.5. Modelling of Sorption Isotherms

The isotherm modelling was performed by applying the Freundlich, Langmuir, Temkin and Scatchard models (Eze et al., 2019; Ogbu et al., 2019) and was well represented respectively by the following linear equations:

$$\log q_e = \log K_F + [1/n] \log C_e \quad (3)$$

$$C_e/q_e = 1/q_L K_L + C_e/q_L \quad (4)$$

$$q_e = B \ln A + B \ln C_e \quad (5)$$

$$q_e/C_e = q_s b - q_e b \quad (6)$$

Where q_L (g/g) denotes the Langmuir maximum monolayer sorption capacity, K_L is the sorption equilibrium constant for Langmuir, q_e (g/g) is the sorption capacity of the sorbent and C_e is the equilibrium concentration, $B = RT/b_T$, T is the temperature (K), R is the constant for ideal gas (8.314 J/mol K) and A , B as well as b_T are constants. A is the equilibrium binding constant (L/g), and constant B is connected to the energy due to sorption, and b_T is the Temkin constant, K_F (L/g) and n are the sorption constants for the Freundlich, and intensity of the sorption model. q_s (g/g) and b (L/g) are the Scatchard model constants.

2.6. Modelling of Sorption Kinetics

The kinetic modelling was performed by applying pseudo-second order, pseudo-first order, liquid film diffusion and intraparticle diffusion models (Nwadiogbu et al., 2016; Ogbu et al., 2019) and well represented respectively by the following linear equations:

$$t/q_t = 1/K_2 q_e^2 + t/q_e \quad (7)$$

$$\log(q_e - q_t) = \log q_e - (K_1 t / 2.303) \quad (8)$$

$$\ln(1 - F) = -K_{fd} t + C \quad (9)$$

$$q_t = K_d t^{1/2} + C \quad (10)$$

Where q_t and q_e in g/g are the sorption capacities at a specified time, t as well as at point of equilibrium correspondingly, K_1 (min⁻¹) is the rate constant for pseudo-first order, K_2 (g/g min) denotes the rate constant for pseudo second order, $h = K_2 q_e^2$ denotes the sorption initial rate constant (g/g min), $F = q_t/q_e$ is the fractional attainment of equilibrium, K_{fd} (g/g min) depicts sorption rate constant and C the intercept. K_d (g/g min^{1/2}) is the rate constant for intraparticle diffusion.



2.7. Sorption Thermodynamics

Sorption thermodynamics was accomplished by applying the following equations (Akpomie et al., 2019):

$$\Delta G^0 = -RT \ln K_c \quad (11)$$

$$\ln K_c = -(\Delta H^0 / RT) + (\Delta S^0 / R) \quad (12)$$

where (ΔG^0), (ΔH^0), (ΔS^0) depict changes in standard free energy, enthalpy and entropy, respectively. $K_c = C_s/C_e$ is the distribution coefficient; C_s (g/L) and C_e (g/L) symbolize the concentration of oil sorbed and concentration at equilibrium, respectively. T (K) is the absolute temperature, and R is the constant for an ideal gas.

2.8. Regeneration and Reusability

Desorption of oil to regenerate the used sorbents from the oil-loaded sorbents was investigated with petroleum ether, acetone and n-hexane as stripping agents. Sorbent loaded with crude oil (0.5 g) was contacted with a solvent (125 mL) in a beaker, perfectly fastened, and kept for 30 min for extraction to take place. It was removed by sieve net, desiccated in an oven for 30 min at 60 °C, weighed and then reused for sorption. The percentage desorption was evaluated by the equation

$$\chi^2 = \sum [(q_{e\text{exp}} - q_{e\text{cal}})^2 / q_{e\text{cal}}] \quad (13)$$

$$SSE = \sum (q_{e\text{exp}} - q_{e\text{cal}})^2 \quad (14)$$

Where $q_{e\text{cal}}$ and $q_{e\text{exp}}$ are, respectively, the calculated and experimental q_e values. The most fitted model is the one with the highest regression (R^2) and the minimum χ^2 and SSE values (Das and Mondal, 2011).

3.0. Results and Discussion

3.1. Analysis of Physicochemical Characteristics of Petroleum

The physicochemical characteristics of petroleum used in the analysis were determined, and the results are depicted in Table 1. °API gravity is regarded as a fundamental property of crude oil and thus very important in oil classification. It is light petroleum (34–39 °), heavy petroleum (< 22°), medium petroleum (22–33 °) and very light petroleum (40–45 °) (Nwadinigwe and Alumonia, 2015). Thus, the oil is a light one, as the value obtained is within the range apportioned for that type. The values obtained for all the parameters analyzed are represented in the table.

Table 1:Physicochemical characteristics of petroleum



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Parameters	Values
Total sulfur (wt %)	0.0000
Water content (ppm)	233.7±1.80
Density (g/cm ³)	0.83±0.43
°API gravity (degrees)	36.50±0.55
Carbon Residue (wt %)	2.68±0.02
Total basicity (mg KOH /g)	2.68±0.02
Total acidity (mg KOH /g)	0.23±0.01
Flash point °C	-19±0.72
Pour point °C	-37±0.81
Refractive index	1.44±0.03

3.2. Analysis of BET surface areas and pore properties of RVSH and EVSH

The BET surface area (S_{BET}), pore volume and pore size values for the sorbents are presented in Table 2. The result showed that the modified sample was relatively better in terms of surface area and pore properties using various standard methods, and thus can trap more oil molecules during sorption

Table 2: BET Surface areas and pore properties of RVSH and EVSH

Parameters	Sorbents	
	RVSH	EVSH
Surface area values (m ² /g)		
BET single-point method	---	275.7±0.817
BET multi-point method	345.2±0.384	376.5±0.515
Langmuir method	821.3±0.372	1016.0±1.217
BJH method	446.4±0.506	472.1±0.715
DH method	476.0±0.441	502.6±0.816
DFT method	110.9±0.417	112.7±0.555
Pore volume values (cm ³ /g)		
BJH method	0.216±0.009	0.230±0.12
DH method	0.221±0.005	0.235±0.13
DR method	0.154±0.003	0.165±0.014
HK method	0.078±0.002	0.079±0.085
SF method	0.027±0.001	0.025±0.004
DFT method	0.126±0.004	0.130±0.009
Pore size values (mm)		
BJH method	2.105±0.007	2.118±0.016
DH method	2.107±0.003	2.118±0.008
DR method	5.428±0.047	5.676±0.225
HK method	0.368±0.015	0.368±0.037
SF method	0.452±0.005	0.452±0.225
DFT method	2.647±0.031	2.647±0.198

3.3. Analysis of SEM images of RVSH and EVSH

The SEM images of RVSH and EVSH are depicted in Fig. 1a and b, respectively, and describe the surface morphologies of the materials. More pores were observed in the modified sample (EVSH) which led to improved oil diffusion onto the surface of the sorbent than in the raw sample (RVSH) (Gautam et al., 2014).

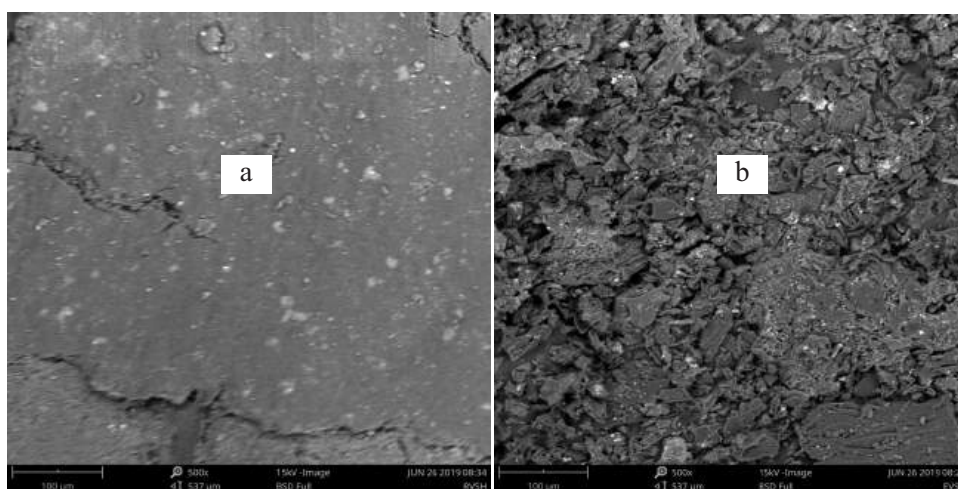
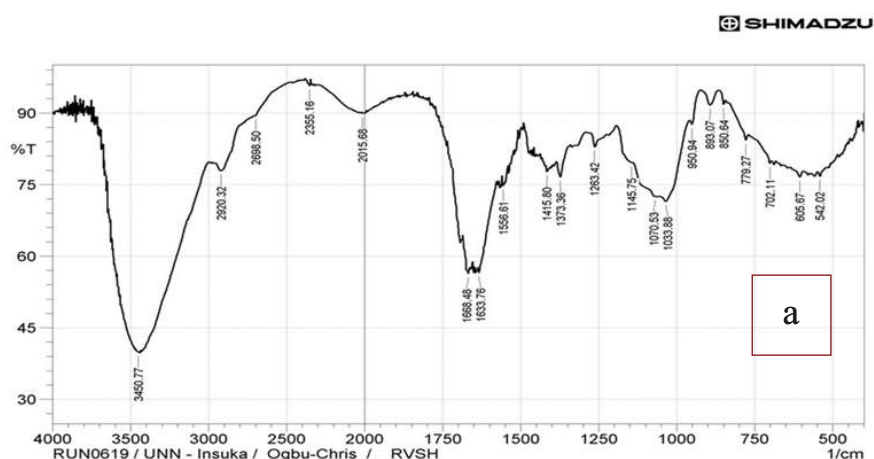


Fig 1: SEM image of (a) RVSH and (b) EVSH

3.4. Analysis of FT-IR Spectra of RVSH and EVSH

FT-IR spectra of RVSH and EVSH are depicted in Fig. 2a and b, respectively. The spectrum of RVSH with --OH stretching at 3450 cm^{-1} , indicates the occurrence of water molecules in the sample (Fathy et al., 2017). The band at 2920 cm^{-1} symbolizes C–H vibrations, while the one at 2015 cm^{-1} is due to $\text{C}\equiv\text{C}$ functionality of alkynes (Behnood et al., 2014). The FT-IR spectrum of EVSH showed the appearance of the band at 3458 cm^{-1} , which shows (--OH) stretching (Sokker et al., 2011), whereas the one at 2924 cm^{-1} is mainly because of --CH stretching (Behnood et al., 2014). A sharp band at 1631 cm^{-1} correspond to the carboxyl group (C=O) stretching, which is a proof of the esterification reaction due to the addition of oleic acid to the --OH group of the RVSH during the modification (Banerjee et al., 2006).



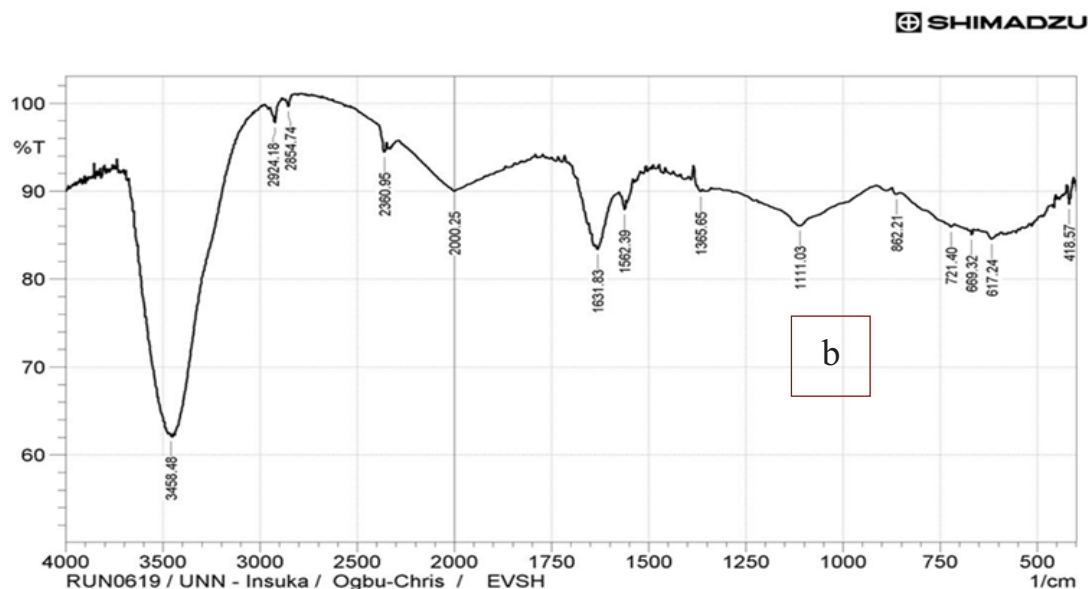
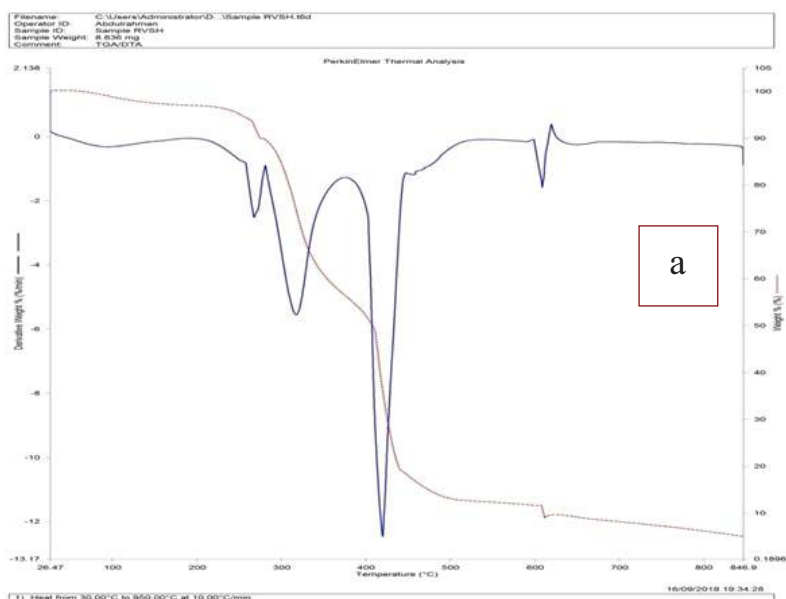


Fig 2: FT-IR spectral data for (a) RVSH and (b) EVSH

3.5. Thermal Analysis of RVSH and EVSH

The approximation of the thermal stabilities of RVSH and EVSH was attained at a temperature between 30 and 950 °C and a heating rate of 10 °C/min, and depicted in Fig. 3a and b, respectively. The TGA curve of the raw sample (RVSH) revealed reasonable weight loss between 270 and 605 °C, during which fairly thermal stability was attained. However, modification of the raw sample by treatment with oleic acid (esterification) produced EVSH, and its TGA curve revealed a weight loss between 300 and 480 °C, hence signifying a reduction in thermal stability.



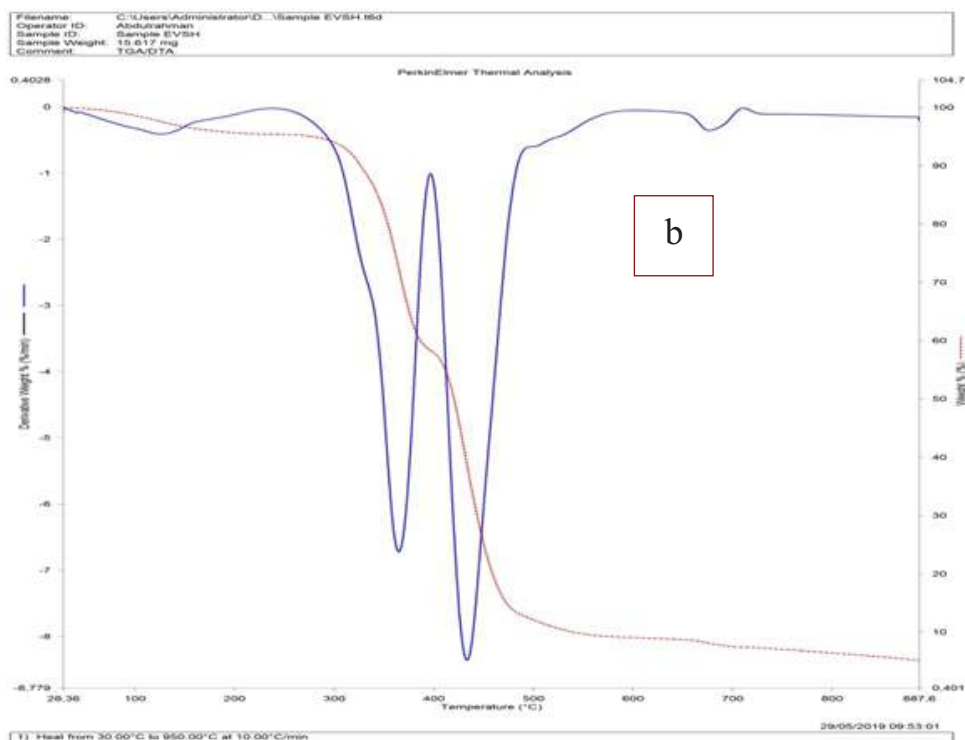
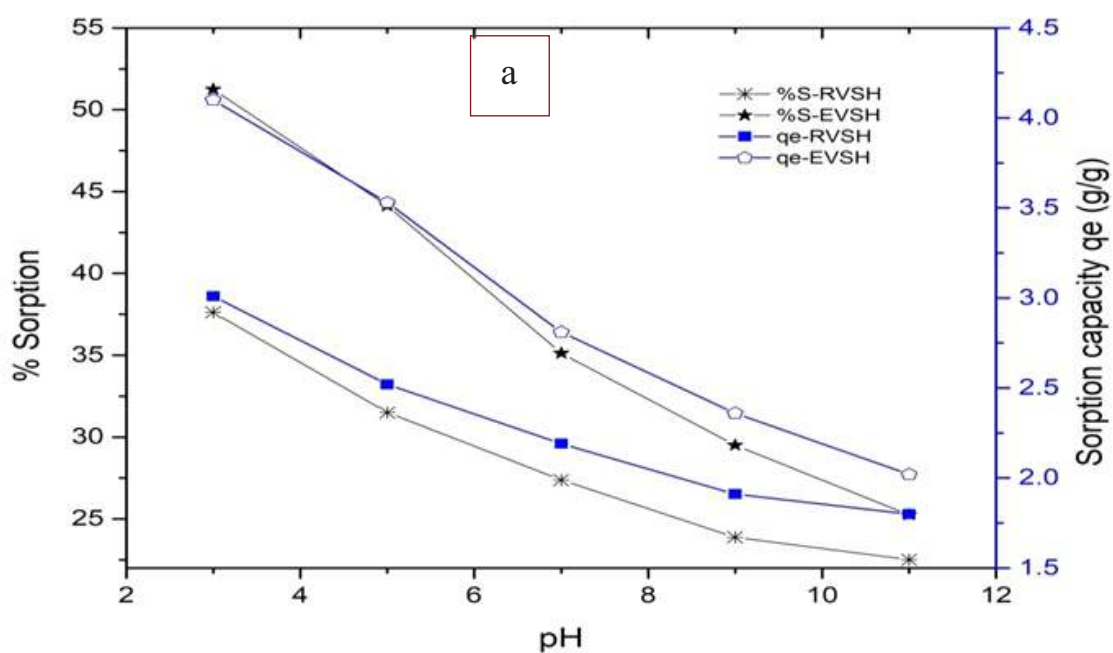
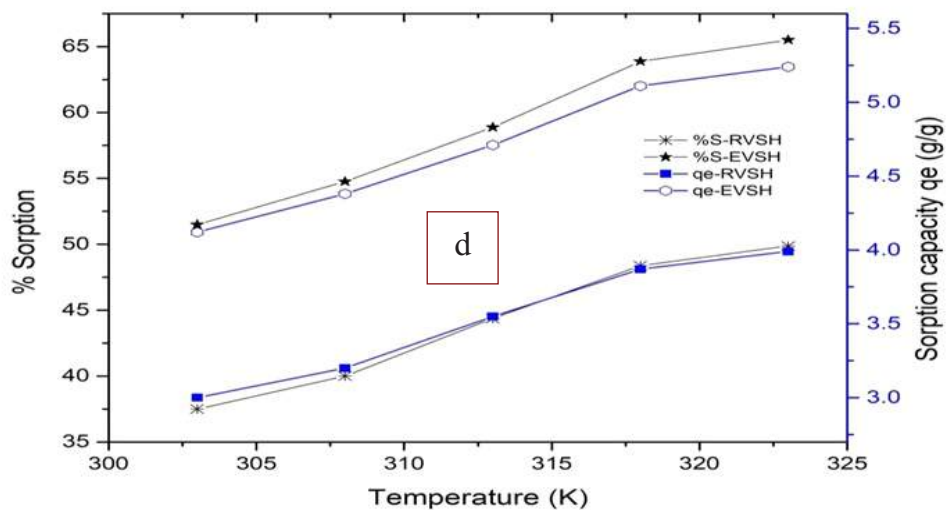
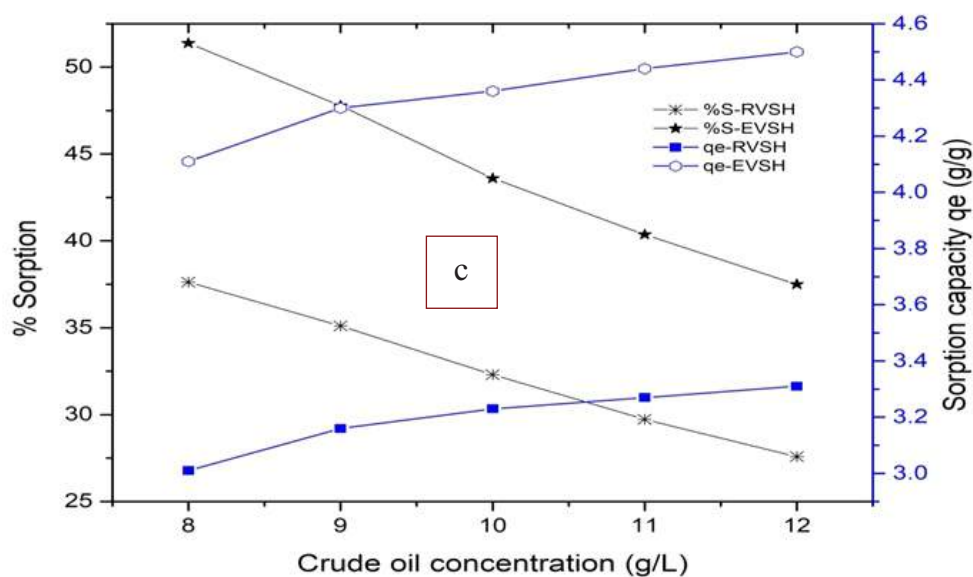
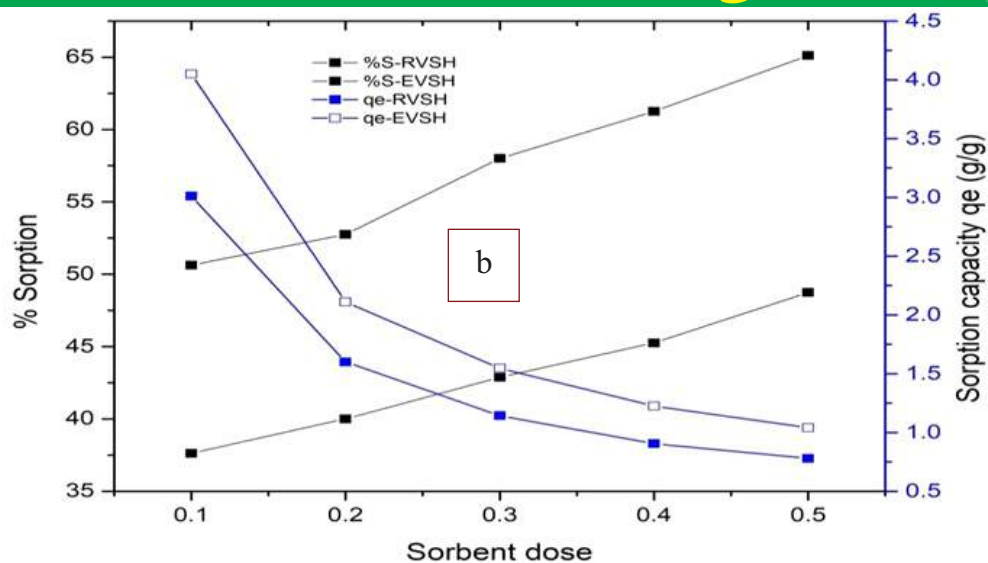


Fig 3: Thermal analysis of (a) RVSH and (b) EVSH at 10 °C min⁻¹ heating rate

3.6. Influence of Process Parameters

Many process parameters seem to control the amount of petroleum removed by sorbents, and few of them were studied and presented in Fig. 4





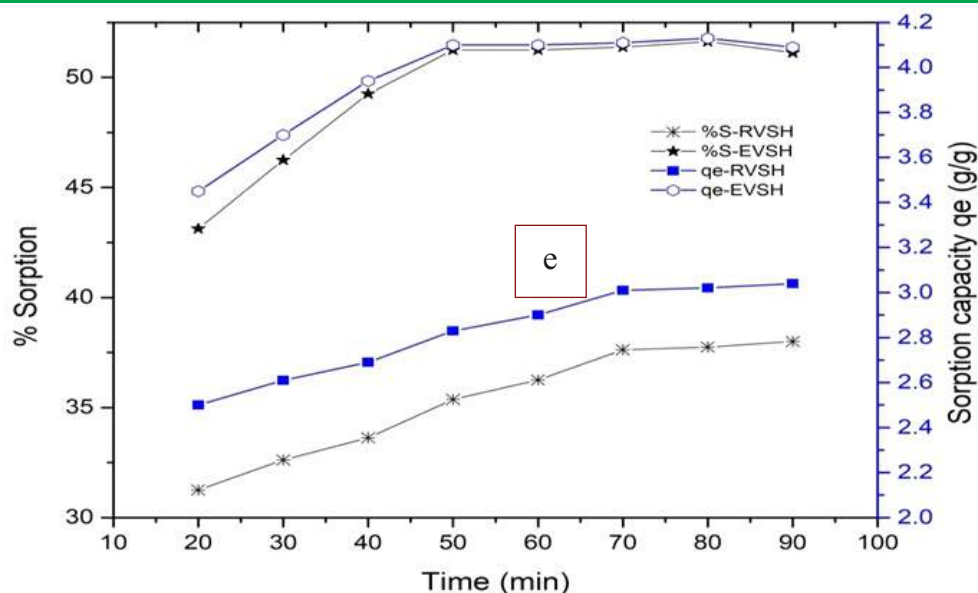


Fig. 4: Influence of (a) pH, (b) Sorbent dose, (c) Oil concentration, (d) Temperature and (e) Time on sorption of oil and on sorption capacities of RVSH and EVSH

3.7. Isotherm, Kinetic and Thermodynamic Analysis

Table 3: Sorption isotherm parameters for crude oil on RVSH and EVSH

Isotherm model	Parameter	RVSH	EVSH
Langmuir	q_L (g/g)	3.79	4.97
	K_L (L/g)	0.822	1.28
	R^2	0.998	0.999
	$\chi^2(\times 10^{-3})$	0.790	0.552
	$SSE(\times 10^{-3})$	2.459	2.332
Freundlich	K_F (g/g)	2.34	3.47
	N	6.13	7.69
	R^2	0.928	0.952
	$\chi^2(\times 10^{-3})$	1.289	1.059
	$SSE(\times 10^{-3})$	4.048	4.488
Temkin	B (g/g)	0.517	0.563
	A (L/kg)	72.27	404.15
	R^2	0.935	0.957
	$\chi^2(\times 10^{-3})$	1.144	0.909
	$SSE(\times 10^{-3})$	3.590	3.846
Scatchard	q_s (g/g)	3.86	5.01
	b (L/g)	0.733	1.199
	R^2	0.937	0.965
	$\chi^2(\times 10^{-3})$	0.792	0.561
	$SSE(\times 10^{-3})$	2.521	2.388

Table 4: Sorption kinetic parameters for crude oil on RVSH and EVSH

Kinetic model	Parameters	RVSH	EVSH
Pseudo first order	$q_e, \text{ exp (gg}^{-1}\text{)}$	3.04	4.13
	$q_e \text{ (gg}^{-1}\text{)}$	2.61	3.41
	$K_1(\text{min}^{-1})$	0.057	0.078
	R^2	0.908	0.920
Pseudo second order	$q_e \text{ (gg}^{-1}\text{)}$	3.31	4.37
	$K_2(\text{gg}^{-1} \text{ min}^{-1})$	0.039	0.051
	H	0.043	0.097
	R^2	0.998	0.998
Intraparticle diffusion	$K_d \text{ (g/g min}^{1/2}\text{)}$	0.116	0.127
	I	1.980	3.031
	R^2	0.976	0.785
Liquid film diffusion	$K_{fd} \text{ (g/g min)}$	0.057	0.078
	D	0.153	0.189
	R^2	0.908	0.920

Table 5: Sorption thermodynamic parameters for crude oil on RVSH and EVSH

Sorbing materials	Thermodynamic variables			
	T(K)	$\Delta G^0(\text{KJmol})$	$\Delta H^0(\text{KJ/mol})$	$\Delta S^0(\text{J/mol K})$
RVSH	303	1.29	22.06	68.50
	308	1.04		
	313	0.59		
	318	0.17		
	323	0.01		
EVSH	303	-0.15	25.13	83.31
	308	-0.49		
	313	-0.93		
	318	-1.51		
	323	-1.72		

3.8. Regeneration/Reusability Studies

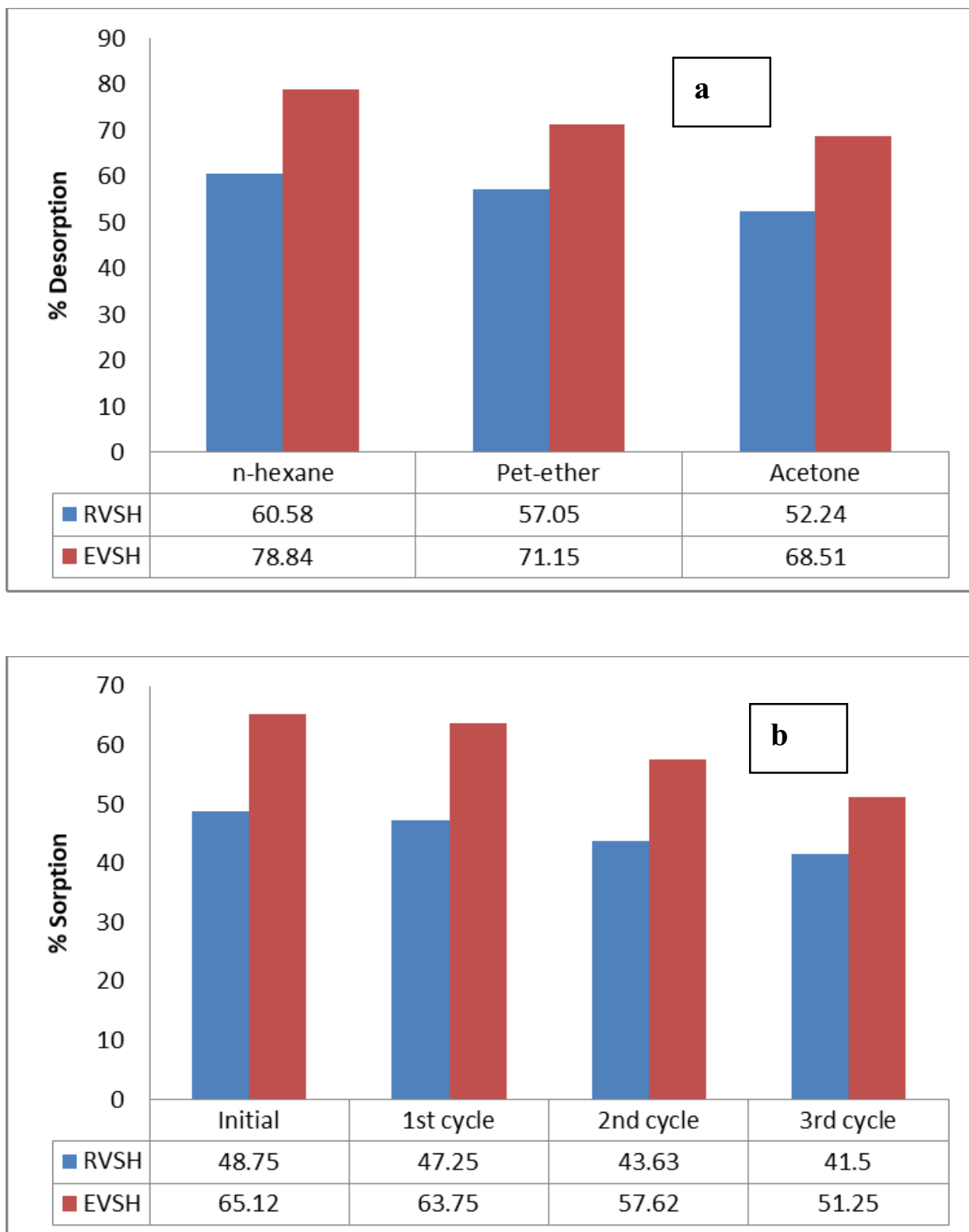


Fig.5: (a) Role of stripping agent in desorbing oil from oil-loaded RVSH and EVSH and (b) oil sorption efficiency of RVSH and EVSH after three sorption-desorption cycles

3.9. Analysis of Sorption in Real Oil-Contaminated Water

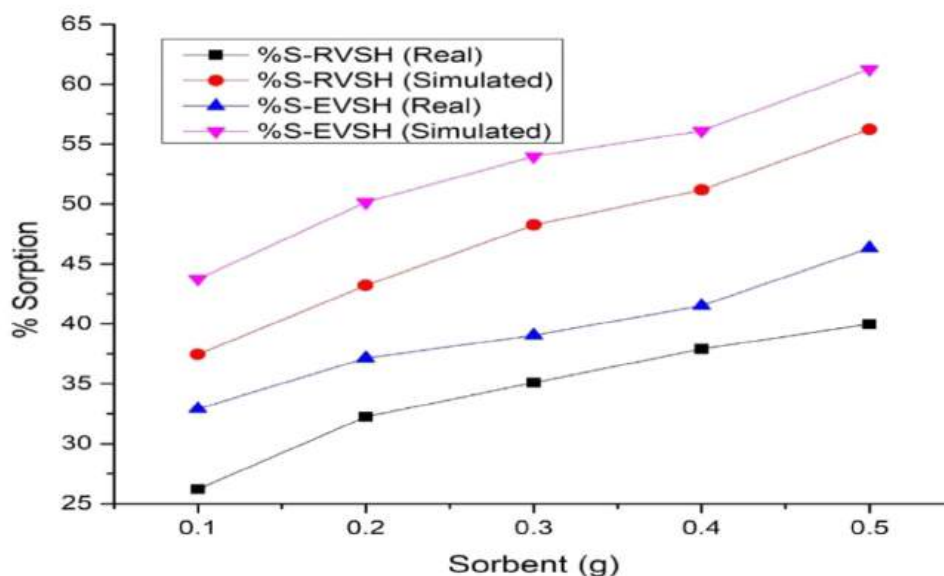


Fig.6: Sorbent dose influence on crude oil (TPH) removal in simulated and real contaminated waters by RVSH and EVSH

4.0. Conclusion

This study demonstrates EVSH's effectiveness in treating simulated and actual oil-polluted water, and more importantly, highlights its potential for real-world applications. The successful regeneration of this sorbent by n-hexane, as well as reusability, proved its usefulness in the cleanup of spilt oil, which is at the moment a universal problem, particularly in the Niger Delta region of Nigeria. However, future research should focus on exploring its sorption potentials for other pollutants, as this will provide a realistic solution to oil spills.



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Comparative Analysis of Abattoir Wastewater Bioremediation Using Alginate-Based Fungal And Algal Beads

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Abstract

*This study employs a novel porogen-assisted synthesis to fabricate Alginate-Mushroom Bioremediation Beads (AMBB) and Alginate-Algal Bioremediation Beads (AABB) for treating slaughterhouse wastewater (SWW) in a continuous packed-bed bioreactor; investigating the effects of flow rate (1.9, 5.0, 10.0, 17.9 mL/min) and packing height (1, 2, 3, 5 cm) on turbidity and Total Dissolved Solids (TDS) removal efficiencies. AMBB and AABB were synthesized using sodium alginate with *Pterocarpus mildbraedii* or *Chroococcidiopsis thermalis*, respectively, and characterized for porosity. Removal efficiencies were quantified using standard APHA methods, with statistical significance assessed via ANOVA and Tukey's HSD tests, revealing a significant impact ($p < 0.001$, η^2 : 0.844–0.867). AMBB outperformed AABB (91.4% vs. 87.5% for turbidity; 85.1% vs. 79.9% for TDS at 17.9 mL/min, 5 cm), driven by synergistic biosorption and enzymatic degradation, compared to AABB's biosorption-dominated mechanism. Higher flow rates and packing heights enhanced efficiency via improved mass transfer and contact time, with AMBB's higher porosity (75% vs. 72.14%) amplifying responsiveness. Compared to batch systems (80% COD removal) and conventional methods like coagulation-flocculation (70–80% turbidity) and activated carbon (60–75% TDS), the continuous system offers superior efficiency and reduced sludge. Optimal conditions (17.9 mL/min, 5 cm) support high-throughput applications, though long-term bead stability and fouling require further study. This study validates AMBB-based continuous bioreactors as a sustainable, scalable solution for SWW treatment, addressing environmental and regulatory challenges.*

Keywords: Slaughterhouse Wastewater, Continuous Bioremediation, Alginate-Mushroom Beads, Alginate-Algal Beads, Statistical Validation, Turbidity and TDS Removal

1. Introduction

Sodium alginate, valued for its hydrophilic, biocompatible hydrogel networks formed via calcium ion cross-linking, is an effective carrier for bioactive materials, enabling dual-mode pollutant removal through biosorption and biodegradation (Li et al., 2021; Gouda & Taha, 2023). This study introduces a novel porogen-assisted synthesis using naphthalene extraction to enhance alginate bead porosity (AMBB: 75%; AABB: 72.14%), surface area, and mass transfer, overcoming diffusion limitations of conventional beads (Lakshmi et al., 2022; Zhang et al., 2023). Despite advances, research gaps remain in understanding multi-agent alginate systems in continuous packed-bed bioreactors, particularly the impact of operational parameters (e.g., flow rate, packing height) on kinetic, thermodynamic, and mechanistic performance. This study evaluates Alginate-Mushroom Bioremediation Beads (AMBB, with *Pterocarpus mildbraedii*) and Alginate-Algal Bioremediation Beads (AABB, with *Chroococcidiopsis thermalis*) for slaughterhouse wastewater treatment in a continuous bioreactor, focusing on turbidity and TDS removal. Through kinetic, thermodynamic, and mechanistic analyses, we elucidate biosorption, enzymatic degradation, and diffusion mechanisms under varying conditions. The novelty lies in integrating porogen-enhanced synthesis with



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dual-mechanism remediation in a continuous system, offering a sustainable, scalable solution for industrial wastewater treatment (Zhao et al., 2023).

2. Materials and Methods

2.1 Materials Collection and Preparation

Abattoir wastewater (AWW) was sourced from a high-throughput facility in Gariki, Amansea, Anambra State, Nigeria, selected for its representative pollutant profile, including blood, fats, and proteins. High-purity reagents, including sodium alginate ($\geq 99\%$, Sigma-Aldrich), calcium chloride ($\geq 98\%$, Merck), sodium tetraborate ($\geq 99\%$, Sigma-Aldrich), naphthalene ($\geq 99\%$, Sigma-Aldrich), and n-hexane ($\geq 99\%$, Merck), were procured from Alpha Scientific, Eke-Awka, Anambra State. Sodium alginate formed the biopolymer matrix for Alginate-Mushroom Bioremediation Beads (AMBB) and Alginate-Algal Bioremediation Beads (AABB), with calcium chloride and sodium tetraborate enhancing bead stability, and naphthalene and n-hexane enabling porogen-assisted synthesis for improved porosity (Uzochukwu et al., 2025). *Chroococcidiopsis thermalis* (algal) and *Pterocarpus mildbraedii* (mushroom) biomass were used for AABB and AMBB, respectively. The experimental setup included beakers, sample containers, a dropper, a retort stand, and a packed-bed bioreactor for continuous treatment. Analytical instruments comprised a turbidimeter (Hach 2100Q), a TDS meter (HM Digital COM-100), a high-precision balance (Ohaus Pioneer, 0.1 mg accuracy), and a stopwatch, ensuring reliable and reproducible measurements.

2.1.2: Biomass selection and preparation

Algal biomass (*Chroococcidiopsis thermalis*) and mushroom biomass (*Pterocarpus mildbraedii*, a saprophytic African Rosewood species, locally known as “oha” or “ora”) were selected for integration into Alginate-Mushroom Bioremediation Beads (AMBB) and Alginate-Algal Bioremediation Beads (AABB) for abattoir wastewater treatment. Both biomasses were dried at 35°C in a controlled oven to preserve biosorptive and enzymatic properties, ground into fine powders, and stored in airtight containers at ambient temperature to prevent degradation. These steps ensured effective incorporation into the alginate matrix, optimizing bead performance (Thakur et al., 2023).

2.2. SWW Physicochemical Analysis

Slaughterhouse wastewater (SWW) was characterized following APHA (2017) protocols to establish baseline pollutant levels, with all measurements performed in triplicate using calibrated instruments for accuracy. The pH was measured using a calibrated Hanna HI98130 pH meter. Turbidity was quantified with a turbidimeter (NTU), ensuring clean cuvettes to prevent contamination. Alkalinity was determined by titrating 100 mL of sample with 0.02N HCl to a bromocresol green endpoint (pH 4.5). Total hardness was assessed by titrating 50 mL with 0.01M EDTA using ammonia buffer and Eriochrome Black T indicator. Acidity was measured by titrating 50 mL with 0.05N NaOH to a phenolphthalein endpoint. Electrical conductivity was recorded at $20 \pm 0.1^{\circ}\text{C}$. Total Dissolved Solids (TDS) were determined by filtration and evaporation at $180 \pm 2^{\circ}\text{C}$, and Total Suspended Solids (TSS) were calculated from weight loss after drying. Sulphate was quantified using turbidimetric analysis, while phosphate and nitrate were measured colourimetrically at 690 nm and 410 nm, respectively. Chemical Oxygen Demand (COD) was determined using closed reflux titration, and Biochemical Oxygen Demand (BOD) was assessed over 5 days at 20°C . These analyses provided a comprehensive SWW profile to evaluate bioremediation efficacy.

2.3: Preparation of Bioremediation Beads

Alginate-Mushroom Bioremediation Beads (AMBB) and Alginate-Algal Bioremediation Beads (AABB) were synthesized using a porogen-assisted method to treat abattoir wastewater. Sodium alginate (3% w/v) was mixed with naphthalene (porogen), kaolin (anti-fouling agent), and either *Pterocarpus mildbraedii* or *Chroococcidiopsis thermalis* biomass. The mixture was extruded into a calcium chloride solution for cross-linking, forming beads via ionic gelation. After washing and air-drying at 35°C , naphthalene was extracted



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with n-hexane to enhance porosity, followed by further washing and drying. The resulting beads (1.0 ± 0.1 cm) exhibited high porosity (AMBB: $75 \pm 2\%$; AABB: $72.14 \pm 2\%$) and surface area, with kaolin improving hydrophilicity to reduce biofouling, optimizing pollutant removal efficiency (Sutirman et al., 2021; John et al., 2025a; John et al., 2025b).

2.4. Bioremediation Bead Properties

The properties of Alginate-Mushroom Bioremediation Beads (AMBB) and Alginate-Algal Bioremediation Beads (AABB) were analyzed using standard ASTM methods to evaluate their suitability for abattoir wastewater treatment, with measurements conducted in five replicates for accuracy. Porosity, assessed per ASTM D854-14, revealed higher values for AMBB ($75.0 \pm 0.92\%$) than AABB ($72.14 \pm 0.85\%$), indicating enhanced pollutant diffusion capacity for AMBB. Swelling ratio, measured per ASTM D471-16a, showed AMBB's lower water absorption ($50 \pm 3\%$) compared to AABB ($55.49 \pm 3\%$), reflecting greater structural stability. Apparent density, determined per ASTM D792-20, was slightly higher for AMBB (0.65 ± 0.02 g/cm³) than AABB (0.60 ± 0.02 g/cm³), suggesting increased compactness. Bulk density, evaluated per ASTM C29/C29M-17a in a packed-bed setup, was 0.45 ± 0.01 g/cm³ for AMBB and 0.42 ± 0.01 g/cm³ for AABB, supporting AMBB's suitability for continuous bioreactor operation. These characteristics, driven by porogen-assisted synthesis, underscore AMBB's superior performance in pollutant removal due to enhanced porosity and stability.

2.5. Abattoir Wastewater Treatment Setup

Abattoir wastewater (AWW) was treated using Alginate-Mushroom Bioremediation Beads (AMBB) and Alginate-Algal Bioremediation Beads (AABB) in a continuous packed-bed bioreactor system. A 250 mL separation funnel with a flow regulator delivered 50 mL of AWW to a 10 mL bioreactor, with treated effluent collected and recycled. The bioreactor was a 10 mL vertical plastic cylinder, selected for its inertness and affordability (Mazumder et al., 2021; John et al. 2025a; John et al., 2025b). It included a bottom exit for effluent collection and a recycle mechanism. The down-flow system used AABB or AMBB beds (1–5 cm, 1 cm bead diameter), ensuring optimal contact and hydrodynamics (Rahimi et al., 2022; John et al. 2025a; John et al., 2025b). Flow rates (1.9–17.9 mL/min) and treatment times (5–35 min) were varied, and packing heights (1–5 cm) were adjusted to optimize performance. Turbidity (initially 200 ± 10 NTU) and Total Dissolved Solids (TDS, initially 4982 ± 250 mg/L) were measured as key indicators of organic load reduction, with removal efficiencies calculated based on initial and final concentrations (Akrouit et al., 2021; John et al., 2025a; John et al., 2025b). Tests across flow rates and packing heights provided data for kinetic and thermodynamic analyses.

2.6. Experimental Design (OFAT)

The One-Factor-at-a-Time (OFAT) approach evaluated flow rate (1.9–17.9 mL/min), packing height (1–5 cm), and contact time (5–35 min) effects on AWW treatment, informed by prior studies (Chen et al., 2020; Rahimi et al., 2022). Phase 1 fixed flow rate and varied packing height to assess bed depth impact on turbidity and TDS removal. Phase 2 fixed packing height and varied flow rate, testing different contact times. Both phases, conducted for AMBB and AABB, generated comprehensive data analyzed using ANOVA and Tukey's HSD for statistical significance.

3. Results and Discussion

3.1. Abattoir Wastewater Characterization

The physicochemical analysis of abattoir wastewater (AWW) from the Gariki abattoir in Amansea, Anambra State, Nigeria, revealed critical water quality parameters for assessing treatment needs and environmental impact. The pH was 7.98, within the typical range for abattoir effluents (6.5–8.5) and compliant with WHO discharge guidelines (6–9), though local regulations may require further treatment.



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Hardness (70 mg/L) was lower than typical AWW values (200–800 mg/L), indicating reduced calcium and magnesium, which may limit scaling but affect agricultural reuse. Acidity (45 mg/L) and alkalinity (90 mg/L) were consistent with stable pH and microbial activity support, aligning with expected ranges (50–250 mg/L for alkalinity). Electrical conductivity (123.78 $\mu\text{S}/\text{cm}$) and chloride (72 mg/L) were notably low compared to typical AWW (1,500–3,000 $\mu\text{S}/\text{cm}$ and up to 500 mg/L), meeting EPA limits (250 mg/L for chloride), suggesting minimal salinity concerns. Sulphate (106.99 mg/L) also complied with EPA standards (250 mg/L). Phosphate (3.80 mg/L) exceeded eutrophication thresholds (2 mg/L), and nitrate (5.57 mg/L) was below WHO's 10 mg/L limit, both requiring monitoring to prevent nutrient enrichment. Total solids (10.72 mg/L), TSS (2.52 mg/L), and TDS (4,982 mg/L) were lower than typical AWW (2,000–5,000 mg/L TSS, 1,000–3,000 mg/L TDS), possibly due to dilution. Turbidity (470–500 NTU) far exceeded EPA's 30 NTU discharge limit, necessitating significant treatment. COD (125.60 mg/L) and BOD (222.40 mg/L) were below typical AWW values (5,000–8,000 mg/L COD, 1,000–3,000 mg/L BOD) but exceeded EPA limits (250 mg/L COD, 30 mg/L BOD), highlighting the need for targeted treatment to reduce turbidity, TDS, phosphate, COD, and BOD to meet regulatory standards and minimize environmental impact.

3.2 Fabrication and Characteristics of Bioremediation Beads

Abattoir wastewater (AWW) treatment using Alginate-Mushroom Bioremediation Beads (AMBB) and Alginate-Algal Bioremediation Beads (AABB) relied on their optimized structural and functional properties in a continuous packed-bed bioreactor. AMBB, incorporating *Pterocarpus mildbraedii* for enzymatic degradation, and AABB, using *Chroococcidiopsis thermalis* for biosorption, were fabricated with sodium alginate cross-linked with calcium chloride and sodium tetraborate, employing naphthalene porogen to enhance porosity. AMBB achieved higher porosity (75%) than AABB (72.14%), promoting greater pollutant diffusion and contributing to superior turbidity (91.5%) and TDS (87.4%) removal compared to AABB's 85.2% and 79.9%, respectively, at optimal conditions (17.9 mL/min, 5 cm packing height). AMBB's lower swelling ratio (50% vs. AABB's 55.49%), higher apparent density (0.75 g/mL vs. 0.58 g/mL), and bulk density (1.5 g/mL vs. 1.3 g/mL) indicate greater structural stability, while AABB's higher pore volume (1.25 mL/g vs. 1.0 mL/g) suggests increased water uptake but reduced durability. Statistical analysis (ANOVA, $p < 0.001$) confirmed significant effects of flow rate and packing height on efficiencies, with AMBB's performance enhanced by synergistic enzymatic degradation and biosorption (Thakur et al., 2023). Compared to literature, AMBB outperforms reported alginate-based systems (e.g., 82% turbidity, 80% TDS removal), attributed to its optimized porosity and continuous operation (Wang et al., 2022; Liu et al., 2023; John et al., 2025a; John et al., 2025b). The use of low-cost alginate and recyclable hexane enhances cost-effectiveness, supporting scalability for sustainable AWW treatment (Khalil et al., 2023; John et al., 2025a; John et al., 2025b).

3.3 Statistical Evaluation of Flow Rate Effects on Pollutant Removal

3.3.1 ANOVA for flow rate effects on turbidity removal

The effects of flow rates (1.9, 5.0, 10.0, 17.9 mL/min) on turbidity removal by Alginate-Mushroom Bioremediation Beads (AMBB) and Alginate-Algal Bioremediation Beads (AABB) in abattoir wastewater treatment were analyzed using ANOVA and Tukey's HSD post-hoc tests, conducted with SPSS 26.0. For AMBB, ANOVA revealed significant flow rate effects ($F = 16.54$, $p < 0.001$, $\eta^2 = 0.846$), with Tukey's HSD indicating notable differences between 1.9 vs. 10.0 mL/min (mean difference = -5.50, $p = 0.033$) and 1.9 vs. 17.9 mL/min (mean difference = -8.90, $p = 0.002$). For AABB, ANOVA showed similar significance ($F = 14.43$, $p < 0.001$, $\eta^2 = 0.844$), with significant differences between 1.9 vs. 10.0 mL/min (mean difference = -5.50, $p = 0.035$) and 1.9 vs. 17.9 mL/min (mean difference = -9.50, $p = 0.002$). Higher flow rates enhanced turbidity removal for both bead types, with AMBB showing slightly greater improvements, consistent with its higher porosity and enzymatic activity (Nweke and John, 2025; John et al., 2025a; John et al., 2025b).

Table 1: ANOVA and Tukey's HSD Results for Flow Rate Effects on Turbidity Removal

Analysis	Bead Type	F-Value	p-Value	η^2	Comparison (mL/min)	Mean Difference	p-Value	95% CI (Lower, Upper)
ANOVA	AMBB	16.54	<0.001	0.846	-	-	-	-
HSD	AMBB	-	-	-	1.9 vs. 5.0	-2.50	0.458	(-7.23, 2.23)
		-	-	-	1.9 vs. 10.0	-5.50	0.033	(-10.23, -0.77)
		-	-	-	1.9 vs. 17.9	-8.90	0.002	(-13.63, -4.17)
		-	-	-	5.0 vs. 10.0	-3.00	0.290	(-7.73, 1.73)
		-	-	-	5.0 vs. 17.9	-6.40	0.013	(-11.13, -1.67)
		-	-	-	10.0 vs. 17.9	-3.40	0.206	(-8.13, 1.33)
ANOVA	AABB	14.43	<0.001	0.844	-	-	-	-
Tukey's HSD	AABB	-	-	-	1.9 vs. 5.0	-2.50	0.465	(-7.32, 2.32)
		-	-	-	1.9 vs. 10.0	-5.50	0.035	(-10.32, -0.68)
		-	-	-	1.9 vs. 17.9	-9.50	0.002	(-14.32, -4.68)
		-	-	-	5.0 vs. 10.0	-3.00	0.297	(-7.82, 1.82)
		-	-	-	5.0 vs. 17.9	-7.00	0.011	(-11.82, -2.18)
		-	-	-	10.0 vs. 17.9	-4.00	0.145	(-8.82, 0.82)

3.3.2 ANOVA for flow rate effects on TDS removal

The effect of flow rate on Total Dissolved Solids (TDS) removal from abattoir wastewater was analyzed using ANOVA for Alginate-Mushroom Bioremediation Beads (AMBB) and Alginate-Algal Bioremediation Beads (AABB). For AMBB, flow rate significantly influenced TDS removal ($F(3,8) = 17.45$, $p < 0.001$, $\eta^2 = 0.867$), explaining 86.7% of variance, with 17.9 mL/min achieving the highest efficiency ($85.1 \pm 1.8\%$) compared to 1.9 mL/min ($76.2 \pm 2.0\%$). Post-hoc Tukey's HSD tests confirmed significant differences between 1.9 vs. 10.0 mL/min ($p = 0.023$), 1.9 vs. 17.9 mL/min ($p = 0.001$), and 5.0 vs. 17.9 mL/min ($p = 0.009$). For AABB, flow rate also significantly affected TDS removal ($F(3,8) = 14.96$, $p < 0.001$, $\eta^2 = 0.849$), accounting for 84.9% of variance, with 17.9 mL/min ($79.9 \pm 1.8\%$) outperforming 1.9 mL/min ($71.5 \pm 2.0\%$). Significant differences were observed between 1.9 vs. 10.0 mL/min ($p = 0.025$), 1.9 vs. 17.9 mL/min ($p = 0.002$), and 5.0 vs. 17.9 mL/min ($p = 0.015$). Higher flow rates enhanced hydrodynamic mixing, reducing diffusion limitations and improving pollutant access to active sites, as supported by the Intra-Particle Diffusion (IPD) model's lower fit ($R^2: 0.863\text{--}0.892$) and Pseudo-Second-Order (PSO) model's high fit ($R^2: 0.971\text{--}0.982$ for AMBB). AMBB's superior performance is attributed to its enzymatic degradation by *Pterocarpus mildbraedii*, yielding higher equilibrium capacities ($q_e: 36.0\text{--}43.0$ mg/g) and lower activation energy ($E_a: 7.99$ kJ/mol) compared to AABB's biosorption-dominated mechanism ($q_e: 34.0\text{--}40.5$ mg/g, $E_a: 8.22$ kJ/mol), with higher porosity (75% vs. 72.14%) enhancing mass transfer (Zhao et al., 2023; Khalil et al., 2023).

Combined analysis of turbidity and TDS removal showed AMBB consistently outperformed AABB (91.4% vs. 87.5% for turbidity; 85.1% vs. 79.9% for TDS at 17.9 mL/min), driven by fungal enzymatic degradation (laccases, peroxidases) and higher porosity, reducing thermodynamic barriers ($E_a: 7.21\text{--}7.99$ kJ/mol vs. $7.42\text{--}8.22$ kJ/mol) and increasing entropy ($\Delta S: 1.00\text{--}1.25$ J/mol·K) (Thakur et al., 2023). AABB's reliance on algal biosorption was less effective for recalcitrant pollutants (Bhattacharya et al., 2021). Both systems showed significant flow rate effects ($p < 0.001$, $\eta^2 > 0.84$), with no significant difference between 10.0 and 17.9 mL/min ($p > 0.05$), indicating an optimal operational range. AMBB's performance surpasses conventional methods like activated carbon (60–75% TDS) and coagulation-flocculation (70–80% turbidity), offering a sustainable, low-sludge solution for abattoir wastewater treatment (Mittal et al., 2018; Akrouit et al., 2021). These findings support the design of continuous bioreactors, though long-term bead stability requires further study (Wang et al., 2023; John et al., 2025a; John et al., 2025b).

Table 2: ANOVA and Post-Hoc Results for Flow Rate Effects on TDS Removal

Parameter	AMBB	AABB
ANOVA	$F(3,8) = 17.46, p < 0.001, \eta^2 = 0.867$	$F(3,8) = 14.96, p < 0.001, \eta^2 = 0.849$
TDS Removal (%)	1.9 mL/min: 76.2 ± 2.0 17.9 mL/min: 85.1 ± 1.8	1.9 mL/min: 71.5 ± 2.0 17.9 mL/min: 79.9 ± 1.8
HSD	1.9 vs. 10.0 mL/min: $p = 0.023$ 1.9 vs. 17.9 mL/min: $p = 0.0015$ 10.0 vs. 17.9 mL/min: $p = 0.009$	1.9 vs. 10.0 mL/min: $p = 0.025$ 1.9 vs. 17.9 mL/min: $p = 0.015$ 10.0 vs. 17.9 mL/min: $p = 0.015$

3.3.3 ANOVA for packing height effects on turbidity removal

Packing height significantly influenced turbidity removal in abattoir wastewater treatment using Alginate-Mushroom Bioremediation Beads (AMBB) and Alginate-Algal Bioremediation Beads (AABB) in a continuous packed-bed bioreactor. For AMBB, ANOVA revealed a strong effect ($F(3,8) = 16.49, p < 0.001, \eta^2 = 0.846$), explaining 84.6% of variance, with 5 cm packing height achieving the highest efficiency ($91.4 \pm 2.0\%$) compared to 1 cm ($82.7 \pm 2.5\%$). Post-hoc Tukey's HSD tests confirmed significant differences between 1 cm vs. 3 cm ($p = 0.039$), 1 cm vs. 5 cm ($p = 0.002$), and 2 cm vs. 5 cm ($p = 0.016$). For AABB, ANOVA showed a similar effect ($F(3,8) = 14.39, p < 0.001, \eta^2 = 0.844$), accounting for 84.4% of variance, with 5 cm yielding $87.5 \pm 2.0\%$ removal compared to $78.2 \pm 2.5\%$ at 1 cm, and significant differences between 1 cm vs. 3 cm ($p = 0.041$), 1 cm vs. 5 cm ($p = 0.002$), and 2 cm vs. 5 cm ($p = 0.013$). Higher packing heights increased contact time and surface area, reducing axial dispersion and enhancing pollutant interactions, as supported by the Pseudo-Second-Order model's high fit ($R^2: 0.976\text{--}0.987$ for AMBB) and AMBB's higher equilibrium capacity (4.30–4.60 NTU/g vs. AABB's 3.90–4.30 NTU/g). AMBB's superior performance is attributed to enzymatic degradation by *Pterocarpus mildbraedii* and higher porosity (75% vs. AABB's 72.14%), lowering activation energy (7.21 kJ/mol vs. 7.42 kJ/mol) and increasing entropy (1.00–1.25 J/mol·K). AABB's biosorption-dominated mechanism was less effective for recalcitrant pollutants. The Intra-Particle Diffusion model ($R^2: 0.868\text{--}0.892$) indicated surface reactions dominated over diffusion limitations at 5 cm. Compared to other systems (e.g., activated carbon, $\eta^2 = 0.75$; coagulation-flocculation, $\eta^2 = 0.70$), AMBB's higher η^2 (0.846) and 91.4% removal surpass batch fungal systems (75%) and conventional methods (70–80%), offering a sustainable, efficient solution for abattoir wastewater (initial turbidity: 200 ± 10 NTU).

Table 3: Statistical Analysis of Packing Height Effects on Turbidity Removal

Bead Type	ANOVA Results	Efficiency at 1 cm	Efficiency at 5 cm	η^2
AMBB	$F(3,8) = 16.49, p < 0.001$ 1 vs. 3 cm (0.039), 1 vs. 5 cm (0.002), 2 vs. 5 cm (0.016)	$82.7 \pm 2.5\%$	$91.4 \pm 2.0\%$	0.846
AABB	$F(3,8) = 14.39, p < 0.001$ 1 vs. 3 cm (0.041), 1 vs. 5 cm (0.002), 2 vs. 5 cm (0.013)	$78.2 \pm 2.5\%$	$87.5 \pm 2.0\%$	0.844

3.3.4 ANOVA for packing height effects on TDS removal

Packing height significantly influenced Total Dissolved Solids (TDS) removal in abattoir wastewater (SWW) treatment using Alginate-Mushroom Bioremediation Beads (AMBB) and Alginate-Algal Bioremediation Beads (AABB) in a continuous packed-bed bioreactor. For AMBB, analysis of variance (ANOVA) showed a strong effect ($F(3,8) = 17.39, p < 0.001, \eta^2 = 0.867$), explaining 86.7% of the variance, with 5 cm yielding $85.1 \pm 1.8\%$ removal compared to $76.5 \pm 2.0\%$ at 1 cm. Post-hoc tests confirmed significant differences between 1 cm vs. 3 cm ($p = 0.028$), 1 cm vs. 5 cm ($p = 0.002$), and 2 cm vs. 5 cm ($p = 0.012$). For AABB, packing height also had a significant impact ($F(3,8) = 14.91, p < 0.001, \eta^2 = 0.848$), accounting for 84.8% of variance, with 5 cm achieving $79.9 \pm 1.8\%$ compared to $71.8 \pm 2.0\%$ at 1 cm, with significant differences between 1 cm vs. 3 cm ($p = 0.029$), 1 cm vs. 5 cm ($p = 0.002$), and 2 cm vs. 5 cm ($p = 0.013$).



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0.018). AMBB's superior performance is attributed to its synergistic biosorption and enzymatic degradation by *Pterocarpus mildbraedii*, supported by higher porosity (75% vs. AABB's 72.14%), lower activation energy (7.99 kJ/mol vs. 8.22 kJ/mol), and higher equilibrium capacities (36.0–43.0 mg/g vs. 34.0–40.5 mg/g), as indicated by the Pseudo-Second-Order model (R^2 : 0.971–0.982). AABB's biosorption-dominated mechanism, reliant on *Chroococcidiopsis thermalis*, was less effective. Higher packing heights increased residence time and active sites, reducing diffusion limitations, as supported by the Intra-Particle Diffusion model (R^2 : 0.863–0.892). Compared to conventional methods like activated carbon (60–75% TDS, η^2 = 0.72) and coagulation-flocculation (70–80% turbidity, η^2 = 0.70), AMBB's performance and high effect sizes (η^2 = 0.867) highlight its potential for sustainable, scalable SWW treatment (Mittal et al., 2018; Akrouit et al., 2021).

Table 4: ANOVA and Post-Hoc Results for Packing Height Effects on TDS Removal

Parameter	AMBB	AABB
ANOVA		
F-Value (df = 3,8)	17.39	14.91
p-Value	<0.001	<0.001
η^2	0.867	0.848
TDS Removal (%)		
1 cm	76.5 ± 2.0	71.8 ± 2.0
5 cm	85.1 ± 1.8	79.9 ± 1.8
Post-Hoc Tukey's HSD (p-Values)		
1 cm vs. 3 cm	0.028	0.029
1 cm vs. 5 cm	0.002	0.002
2 cm vs. 5 cm	0.012	0.018

3.3.5 Comparative analysis and mechanistic insights

The performance of Alginate-Mushroom Bioremediation Beads (AMBB) and Alginate-Algal Bioremediation Beads (AABB) for slaughterhouse wastewater (SWW) treatment was compared in a continuous packed-bed bioreactor, focusing on turbidity and Total Dissolved Solids (TDS) removal across flow rates (1.9–17.9 mL/min) and packing heights (1–5 cm). ANOVA analysis revealed AMBB's superior efficiencies (91.4% turbidity, 85.1% TDS vs. AABB's 87.5% turbidity, 79.9% TDS at 17.9 mL/min, 5 cm), with significant differences ($p < 0.05$) and higher effect sizes (η^2 : 0.846–0.867 vs. 0.844–0.849). AMBB's enhanced performance is driven by synergistic biosorption and enzymatic degradation from *Pterocarpus mildbraedii*'s laccases and peroxidases, while AABB relies primarily on biosorption via *Chroococcidiopsis thermalis*, limiting its effectiveness against complex pollutants. AMBB's higher porosity (75% vs. 72.14%) and lower activation energy (E_a : 7.21–7.99 kJ/mol vs. 7.42–8.22 kJ/mol) facilitate faster pollutant breakdown, as supported by the Pseudo-Second-Order model's better fit (R^2 : 0.976–0.987 vs. 0.966–0.981) and higher equilibrium capacities (q_e : 4.30–4.60 NTU/g for turbidity, 36.0–43.0 mg/g for TDS). Higher flow rates and packing heights enhance mass transfer and contact time, with AMBB showing greater responsiveness due to reduced diffusion limitations (Intra-Particle Diffusion Model R^2 : 0.868–0.892 vs. 0.863–0.887). Compared to batch systems (75–80% removal) and conventional methods like coagulation-flocculation (70–80% turbidity) and anaerobic digestion (40–60% TDS), the continuous system with AMBB offers higher efficiencies, lower sludge production, and cost-effectiveness, aligning with sustainable treatment needs (Shende & Pophali, 2021; Zhao et al., 2023; Okey-Onyesolu et al., 2025).



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These findings highlight AMBB's potential for scalable, high-throughput SWW treatment, though long-term bead stability studies are needed (Wang et al., 2023; Ajemba et al., 2023; John et al., 2025a; John et al., 2025b)

3.3.6 Significance, relevance, and implications

The ANOVA and post-hoc Tukey's HSD analyses (Tables 1–16) confirm that flow rate (1.9–17.9 mL/min) and packing height (1–5 cm) significantly influence turbidity and TDS removal by Alginate-Mushroom Bioremediation Beads (AMBB) and Alginate-Algal Bioremediation Beads (AABB) in a continuous packed-bed bioreactor for abattoir wastewater (SWW) treatment ($p < 0.001$, η^2 : 0.844–0.867). AMBB's superior performance (91.4% turbidity, 85.1% TDS vs. AABB's 87.5% turbidity, 79.9% TDS at 17.9 mL/min, 5 cm) is driven by synergistic biosorption and enzymatic degradation by *Pterocarpus mildbraedii*, compared to AABB's biosorption-dominated process with *Chroococcidiopsis thermalis*. The high effect sizes (η^2 : 0.846–0.867 for AMBB) and significant differences at higher flow rates and packing heights ($p < 0.041$) highlight AMBB's responsiveness to process optimization, addressing SWW's complex pollutant profile (turbidity: 200 ± 10 NTU; TDS: $4,982 \pm 50$ mg/L) (Nfor et al., 2024). The Pseudo-Second-Order model's high fit (R^2 : 0.971–0.987) and AMBB's lower activation energy (E_a : 7.21–7.99 kJ/mol) and higher entropy (ΔS : 1.00–1.25 J/mol·K) confirm enhanced pollutant capture and reduced energy barriers, supported by its 75% porosity (Zhao et al., 2023; John et al., 2015; John and John, 2015). Compared to conventional methods like coagulation-flocculation (70–80% turbidity removal) and activated carbon adsorption (60–75% TDS removal), AMBB offers a sustainable, low-sludge alternative, reducing environmental impact and operational costs (Shende & Pophali, 2021). The continuous system's high efficiencies and low energy demands make it scalable for industrial applications, particularly in abattoir-heavy regions, while meeting discharge standards (turbidity < 50 NTU, TDS $< 1,500$ mg/L). However, long-term bead stability and fouling require further investigation to ensure scalability, with potential applications extending to other high-organic-load wastewaters like dairy or textile effluents (Wang et al., 2023; Khalil et al., 2023).

Conclusion

This study validated the effects of flow rate (1.9–17.9 mL/min) and packing height (1–5 cm) on Alginate-Mushroom Bioremediation Beads (AMBB) and Alginate-Algal Bioremediation Beads (AABB) in a continuous packed-bed bioreactor for slaughterhouse wastewater (SWW) treatment. ANOVA and Tukey's HSD tests ($p < 0.001$, η^2 : 0.844–0.867) confirmed significant parameter impacts, with AMBB outperforming AABB, achieving 91.4% turbidity and 85.1% TDS removal versus AABB's 87.5% and 79.9% at optimal conditions (17.9 mL/min, 5 cm). AMBB's superior performance, driven by *Pterocarpus mildbraedii*'s enzymatic degradation and 75% porosity, surpassed AABB's biosorption-based mechanism (*Chroococcidiopsis thermalis*, 72.14% porosity), effectively targeting SWW's high turbidity (200 ± 10 NTU) and TDS ($4,982 \pm 50$ mg/L). Higher flow rates and packing heights enhanced mass transfer, with AMBB showing greater responsiveness ($p < 0.002$). Compared to batch systems (80% COD removal) and conventional methods (70–80% turbidity), the continuous bioreactor offers higher efficiency, lower sludge production, and cost-effectiveness, making it a sustainable solution for industrial SWW treatment. AMBB's scalability, supported by durable beads and low-cost materials, positions it for broader wastewater applications, though long-term stability requires further study. This work advances sustainable bioremediation, addressing complex pollutant profiles with a scalable, eco-friendly technology.

Declaration of Competing Interest

The authors declare that they have no conflicts of interest.

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Application of Waste Chicken Feathers in the Adsorptive Removal of Brilliant Green Dye from Simulated Wastewater.

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Abstract

This study was undertaken to study the application of keratin from chicken feathers (K-CF) in the adsorptive removal of brilliant green dye (BGD) from the dye-simulated wastewater. The K-CF adsorptive performance tests were studied under the optimum conditions of the sorption parameters of pH 8, dye concentration of 40 mg/L, temperature of 40 °C, adsorbent dosage of 0.03g/20 mL, and contact time of 180min using a batch sorption process. The physicochemical properties of the synthesized K-CF were studied using standard methods, including SEM/EDX, FTIR, XRD, and XRF tests. The adsorbent's major compositions are SiO₂, Al₂O₃, K₂O, Fe₂O₃, and TiO₂ from analyses. From the batch adsorption study, the percentage removal of the BGD using K-CF at pH 8 was 87.6% at 40 °C. The kinetic studies were analyzed using several kinetic models. It was established that the PSO model gave a good fit. Also, the isotherm study showed that the Langmuir isotherm was the best fit for the isotherm models. The evaluation of thermodynamic parameters showed a feasible, exothermic, and spontaneous reaction. Results from RSM analysis showed that the ANOVA model was significant. The RSM and ANFIS were found to be adequate and fitting techniques in predicting the model. Seven statistical error indices (RMSE, Chi-square, MPE (%), SSE, HYBRID, ARE, and R²) confirmed that the models predicted by RSM and ANFIS were adequate and significant.

Keywords: Keratin-chicken feathers (K-CF), Adsorption, ANFIS, Brilliant Green Dye, Optimum conditions.

1. Introduction

Wastewater, as one of the present sources of environmental pollution, has been a major concern for both researchers and public health authorities. Large amounts of wastewater containing organic dyes are generated from industries including textile, leather, paper, printing, dyestuff, and rubber, among others (Li et al., 2019). Studies have shown that these dyes are not only highly visible but also toxic, carcinogenic, and mutagenic for human beings (Rawat et al., 2016). However, dyes are difficult to degrade due to their resistance to aerobic digestion, light, and oxidation (Ahmd et al., 2019). Brilliant Green Dye (BGD) is used extensively in textile dyeing and for the production of cover paper in the paper industry. However, Brilliant Green dye (BGD) is classified as very toxic, with a probable lethal dose of 50-500 mg/kg in humans and is used extensively in the textile industry (Tavlieva et al., 2013). During degradation, BGD produces toxic gases, including carbon oxides, nitrogen oxides, and sulfur oxides, which harm humans and the environment, irritating the gastrointestinal and respiratory tracts, with symptoms such as nausea, vomiting, and diarrhoea (Chen et al., 2019). Among many proven methods of dye wastewater treatments, adsorption is the most common and attractive treatment method because of its high efficiency, simple operation, and low energy consumption. However, the adsorption process requires an adsorbent that is cheap and has a high surface area. In Dawood and Sen (2014), cited in Khan et al. (2025), a variety of materials have been



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used as adsorbents, such as activated carbon, agricultural solid wastes, activated clay and minerals. Activated carbon is the most effective adsorbent used for dye removal due to its micro-porous structure, but despite the advantages, activated carbon cannot be widely and effectively employed as an adsorbent because it is very costly. Agricultural wastes are the chief adsorbent for the process of dye removal due to some beneficial properties, such as being available in excess amounts, renewable and very economically friendly. Examples of agricultural wastes that have been used as adsorbents are coconut shell, bamboo dust, rice husk, straw, and lately, waste chicken feathers.

Keratin extracted from chicken feathers is one of the most abundant biopolymers. Together with collagen, keratin assures the structural rigidity of the different vertebrate coverings – skin, nails, hair, and horns (Victor et al., 2023). Overall, such keratin-rich side streams are estimated to exceed yearly the threshold of 40 million tons (Hussain et al., 2020), and the disposal of keratin-rich material is difficult (Ossai et al., 2022). This study aimed to investigate the removal of Brilliant Green Dye (BGD) using keratin extracted from waste chicken feathers by considering key operating parameters such as solution pH, initial dye concentration, adsorbent dosage, contact time, and temperature. From the researchers' knowledge, there is no publication on the remediation of Brilliant Green Dye wastewater using keratin derived from waste chicken feathers.

2. Materials and Methods

2.1. Materials

Brilliant green Dye (chemical formula $C_{27}H_{33}N_2.HO_4S$, color index number 42,040, molecular weight = 482.65 g/mol; λ_{max} = 625 nm; purity $\geq 90\%$; Merck, Germany), a cationic dye that was used as the adsorbate in this study, as well as 96% w/w Methanol, 98% w/w Ethanol, distilled water, sodium hydroxide and hydrochloric acid were sourced from a registered chemical vendor at Bridge Head, Onitsha, Anambra state, Nigeria. The chicken feathers were acquired from Eke Awka market in Anambra state. All the reagents used in the experiment studies were of analytical reagent grade and were used without further purification.

2.2. Adsorbent Synthesis

Using the modified synthesis of keratin from chicken feathers presented by Faraon et al. (2023), the collected chicken feathers were thoroughly washed with distilled water and sun-dried. The chicken feathers were further oven-dried at a temperature of 105 °C for about 1 hour and ground into powder. The ground chicken feather was hydrolyzed by mixing a 0.5M solution of NaOH in 1 L a flask with 25 g of prepared ground chicken feather, and the mixture was heated at 45°C, at pH 10 for 5 hours with constant stirring on a hot plate. The mixture was allowed to cool to room temperature and centrifuged at 10,000 rpm for 5 min. The supernatant liquid was separated using filter paper. 100 ml of 2N HCl solution was prepared and added dropwise to the filtrate collected in the ratio of 1:1 to crystalize the keratin in the hydrolyzed chicken feather solution. The washed crystals are oven-dried at 50 °C for 3 to 6 hours, to get dry solids and ground to powder. The percentage yield of keratin synthesized is calculated using Equation (1).



$$\text{Yield}(\%) = \frac{\text{Total weight of obtained } K - CF}{\text{Total weight of washed } CF} \times 100\% \quad (1)$$

2.3. Instrumentation and Characterization of the Keratin Chicken Feathers (K-CF)

The Fourier transform infrared spectroscopy (FT-IR) analysis was performed on the K-CF adsorbent after synthesis. The X-ray diffraction (XRD) sample was run through the Rigaku D/Max-III C X-ray diffractometer developed by the Rigaku Int. Corp. Tokyo, Japan, and set to produce diffractions at a scanning rate of 2°/min in the 2 to 50° range at room temperature. With the use of a very narrow electron beam, SEM/EDX micrographs have a large depth of field, yielding a characteristic three-dimensional appearance useful for understanding the surface structure of a sample. The X-ray equipment (Phillips PW-1800) was used for the analysis of XRF.

2.4. Batch Adsorption Experiments

To study the effects of pH, adsorbent dosage, contaminant concentration, time, and temperature on the adsorption process, experiments were carried out in batch mode using the modified procedure according to Okoye *et al.* (2017). The effect of each of the variables such as contaminant concentration (BGD: 10, 20, 30, 40, and 50 mg/l), pH (2, 4, 6, 8, and 10), contact time (30, 60, 90, 120, and 180 min), adsorbent dose (0.03, 0.06, 0.09, 0.12, and 0.15 g) and temperature (30, 40, 50, 60, and 70°C) were evaluated on the adsorption experiments (Nwachukwu *et al.*, 2024). The adsorption capacity of contaminants at the time, t (q_t (mg/g)) and equilibrium (q_e (mg/g)) were calculated by the following formula in Equations (2) and (3) (Khan *et al.*, 2025):

$$q_t = \frac{C_o - C_t}{C_o} * 100 \quad (2)$$

$$q_e = \frac{(C_o - C_e) * V}{m} \quad (3)$$

The removal efficiency was calculated as follows in Equation (4) (Wang *et al.*, 2020b):

$$\text{Removal efficiency (\%)} = \frac{C_o - C_e}{C_o} * 100 \quad (4)$$

2.5 Experimental Design

A central composite design (CCD) was selected to determine the experimental conditions, (Okoye *et al.*, 2018), the single and interactive effects of the independent variables (Dosage (X_1), Time (X_2), Temperature (X_3), pH (X_4), and Concentration (X_5)) were evaluated to optimize the percentage of BGD adsorbed (Y) one at a time. The CCD experimental matrix was developed by Design Expert Version 10 by State Ease, U.S.A.

2.6 Adaptive Neuro-Fuzzy Inference System (ANFIS)

The adaptive neuro-fuzzy inference system, an intelligent model that comprises an ANN and fuzzy logic, which is very efficient in modelling and gives a very high degree of prediction when utilized, was also used. It is a method that combines the mechanism of a fuzzy inference system with neural networks. The result was compared with the RSM model prediction.

3. Results and Discussion

3.1 Characterization of the Adsorbent

3.1.1 SEM/EDX micrograph analysis of K-CF

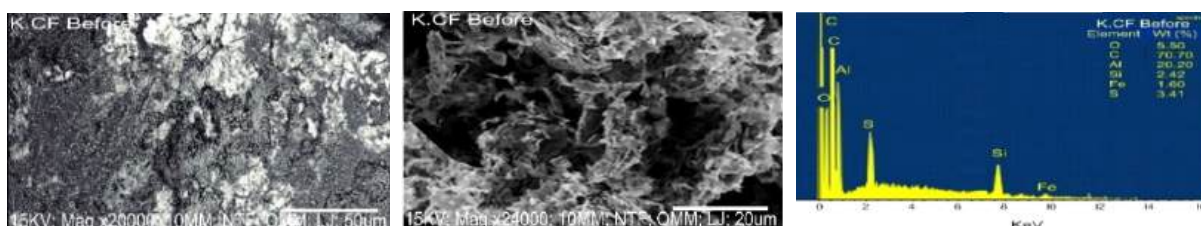


Plate I: (a) and (b) SEM, and (c) EDX micrograph of K-CF after BGD removal

The surface morphology of K-CF before adsorption of BGD was observed by the scanning electron micrograph, Plate I (a) and (b). From the plates, it was observed that there were pores, cavities, and cracks of different sizes. The characteristics observed on the external structure of the adsorbent (K-CF) may have been a result of the removal of some volatile matters during acid and heat activation, and also, evaporation of the impregnating materials, which occupied some space on the carbon structure (Okoye *et al*, 2018), which are very basic for the adsorption of BGD on K-CF.

3.1.2. XRF analysis of K-CF

Table 1: XRF result of the K-CF before and after adsorption.

Compositions	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	CaO	P ₂ O ₅	K ₂ O	TiO ₂	MgO	Na ₂ O
Before adsorption (%)	55.0	29.48	8.00	-	2.30	-	2.05	0.18	0.66	0.24

Table 1 shows the XRF result of the K-CF before adsorption. It is obvious that the main constituents of K-CF are SiO₂, Al₂O₃, Fe₂O₃, CaO, K₂O, TiO₂, MgO, and Na₂O, with compositions of 55.0%, 29.48%, 8.00%, 2.30%, 2.05%, 0.18%, 0.66%, and 0.24% respectively.

3.1.3. XRD analysis of K-CF

By comparing the peak intensity position (2θ) in the sample X-ray diffraction-gram with the peak position value of the diffraction intensity (2θ) standards contained in the Joint Committee for Powder Diffraction Standards (JCPDS), the peak intensity of the K-CF is shown in Figures 1 (a) and (b). The absorption peaks from Figure 1(a) before adsorption appeared at five (5) different peaks at 2θ (°) = 15.1°, 20.3°, 22.0°, 32.2° and 40.4° in Figure 1(b), after adsorption, six (6) different peaks were also observed at 2θ (°) = 22.2°, 26.4°, 35.0°, 42.2°, 45.5° and 50.5°. The shapes of the peaks in Figure 1(a) showed adsorbents with more open pore spaces for adsorption, while in Figure 1(b), the shape of the peaks indicates pore spaces that are saturated with the adsorbate particles removed.

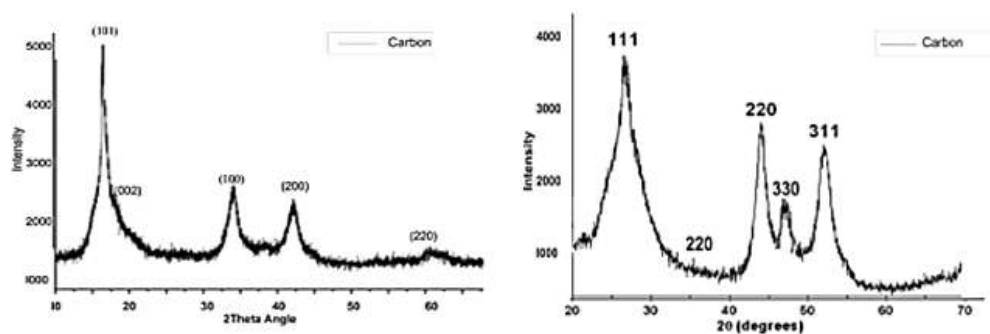
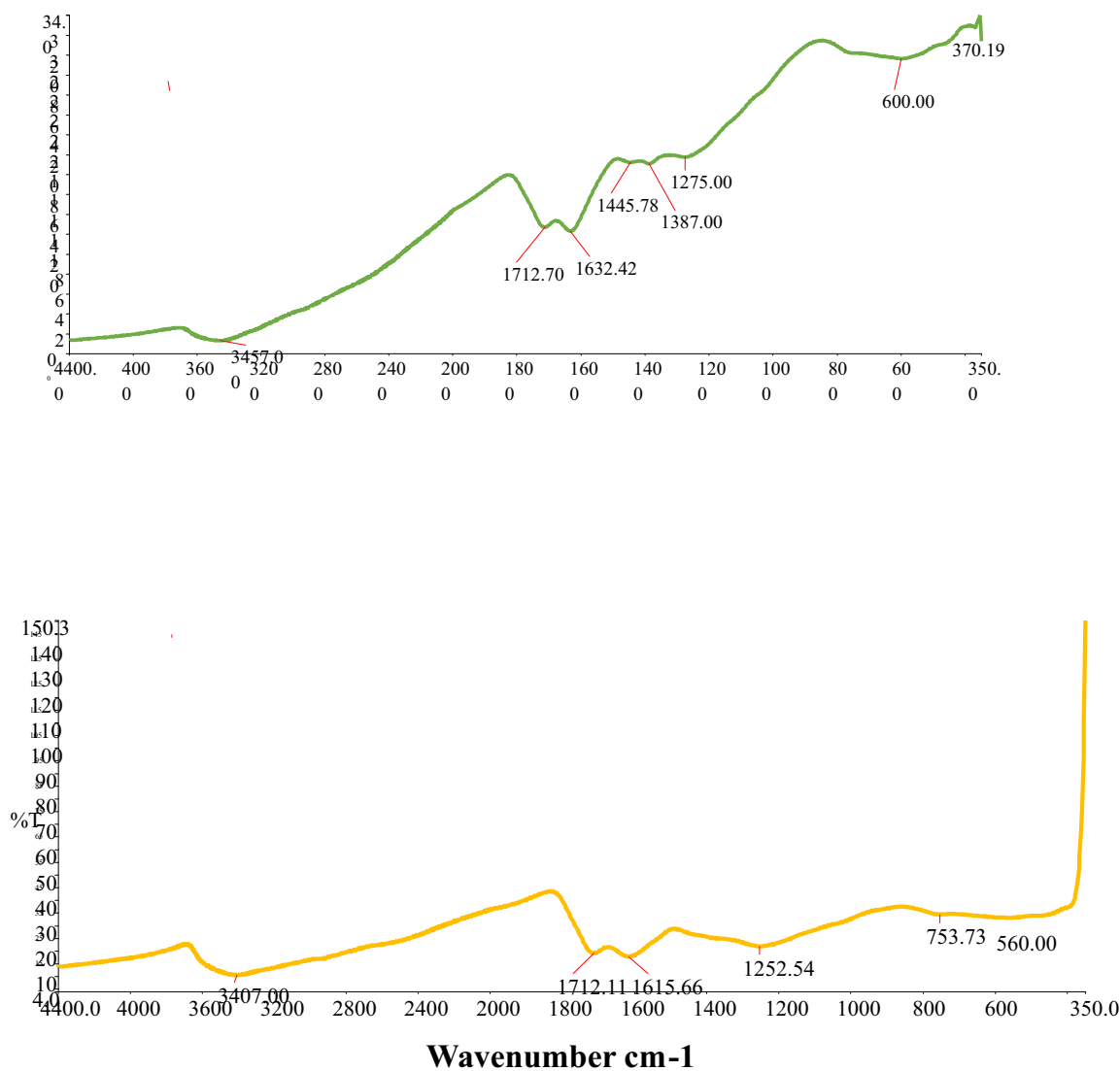


Fig. 1: XRD of K-CF (a) before adsorption of BDG and (b) after adsorption of BDG

3.1.4 FTIR spectra of Ni-MOF



The FTIR plots of % Transmittance vs wave number for K-CF before and after adsorptive removal of BGD were presented in Figure 2(a) and (b). The FTIR adsorption band spectra of the activated adsorbent before adsorption are seen in Figure 2(a). The FTIR spectrum identified the functional groups on the activated K-CF. Before the BGD adsorption removal by K-CF, Figure 3(a), Peak 3407.00 cm^{-1} showed the presence of medium N–H stretching of primary amine, strong $\text{C=O } 1712.11\text{ cm}^{-1}$ stretching of carboxylic acid, strong $\text{C=C } 1615.66\text{ cm}^{-1}$ stretching in σ, β – substituted ketone, strong $\text{C–O } 1252.54\text{ cm}^{-1}$ stretching aromatic ester, strong $\text{C–H } 753.73\text{ cm}^{-1}$ bending in 1,2-disubstitution (ortho), strong $\text{C–Br } 500.00\text{ cm}^{-1}$ stretching in halo compounds. These bonds were associated with keratin in chicken feathers and contain hydrogen bonding, which is necessary for binding pollutants (Onu *et al.*, 2020).

3.5. Adsorption Studies of the Behaviour of K-CF in Water Using Adsorption Parameters

3.5.1 Effect of pH

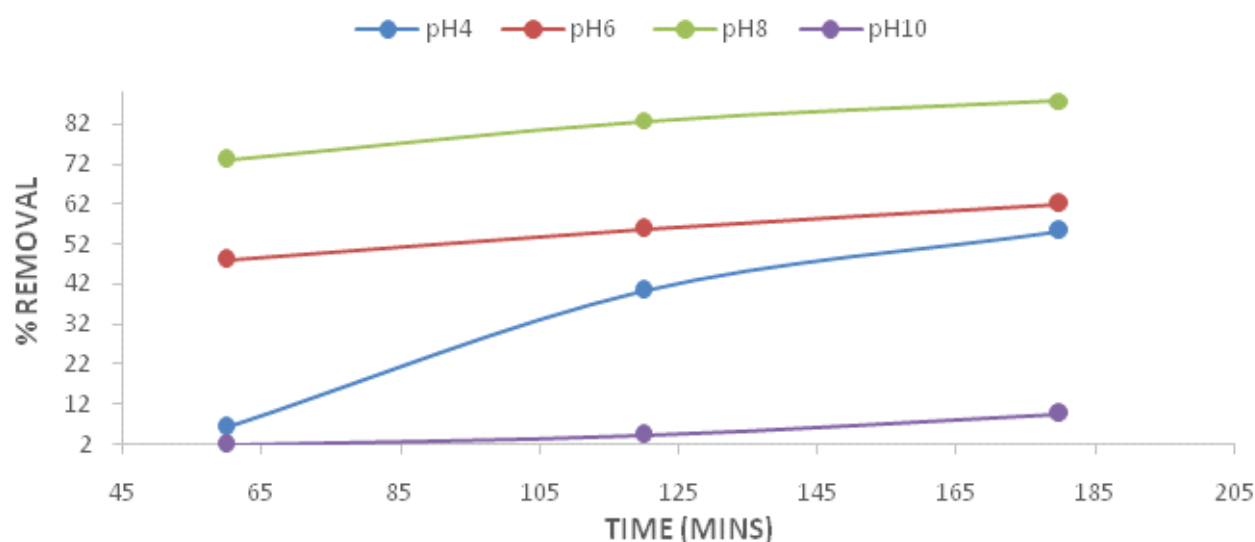


Fig. 3: Influence of initial pH vs. contact time on the adsorption efficiency of BGD using K-CF.

The influence of pH on BGD was performed in the range of pH 2 to 10 for the adsorbent dose = 0.03g, temperature = 40°C , and initial dye concentration = 30 mg/l, as shown in Figure 3. The dye removal responded differently with the three adsorbents at different pH levels. The optimum pH was observed to be at pH 8 for the adsorbent, and the percentage removal increased from 55.3% to 87.6% as the pH changed from acidic to basic.

3.5.2 Effect of adsorbent dosage

Tests were performed with varying adsorbent doses in the scale of (0.03 – 0.15) g/20ml with the initial dye concentration = 30 mg/L, pH = 8, and temperature at 40°C for the K-CF. Figure 4 shows that the percentage of removal improved with a reduction in doses of the K-CF at pH 8, and the optimum dose was 0.09 g/20ml beyond which the adsorption capacity was reduced because of excessive loading of the adsorbent.

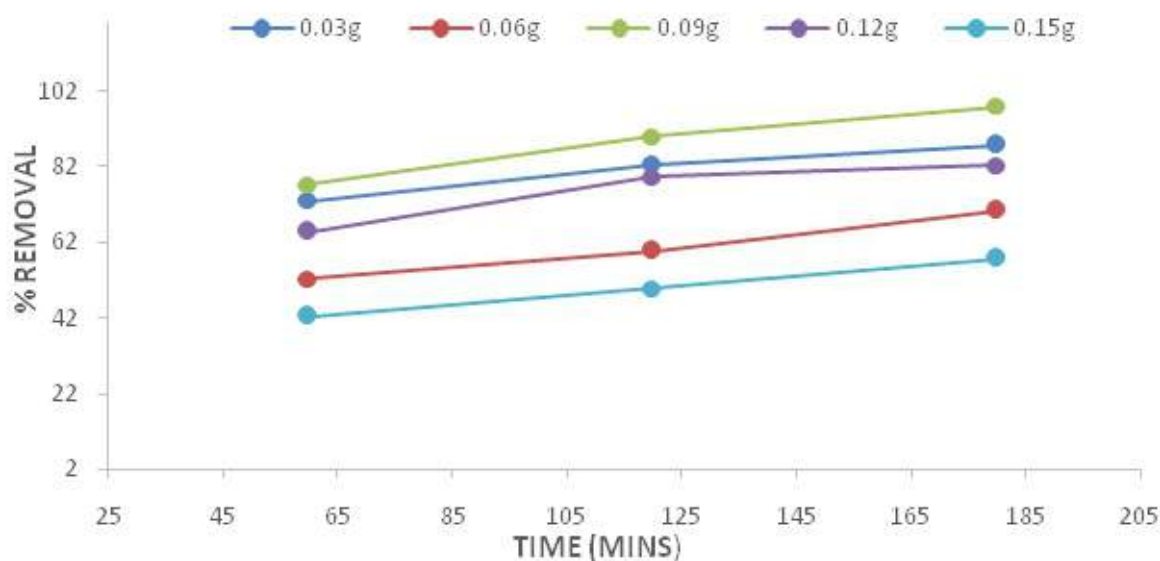


Fig. 4: Influence of adsorbent dosage vs. contact time on the adsorption efficiency of BGD K-CF at pH 8.

3.5.3 Effects of contact time and initial concentration

From the experimental results, it is found that more than 80% of the dye was adsorbed during the first 120 min. It gradually began to slow towards equilibrium in 180 min (Figure 6). Initially, the adsorption rate was fast as the outer surface of the sorbent had a huge number of available sites for adsorption. Figure 5 shows the impact on dye adsorption using K-CF with initial concentrations of 20, 30, 40, and 50mg/l at pH = 8, adsorbent dose = 0.03 g/20ml, and temperature = 40 °C.

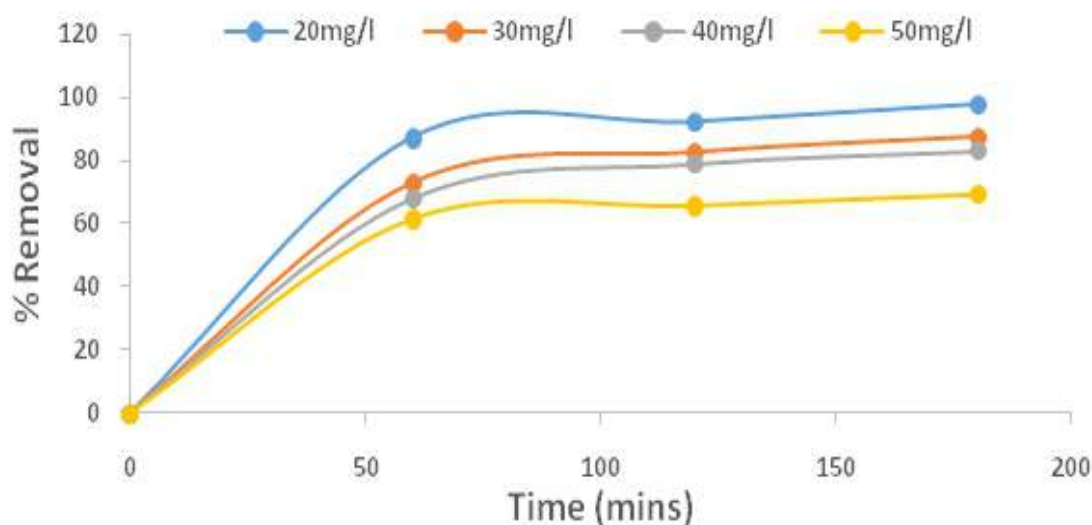


Fig. 5: Influence of BGD concentrations Vs contact time on the adsorption efficiency of BGD for K-CF.

3.6 Adsorption Kinetic Studies

The solute uptake rate is evaluated by an adsorptive kinetics study. The rate at which the dye ions were adsorbed by the adsorbents was studied at varying temperatures (30, 40, and 50 °C) and contact times of 10, 30, 60, 90, 120, 150, 180, and 210 minutes. At a constant pH of 8 for K-CF, and 40 mg/l of BGD were carried out. Pseudo-first-order, pseudo-second-order, Elovich model, Weber-Morris kinetic model, and Intra-particle diffusion model were all employed as shown in Equations (5) to (8). The kinetic parameters and coefficient of determination (R^2) are listed in Table 4.

$$\text{PFO, } \frac{dq_t}{dt} = K_1 (q_e - q_t) \quad (5)$$

$$\text{PSO, } q_t = \frac{K_2 q_e^2 e^t}{1} + K_2 q_e t \quad (6)$$

$$\text{Elovich, } qt = \frac{1}{B} (\ln(ABt + 1)) \quad (7)$$

$$\text{Intra-praticle diffusion } q_t = k_i t^{0.5} \quad (8)$$

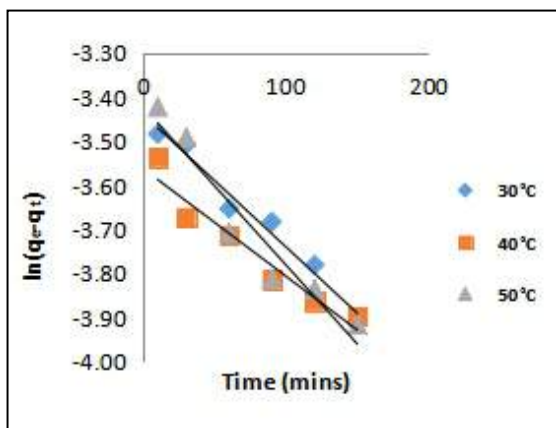


Fig. 6: Pseudo-First-Order plot for BGD on K-CF

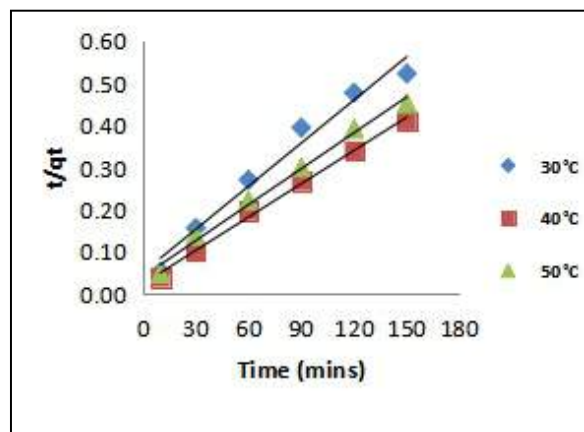


Fig. 7: Pseudo-Second-Order plot for BGD on K-CF

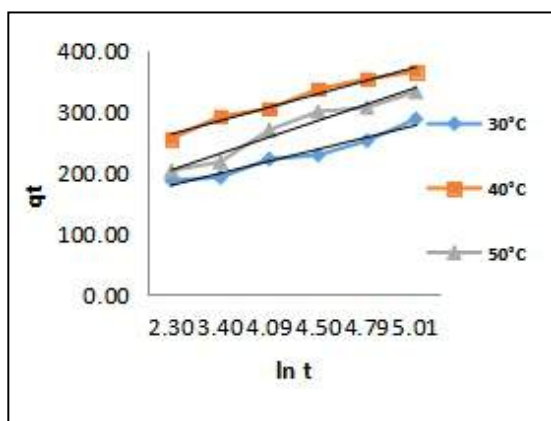


Fig. 8: Elovich plot for BGD on K-CF

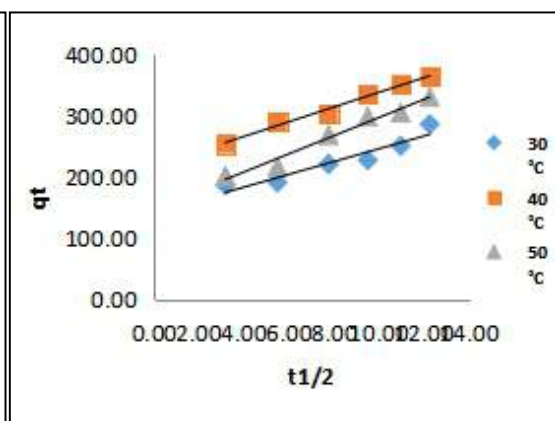


Fig. 9: Intraparticle plot for BGD on K-CF.

Table 4: Adsorption Kinetic Parameters of BGD on K-CF at Concentration of 40mg/l and Different Temperatures

3.7 Adsorption Isotherm

The equilibrium adsorption experiments were carried out by batch process for different initial BGD concentrations (20 to 50 mg/l) at 30 °C, 40 °C, and 50 °C. The equilibrium adsorption data were analyzed by Langmuir, Freundlich, Temkin, and Halsey isotherm models (Table 5).

3.7.1 Langmuir isotherm

The maximum adsorption values calculated from the Langmuir isotherm model were 81.3, 65.36, and 454.55 mg/g for the K-CF at 30 °C, 40 °C, and 50 °C. The essential characteristic of the dimensionless separation factor (R_L) values calculated as Equation (9) was in the range of 0.339 – 0.562 at 20, 30, and 40 °C. The values of $0 < R_L < 1$ indicated that the adsorption of brilliant green was favourable at all temperatures (Kaur *et al*, 2013).

$$\frac{C_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{C_e}{q_{max}} \quad (9)$$

3.7.2 Freundlich isotherm

The Freundlich isotherm model is an empirical model that describes adsorption with a heterogeneous surface. As shown in Table 5, the value for $1/n$ below 1 indicated a normal Freundlich isotherm model and reflected the favourable adsorption (Kaur *et al.*, 2013).

$$\ln q_e = \ln K_F + \frac{1}{n_F} \ln C_e \quad (10)$$

PFO Model					PSO Model			ELOVICH Model			Intra-Particle Diffusion Model		
Temp (K)	qe exp (mg/g)	qe cal (mg/g)	K ₁	R ²	qe cal (mg/g)	K ₂	R ²	Intercept	Ke	R ²	Diffusion Intercept	K _i	R ²
303	5.7	0.032	0.003	0.974	19.49	0.774	0.9738	158.74	0.051	0.95	141.94	10.449	0.9027
313	7.4	0.028	0.002	0.9354	40.65	0.233	0.9953	240.3	0.046	0.9724	218.52	12.022	0.9845
323	6.6	0.033	0.004	0.9264	24.1	0.615	0.9913	176.44	0.037	0.9534	149.21	14.836	0.9722

3.7.3 Temkin isotherm

In Table 5, the Temkin constant, A_T , can be considered a sort of adsorption potential for dye adsorption, and the calculated values were 1.01, 1.02, and 1.007 l/g for the K-CF at 20, 30, and 40 °C. The b_T values, related to the heat of adsorption, were 1.19, 1.17, and 2.11 KJ/mol for K-CF, suggesting a strong interaction between BGD molecules and the adsorbent (Daneshvar *et al.*, 2014).

$$q_e = B_1 \ln K_T + B_1 \ln C_e \quad (11)$$

3.7.4 Halsey isotherm

The Halsey isotherm parameters were calculated and tabulated in Table 5 for the K-CF. It can be deduced from the table that the R^2 values for the K-CF at the same temperature variations were 0.998, 0.452, and 0.366. (Ayawei *et al.*, 2015).

$$\ln q_e = \frac{1}{n_H} \ln K_H - \frac{1}{n_H} \ln C_{qe} \quad (12)$$

Table 5: Isotherm parameters of brilliant green dye adsorption by K-CF at different temperatures of 30, 40, and 50 °C (pH = 8, K-CF dose = 0.09 g, contact time = 180 min).

Isotherms	Temperature °C		
	30°C	40°C	50°C
Langmuir Isotherm (mg/g)			
$q_{\max}$ (mg/g)	81.3	65.36	454.55
R_L	0.0836 - 0.1319	0.0523 - 0.1212	0.3390 - 0.5618
R^2	0.993	0.999	0.993
Freundlich Isotherm			
K_F (L/g)	2.271	2.132	2.226
$1/n$	0.498	0.523	0.474
R^2	0.991	0.996	0.993
Temkin Isotherm			
$B = R_T/B_t$	2.11	2.22	1.27
b_T (KJ/mol)	1.193	1.173	2.113
R^2	0.559	0.644	0.239
Halsey Isotherm			
K_H	3.7×10^{-3}	1.02×10^{-9}	4.3×10^{-7}
n_H	3.394	7.304	6.427
R^2	0.998	0.452	0.366

3.8 Design Matrix for BGD Adsorption on the K-CF Adsorbent

Table 7 shows experimental results showing the percentage of BGD in water samples after adsorption on K-CF. The percentage removal of BGD was calculated using Equation (4).

Table 7: Design Matrix for BGD Adsorption on K-CF

No.	Dosage (g)	Temp (°C)	Factors			Response (%)		
			Conc.(Mg/l)	pH	Time (mins)	Experimental	RSM Predicted	ANFIS Predicted
1	0.06	40	40	4	60	38.00	39.06	38.00
2	0.09	50	30	2	90	46.30	45.39	46.30
3	0.12	60	40	8	120	31.80	32.57	31.80
4	0.09	50	30	6	90	96.21	95.52	95.86
5	0.09	50	30	6	90	95.54	96.11	95.86
6	0.09	50	30	6	90	97.60	98.10	95.86
7	0.12	40	20	4	60	55.50	54.48	55.50
8	0.09	50	30	6	90	92.13	95.85	95.86
9	0.09	50	30	10	90	10.10	11.22	10.10
10	0.06	60	40	8	60	31.50	31.71	31.50
11	0.09	50	30	6	150	56.30	55.78	56.30
12	0.12	60	20	4	120	74.40	73.74	74.40
13	0.06	60	40	4	120	34.50	35.92	34.49
14	0.12	60	40	4	60	77.00	77.58	77.00
15	0.09	50	30	6	30	51.30	52.81	51.30
16	0.15	50	30	6	90	69.30	69.69	69.42
17	0.06	40	20	4	120	62.00	61.83	61.99
18	0.12	60	20	8	60	71.00	69.13	71.00
19	0.03	50	30	6	90	54.60	54.42	54.60
20	0.09	50	30	6	90	99.60	95.85	95.86
21	0.09	50	50	6	90	67.20	63.44	67.20
22	0.12	40	20	8	120	69.00	68.18	69.00
23	0.09	50	10	6	90	99.00	102.92	99.00
24	0.06	60	20	8	120	54.00	52.98	54.00
25	0.09	50	30	6	90	94.24	95.85	95.86
26	0.09	70	30	6	90	99.60	100.31	99.60
27	0.12	40	40	8	60	24.50	24.91	24.50
28	0.06	40	20	8	60	63.00	61.62	63.00
29	0.06	60	20	4	60	97.00	95.78	97.00
30	0.06	40	40	8	120	48.00	49.25	48.00
31	0.12	40	40	4	120	87.00	88.62	86.99
32	0.09	30	30	6	90	95.60	95.02	95.60

3.9 Response Surface Methodology Model

In Table 8, the p-values for the lack-of-fit are presented for Linear (<0.0001) and 2FI (<0.0001) models for K-CF are significant relative to pure error for the three adsorbents studied. As shown in Table 9, the predicted R^2 value of 0.9249 for K-CF was for the quadratic model and is closest to unity when compared with cubic, 2FI, and linear models (Okoye *et al*, 2019).

Table 8: Fit Summary for BGD Adsorption on K-CF

Source	Sequential p-value	Lack of Fit p-value	Adjusted R-Squared	Predicted R-Squared	
Linear	0.2369	< 0.0001	0.0690	-0.1370	
2FI	0.8855	< 0.0001	-0.1690	-3.6543	
<u>Quadratic</u>	<u>< 0.0001</u>	<u>0.3726</u>	<u>0.9877</u>	<u>0.9249</u>	<u>Suggested</u>
Cubic	0.2180	0.8806	0.9915	0.9887	Aliased

Source	Std. Dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	PRESS	
Linear	24.82	0.2192	0.0690	-0.1370	23323.13	
2FI	27.81	0.3967	-0.1690	-3.6543	95469.53	
Quadratic	<u>2.85</u>	<u>0.9956</u>	<u>0.9877</u>	<u>0.9249</u>	<u>1539.63</u>	<u>Suggested</u>
Cubic	2.38	0.9983	0.9915	0.9887	230.95	Aliased

Table 9: Model Summary Statistics for BGD on K-CF

3.10 Analysis of Variance (ANOVA)

An analysis of variance (ANOVA) was used to determine the significance of the RSM models. The results of the ANOVA for the Response Surface Quadratic model for the K-CF are displayed in Table 10.

ANOVA for Response Surface Quadratic model						
Analysis of variance table [Partial sum of squares - Type III]						
Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	20422.64	20	1021.13	125.62	< 0.0001	Significant
A-Dosage	349.61	1	349.61	43.01	< 0.0001	
B-Temp.	43.20	1	43.20	5.31	0.0416	
C-Conc.	2344.33	1	2344.33	288.39	< 0.0001	
D-pH	1751.04	1	1751.04	215.41	< 0.0001	
E-Time	7.26	1	7.26	0.89	0.3649	
AB	9.30	1	9.30	1.14	0.3076	
AC	345.96	1	345.96	42.56	< 0.0001	
AD	244.92	1	244.92	30.13	0.0002	
AE	265.69	1	265.69	32.68	0.0001	
BC	302.76	1	302.76	37.24	< 0.0001	
BD	200.22	1	200.22	24.63	0.0004	
BE	1738.89	1	1738.89	213.91	< 0.0001	
CD	295.84	1	295.84	36.39	< 0.0001	
CE	205.92	1	205.92	25.33	0.0004	
DE	31.36	1	31.36	3.86	0.0753	
A ²	2093.68	1	2093.68	257.56	< 0.0001	
B ²	6.32	1	6.32	0.78	0.3969	
C ²	293.08	1	293.08	36.05	< 0.0001	
D ²	8363.93	1	8363.93	1028.91	< 0.0001	
E ²	3225.33	1	3225.33	396.77	< 0.0001	
Residual	89.42	11	8.13			
Lack of Fit	55.64	6	9.27	1.37	0.3726	not significant
Pure Error	33.77	5	6.75			
Cor Total	20512.06	31				

10: ANOVA for response surface quadratic model for BGD adsorption on K-CF

The resultant quadratic model equation generated after regression analyses from the ANOVA table is given by: In coded value;

$$Y_{K-CF} = 95.85 + 3.82A + 1.34B - 9.88C - 8.54D + 0.55E + 0.76AB + 4.65AC - 3.91AD + 4.07AE - 4.35BC - 3.54BD - 10.43BE - 4.30CD + 3.59CE + 1.40DE - 8.45A^2 + 0.46B^2 - 3.16C^2 - 16.89D^2 - 10.49E^2 \quad (13)$$

3.11 Process optimization using CCD

Table 11 contains the CCD optimum predicted conditions and validation experimental results. It was observed that the percentage of BGD adsorbed (99.29%) obtained from an experiment performed at optimal controllable variable conditions was in close agreement with the CCD predicted optimal response (99.668%) for the K-CF (Okoye *et al.*, 2019).

Table 11. CCD Optimum predicted/validation result.

Adsorbent	Dosage (g)	Temp	Solutions			CCD Optimal Response (%Ads)	Experimental Validation (%Ads)
			Conc. (mg/l)	pH	Time (mins)		
K-CF	<u>0.100</u>	<u>59.439</u>	<u>28.426</u>	<u>4.976</u>	<u>94.565</u>	<u>99.668</u>	<u>99.29</u>

4.0 Conclusion

Based on the problem this research work was meant to solve in our society, which is the removal of BGD from wastewater using synthesized keratin protein from waste chicken feathers, was hugely solved. For instance, the adsorbents were able to remove the dye (BGD) from the wastewater to an environmentally friendly level before disposal. In addition, life-threatening diseases like cancer, cholera, gene mutations, typhoid fever, and death will be hugely reduced and averted with the treatment. It can be concluded from the results obtained that low-cost and eco-friendly materials like K-CF can be used as an available alternative adsorbent for BGD removal in wastewater treatment, and huge amounts of chicken feathers that have been added to environmental pollution are reduced globally.



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C12-Comparative Modelling of Coagulation and Adsorptive Removal of Turbidity and Hexavalent Chromium from Paint Effluent Using Alum and Cactus-Opuntia

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Abstract

This study presents a comparative investigation and mass transfer modelling of the coagulation process for removing turbidity and hexavalent chromium from simulated paint effluent, using both Alum and Cactus-Opuntia Extract (COE) as coagulants. The COE was characterized by its phytochemical content, surface features, and functional groups. SEM analysis revealed a rough surface morphology conducive to adsorption. The influence of key process parameters such as coagulant dosage, pH, and settling time on treatment efficiency was examined. Kinetic and isotherm evaluations showed that the pseudo-second-order and the Freundlich models provided the best fit, with R^2 values of 1.000 and 0.989, respectively. Optimum removal was achieved at a 3 g/L dosage, with COE and Alum showing peak performance at pH 6 and 8, respectively. COE demonstrated superior removal efficiencies for turbidity (99.6%) and chromium (98.14%), compared to Alum (92.63% for turbidity and 96.18% for chromium), highlighting its effectiveness as a sustainable coagulant.

Keywords: Coagulation modeling; Cactus-Opuntia; Chromium (VI); Adsorption kinetics; Paint effluent

1.0 Introduction

Paint formulations typically consist of pigments, binders, solvents, and additives. Depending on the primary solvent used, paints are classified into water-based, solvent-based, or powder-based (solvent-free) types. In industrial settings, significant volumes of wastewater are produced during the cleaning of equipment such as mixers, reactors, blenders, and packaging lines (Ndive et al., 2021). This wastewater is often heavily turbid and contains suspended particles that are difficult to settle without proper treatment (Kakoi et al., 2021; Ezemagu et al., 2021). Furthermore, it commonly harbours hazardous contaminants like hexavalent chromium, a highly soluble and mobile form of chromium that poses serious environmental and health risks (Silva et al., 2016; Mitra et al., 2017). Hexavalent Chromium (Cr (VI)) is considered one of the most toxic and mutagenic heavy metals due to its carcinogenic nature, as confirmed by the International Agency for Research on Cancer (IARC). Upon exposure, it can trigger respiratory complications, reproductive toxicity, immunosuppression, and increased mortality rates in living organisms (Sarankumar et al., 2020). Consequently, untreated discharge of such effluent threatens aquatic ecosystems and contaminates groundwater. Effective pre-treatment of paint wastewater is thus essential before environmental release (Govarthanan et al., 2019). Several treatment methods have been developed for wastewater with high turbidity levels similar to those produced in paint manufacturing. These include chemical precipitation, membrane filtration, ion exchange, photo-catalysis, adsorption, biological treatments, and, more notably, coagulation-flocculation (Sanjay et al., 2018). Among these techniques, coagulation-flocculation is widely favoured due to its simplicity, high efficiency, and economic viability.



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This process is particularly effective in separating colloidal and suspended particles that are otherwise resistant to conventional physical removal methods. It operates by destabilizing particles using metal-based coagulants, typically aluminium or iron salts, which form polymeric aggregates capable of adsorbing contaminants. These complexes interact with pollutants in solution, with efficiency influenced by both coagulant dosage and pH.

However, concerns have emerged over the potential health risks and environmental issues associated with chemical coagulants, such as aluminium and ferric salts. For instance, residual aluminium in treated water has been linked to neurological disorders, including Alzheimer's disease, and the sludge generated often requires additional disposal treatment. These drawbacks have spurred interest in natural, biodegradable alternatives that offer similar or better performance with reduced environmental impact (Huang et al., 2017; Agbovi and Wilson, 2017), membrane filtration (Furuya et al., 2017; Salman et al., 2015), ion exchange [Nouri et al., 2016], photo-catalysis (Huang et al., 2017), coag-flocculation (Okolo et al., 2021; Wang et al., 2017), biological treatment (Yang et al., 2017) and adsorption (Menkiti et al., 2016). *Cactus Opuntia ficus-indica* has recently gained attention as a promising natural coagulant due to its abundance of structured polysaccharides, particularly mucilage, which possesses excellent water-binding and flocculating properties (Okolo et al., 2021; Silva et al., 2016; Wang et al., 2017). The coag-flocculation procedure removes granular or suspended components that stay distributed in a solution and are not eliminated by traditional physical techniques (Silva et al., 2016). While extensively studied for uses in nutrition, cosmetics, and food preservation, its application in water and wastewater treatment is still developing (Kuchelmei and Bauer, 2015). Compared to more established bio-coagulants like *Moringa oleifera*, the coagulative potential of cactus extracts remains underexplored, especially regarding their adsorption-driven mechanisms. (Paula et al., 2014). Although the use of aluminium and ferric salts in coag-flocculation yields adequate removal of turbid particles, this treatment option by itself does not fulfil regulatory discharge conditions, especially when associated health implications such as Alzheimer's disease and sludge toxicity are included (Vishali et al., 2016). These health concerns have motivated researchers to explore other suitable bio-based coagulants with comparable removal efficiency to chemical coagulants. Previous studies have demonstrated the effectiveness of cactus extracts in reducing turbidity and colour from various wastewater streams (Okolo et al., 2021).

Cactus Opuntia, which can be cultivated in most countries of the globe, has long been embedded with numerous benefits, including pharmaceutical and therapeutic (Abdel-Hameed et al., 2014), nutritional food source, cosmetics (Monrroy et al., 2017), exploitation of phytochemicals (Angulo-Bejarano et al., 2014), and bio-coating film for food preservation (Zegbe et al., 2015). However, these investigations centred on the non-adsorptive aspect of coagulation (Rachdi et al., 2017). A few studies have looked into using *cactus opuntia extract* (COE) as a natural organic flocculant rather than chemicals in the coag-flocculation treatment of paint effluent (Zegbe et al., 2017). COE has a strong coagulation potential due to the abundance of structured carbohydrates contained in cactus inner and outer pads, which proves a significant water-holding capacity (Nharingo et al., 2015). From Bustillos et al. (2013), several portions of COE, whether fresh or dried, possess considerable coagulation capability due to the presence of viscous natural polyelectrolytes with negative surface charges under acidic environments. Vishali and Karthikeyan (2014) studied the application of *cactus opuntia* as a coagulant for the treatment of synthetic wastewater. At a coagulant dosage of 30g/L and pH 7.5, the author reported a maximum removal efficiency of 88.37, 78.28 and 82.60 % for colour, COD and turbidity, respectively. Again, in a separate study (Vishali et al., 2016), encapsulated *cactus opuntia* was applied in the breakthrough and mass transfer studies of paint industrial effluent decolonization. The authors recorded a colour removal efficiency of 96% at a flow rate of 5cc/min. It is important to note that all these applications of *cactus opuntia* extract in paint effluent coagulation have



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been centred on the non-adsorptive component of the study, neglecting the adsorptive aspect.

Given the reasonable attention that has been channelled to the non-adsorptive coag-flocculation feature of this study, it becomes critical to investigate the adsorptive aspect of the present by some researchers (Ohale et al., 2018; Menkiti et al., 2018). Adsorption is a technique that uses surface forces to bind solute particles in aqueous solutions to accomplish material detachment (Ohale et al., 2018). To bridge this gap, the present study aims to assess the adsorption characteristics of *Opuntia* extract in the treatment of simulated paint effluent. Specific objectives include: (1) extraction and characterization of the coagulant, (2) evaluation of treatment efficiency under varying process conditions, and (3) modelling the adsorption kinetics and thermodynamics to better understand its underlying removal mechanisms.

2.0 Materials and Methods

2.1 Simulation of Paint Waste Water (PWW)

A synthetic paint effluent representative of water-based paint wastewater was formulated by dispersing 1.7 g of pale-blue emulsion paint into 500 mL of distilled water. The mixture was thoroughly agitated and subsequently diluted to a total volume of 1,000 mL with additional distilled water. This simulated wastewater was then analyzed to determine its baseline physicochemical characteristics and used in subsequent coagulation experiments.

2.2 Collection and Preparation of COE Coagulants

Mature Cactus *Opuntia* (*Opuntia ficus-indica*) pods were harvested from Egbuna Street, off Ezenei Quarter, Oshimili South LGA, Delta State, Nigeria. After thorough washing, the pods were cut into thin slices, sun-dried for two weeks, and then oven-dried at 60 °C for 24 hours to remove residual moisture. The dried material was ground into powder and sieved using a 0.2-mm mesh. To extract the coagulant, 1 g of the powder was suspended in 100 mL of 3N sodium chloride (NaCl) solution. The suspension was stirred for 15 minutes and allowed to settle for another 15 minutes. The supernatant was decanted and filtered using a filter sack, and the resulting eluate was refrigerated for use as a natural coagulant (Ndive et al., 2021).

2.3 Samples Characterization

2.3.1 Simulated paint waste water (PWW) characterization

The synthetic wastewater was characterized using standard analytical methods to evaluate parameters such as total dissolved solids (TDS), turbidity, pH, electrical conductivity, and concentrations of selected heavy metals.

2.3.2 Coagulant characterization

The coagulant extract was subjected to proximate analysis to determine its moisture, ash, crude fibre, protein, fat, and carbohydrate content.

2.3.3 Instrumental analysis of COE

Surface morphology was examined using a JSM-6400 Scanning Electron Microscope (SEM), while functional groups in the extract were identified using a FTIR-8400S Fourier Transform Infrared Spectrophotometer.

2.4 Coagulation Studies

Bench-scale jar tests were conducted to evaluate coagulation performance. 1,000 mL of the prepared synthetic paint wastewater was treated with different dosages (2–5 g/L) of coagulants. Rapid mixing was



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performed at 200 rpm for 3 minutes, followed by slow mixing at 80 rpm for 15 minutes. After settling for time intervals ranging from 5 to 180 minutes, 50 mL of the clarified supernatant was sampled and analyzed for turbidity and hexavalent chromium content. Additional tests assessed the influence of pH and temperature, with pH adjustments made using 0.1 M NaOH or 0.1 M H₂SO₄. Removal efficiency was calculated using the standard percentage removal formula.

$$\text{Removal Efficiency (\%)} = \frac{T_0 - T_t}{T_0} \quad (12)$$

Where T_0 and T_t are initial turbidity of effluent and effluent turbidity at any time.

2.5. Coag-Adsorption Kinetics and Isotherm Studies

The coagulation-adsorption kinetics and isotherm studies were modelled by fitting the coag-flocculation data into adsorption kinetics and isotherm models. This was done to study the adsorption component of the coagulation process. The mathematical expressions for the adsorption kinetics and isotherm models used are presented in Table 1.

Table 1: The mathematical expressions for the adsorption kinetics and isotherm models

Model Name	Non-Linear Mathematical expression	Constants	Reference
Kinetic models			
Pseudo First Order Adsorption	$-\frac{dC}{dt} = K_1 (q_e - q_t)$	K_1	Menkiti, et al., 2016
Pseudo Second Order	$-\frac{dC}{dt} = k_2 (q_e - q_t)$	K_2	Menkiti, et al., 2016
Elovich	$-\frac{dC}{dt} = a \exp(-\beta q_t)$	a, β	Menkiti, et al., 2016
Intra Particle Distribution Model	$\ln(1 - a) = -k_p t$	a, k_p	Menkiti, et al., 2016
Isotherm Models			
Langmuir	$q_e = \frac{q_m b C_e}{1 + b C_e}$	$R_L = q_m, b$	Menkiti, et al., 2016
Freundlich	$q_e = K_f C_e^{1/n}$	K_f, n	Menkiti, et al., 2016
Temkin	$q_e = \left[\frac{A}{n} \right] \ln(AC_e)$	A	Menkiti, et al., 2016

The R_L value of the Langmuir isotherm indicates the shape of the isotherm to be reversible when ($R_L=0$), favourable ($0<R_L<1$), linear ($R_L=1$) or unfavourable ($R_L>1$).

2.6. Mathematical Modelling of Mass/Particles Transfer

Particle movement and interaction within the bulk of the sample generally followed Brownian diffusion (peri-kinetic agglomeration) principles; however, for a system of induced agitation, the movement of particles was studied by Von Smoluchowski, and is represented by Fig. 1 for uniform spherical particles. It is pertinent to observe that the particle transfer is in the direction of the adsorbing particles, which is prompted by coagulation-flocculation. The model describing this movement took its basis from Fick's law. Assuming a one-dimensional particle transfer, a simple homogeneous system, an isothermal process and neglecting an external opposition to particle movement. The model equation that can predict the number of particles transferred in the system at any given time has been detailed below.

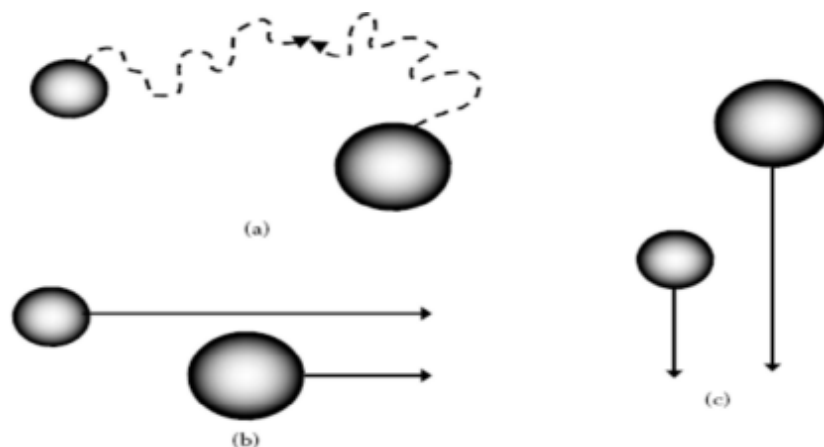


Fig. 1 Spherical particle collision transport showing: (a) diffusion through Brownian movement; (b) hydrodynamic movement; and (c) differential settling.

The governing equation (Fick's law) written in terms of the particles (microscopically spherical particle) of diffusion coefficient, as shown in Equation.

$$I = - D \frac{ac_i}{a_r} \quad (2)$$

I is the diffusive flux, C_i is particle concentration and $\frac{ac_i}{a_r}$ is concentration gradient.

If the system is diffusion controlled, then the motion of the particles in the bulk of the sample has to do with particle movement from a higher concentration to a lower concentration area. Figure 2.2 shows a representation of the motion of a spherical microscopic particle; hence, a basic differential mass balance can be established following a measurable balance over a spherical particle.



Fig. 2 A microscopic system for the spherical particle transfer

$$\text{Time rate of change of particles} = \text{mass inflow of particles} - \text{Mass efflux particles} \quad (2)$$



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Representing Eq. (2.1) mathematically, gives Eq. (3) (Jimoda et al 2013)

$$\frac{\partial(C_i)4\pi r^2}{\partial t} = i4\pi r^2 - \left(i + \frac{\partial_i}{\partial_r}\right) 4\pi r^2 \quad (3)$$

Simplifying Eq. (3) gives Eq. (4) $\frac{r^2 \partial C_i}{\partial t} = - r^2 \frac{\partial_i}{\partial_r}$ (4)

Joining Eq. (2) with Eq. (3) gives Eq. (5) $\frac{\partial C_i}{\partial t} = D \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \frac{\partial C_i}{\partial r})$ (5)

Where C_i is the number of particle concentration, i and r is the radius of the sphere. The equation describing the rate of particle movement during the coagulation-flocculation process is a partial differential equation (Eq. (5)). It is also related to spherical mass transfer according to Coulson and Richardson (2008). Replacing C_{j2} for C , Eq. (5) turn out to be Eq. (6)

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial r} D \frac{\partial C}{\partial r} \quad (6)$$

For the initial condition in Eq. (6) (Coulson et. al 1999)

$$C_i(t = 0, r) = C_{io} \quad (7)$$

Also, the boundary conditions are Eq. (8) - (9)

$$C_i(r = 0, t) = C_{io} \quad (8)$$

$$C_i(r = a, t) = C_{eo} \quad (9)$$

Where C_{eo} is the equilibrium particle concentration in the system, and C_{io} is the primary particle concentration.

Proceeding to dimensionless and normalized dependent variables and also boundary conditions, making use of the dimensionless parameters of Eqs. (10) – (11)

Position variable, $\eta = \frac{r}{R_n}$ (10)

Time variable, $\tau = \frac{D_1 t}{R_n^2}$ (11)

Dimensionless concentration, $C = \frac{C_t - C_s}{C_0 - C_s}$ (12)

The initial and boundary condition changes result in Eq. (13) – (15) ()

$$C(\tau = 0, \eta) = 1 \quad (13)$$

$$C(\tau, 0) = 0 \quad (14)$$

$$C(\tau, 1) = 0 \quad (15)$$



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Then, substituting the dimensionless variables into Eq. (6) results to Eq. (16):

$$\frac{\partial C}{\partial \tau} = \frac{\partial^2 C}{\partial \eta^2} \quad (16)$$

Eq. (2.15) predicts the speed at which the particle is transferred at different operating conditions. The method of separating variables was applied in solving the partial differential, Eq. (16). It involves looking for an explanation by which the time variable (τ) is separated from the space variable (η)

Then, reducing the incomplete differential Eq. (16) to a normal differential equation and applying the essential boundary conditions and also substituting all dimensionless parameters, gives Eq. (17)

$$\frac{C_t - C_e}{C_0 - C_e} = 2 \sum_{n=0}^{\infty} \frac{1 - \cos n\pi}{n\pi} \left(\sin n\pi \frac{r}{R_0} \right) \left(e^{-\frac{(n\pi)^2 K_1 t}{16\pi r R_0^2}} \right) \quad (17)$$

Thus, expressing Eq. (17) as C_t to define the concentration of particles at some process time t , we have Eq. (18) (Jimoda et al 2013)

$$C_t = C_e + 2 (C_0 - C_e) \sum_{n=0}^{\infty} \frac{1 - \cos n\pi}{n\pi} \left(\sin n\pi \frac{r}{R_0} \right) \left(e^{-\frac{(n\pi)^2 K_1 t}{16\pi r R_0^2}} \right) \quad (18)$$

where C_t is the particle concentration at any process time, C_0 is the initial particle concentration, and C_e is the equilibrium particle concentration.

As a result, Eq. (18) represents the model equation that can predict the number of particles transferred in the system at any given time.

3.0 Results and Discussion

3.1 Simulated Paint Waste Water Characterization Results

The initial analysis of the synthetic paint wastewater revealed highly turbid and contaminated conditions. The effluent exhibited a pH of 7.11, indicating near-neutral characteristics. The turbidity level reached 1700 NTU, confirming the presence of dense suspended particulates. Electrical conductivity was measured at 136.0 μ S/cm, while total dissolved solids (TDS) were found to be 54 mg/L, as shown in Table 3.1. Heavy metal analysis showed elevated concentrations of hexavalent chromium (4.966 mg/L), significantly surpassing acceptable limits. Other detected metals included magnesium (10.688 mg/L), arsenic (0.127 mg/L), cobalt (0.017 mg/L), and manganese (0.112 mg/L). Several metals, such as aluminium, nickel, and lead, were either absent or below detection limits, as shown in previous studies [1]

3.2 Proximate Analysis Results

The dried Cactus opuntia powder at 60°C drying temperature used in this study was analyzed to determine its nutritional and chemical composition. The high carbohydrate and fibre content (61.94% and 6.15%), particularly mucilage polysaccharides, is indicative of the extract's flocculating potential, enabling it to function effectively as a natural coagulant [1]

3.3 Instrumental Results (SEM and FTIR)

3.3.1 SEM result

The SEM technique is used to analyze the surface morphology of the polymeric coagulant. The figures 3.1, 3.2 and 3.3 show the SEM micrographs of the sample at different magnifications. The SEM images of the coagulant material revealed a rough surface morphology with numerous pores and irregular structures. These features support the presence of adsorption-active sites that enhance the physical binding of suspended contaminants. The compact, net-like structure observed suggests the potential for bridging and floc formation during coagulation. The pores and rough surfaces shown on the SEM images confirm that adsorption would play an important role in the treatment processes (Menkiti et al., 2016). The FTIR spectrum of the *Cactus opuntia* extract identified several functional groups associated with coagulant activity. A broad peak at 3406 cm^{-1} was attributed to hydroxyl and amine stretching, while the 3000 cm^{-1} region indicated aromatic C=C-H vibrations as shown in Figure 3.4. Other significant bands included peaks for carboxylic salts, aromatic amines, and C-N and C=C bonds, confirming the presence of active sites conducive to coagulation and adsorption mechanisms.

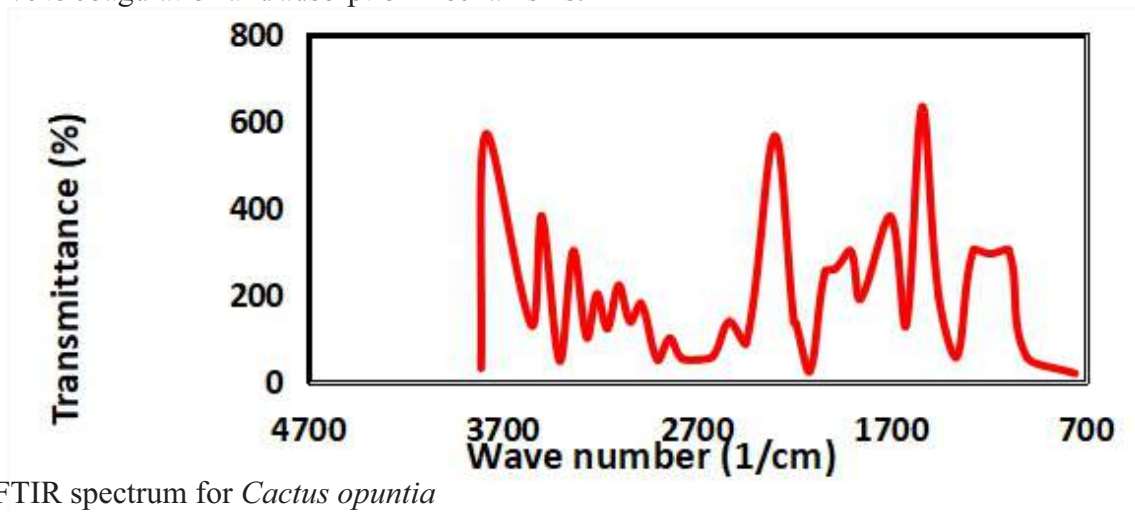


Fig. 3 FTIR spectrum for *Cactus opuntia*

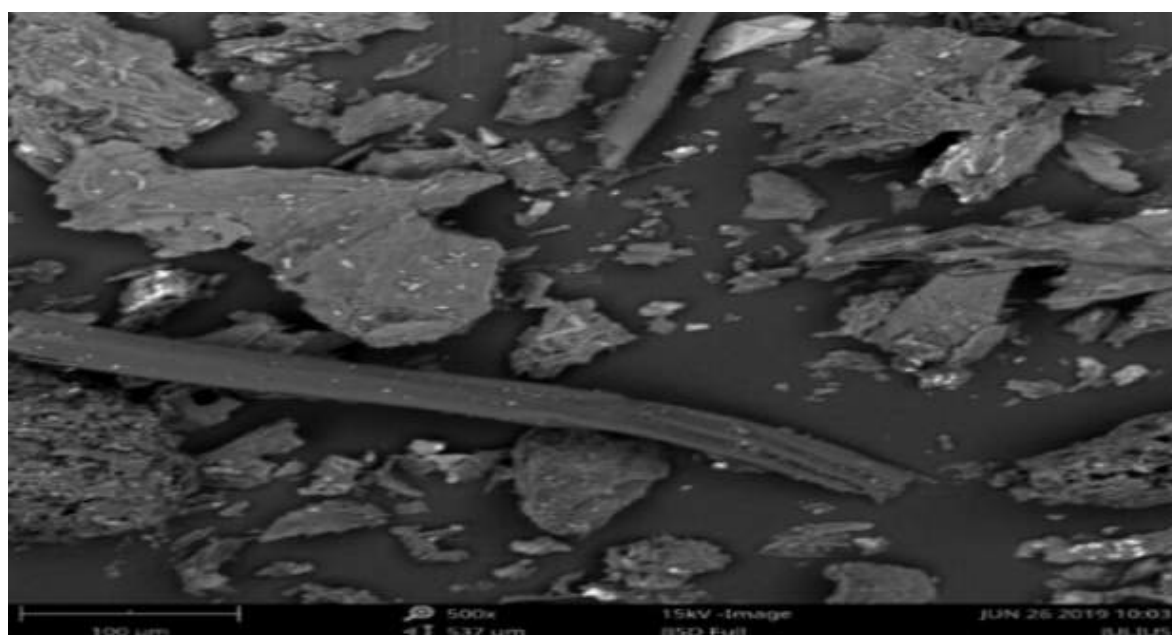


Fig. 4: SEM 500 X Cactus Opuntia

3.3.4 Phytochemical analysis

The phytochemical screening revealed various bioactive constituents such as phenolics, tannins, flavonoids (e.g., naringin, kaempferol), and alkaloids.

3.4.1. Effect of effluent pH on turbidity and chromium ion concentration on PWW using COE and alum

The pH of the effluent played a significant role in determining the performance of both Cactus Opuntia Extract (COE) and Alum. As the pH increased, removal efficiency initially improved due to enhanced protonation, which facilitated the interaction of coagulant molecules with negatively charged contaminants. Peak removal of turbidity reached 99.69% with COE and 99.70% with Alum at pH 6 and 8, respectively. For hexavalent chromium, optimal removal occurred at the same pH values, with COE achieving 99.79% and Alum reaching 97.47%. Beyond these pH values, efficiency declined due to overcharging and destabilization of particles, which impaired coagulation performance as shown in Figures 5 (a, b, c, d, e, f) and 6 (a, b, c, d, e, f), respectively.

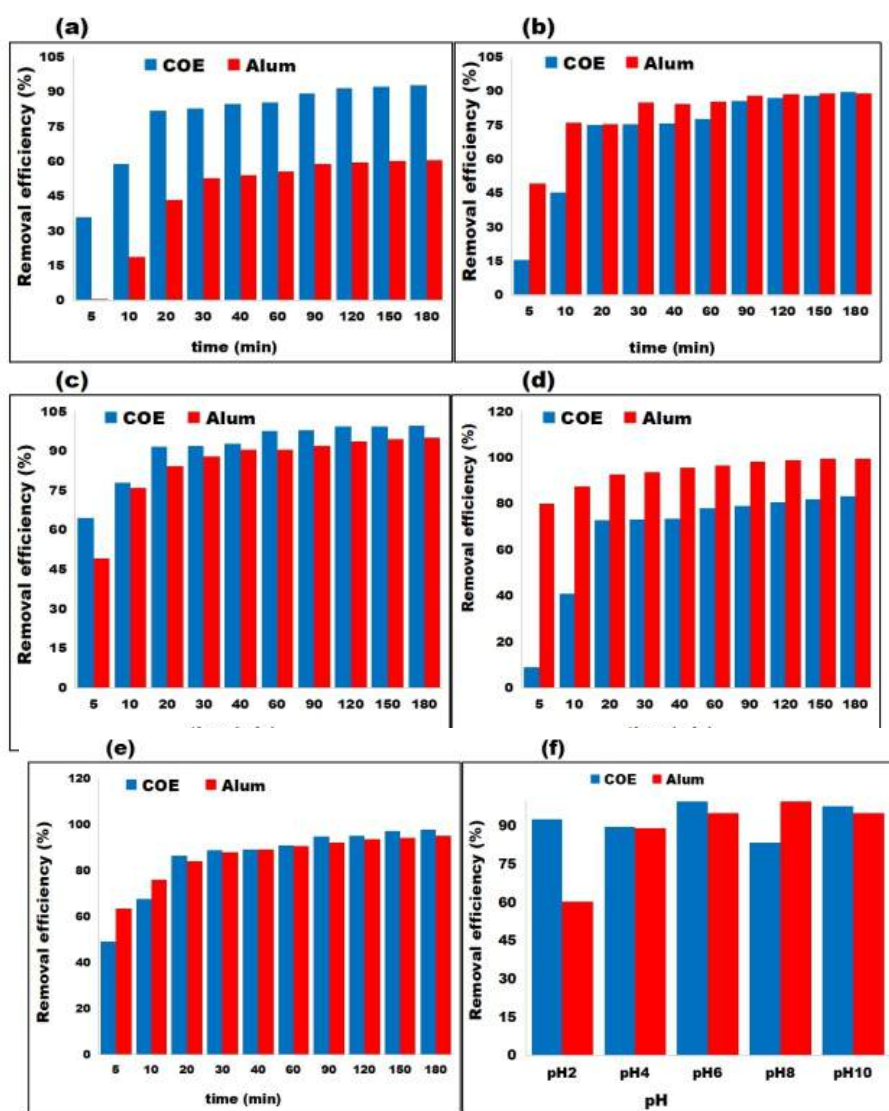


Fig 5 (a, b, c, d, e, f): Effect of pH on Turbidity removal using COE and Alum

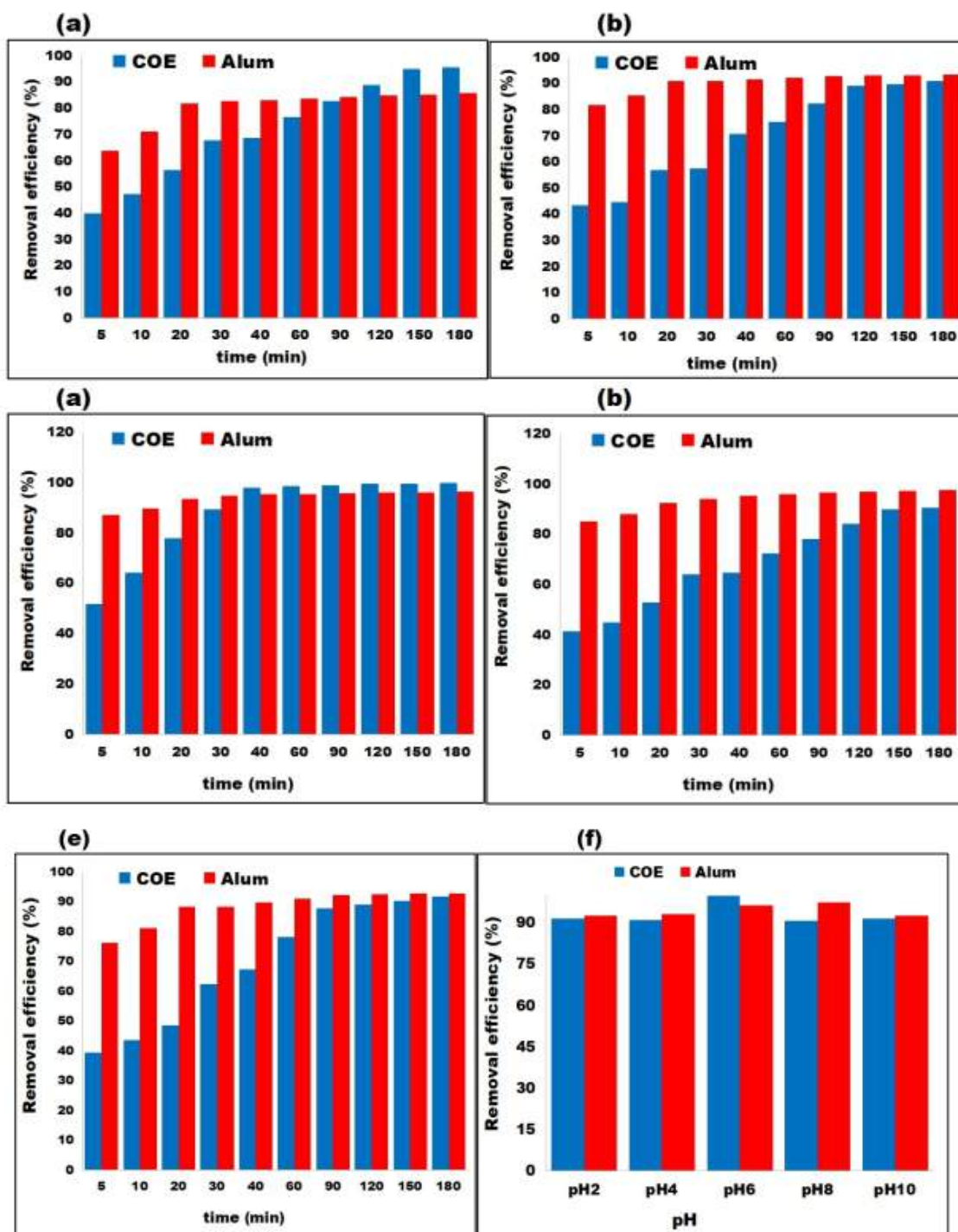


Fig. 6 (a, b, c, d, e, f): Effect of pH on Chromium ion removal using COE and Alum

3.4.2. Effect of coagulant dosage on the removal of turbidity and chromium ion concentration from PWW using COE and alum

The effect of coagulant dosage on the removal of turbidity and chromium ion concentration was shown in the figure 7 (a, b, c, d, e, f) and 8 (a, b, c, d, e, f).

Varying the dosage of coagulants between 1 and 5 g/L revealed a distinct optimum at 3 g/L for both COE and Alum. At this dosage, turbidity removal was 99.6% with COE and 92.63% with Alum. Hexavalent chromium was also effectively removed, with COE achieving 98.14% and Alum 96.18%. The enhanced removal at 3 g/L is likely due to the optimal availability of active sites for bridging and charge neutralization. However, increasing the dosage beyond this point led to a decline in performance, attributed to particle overdosing and re-dispersion, which interferes with floc formation.

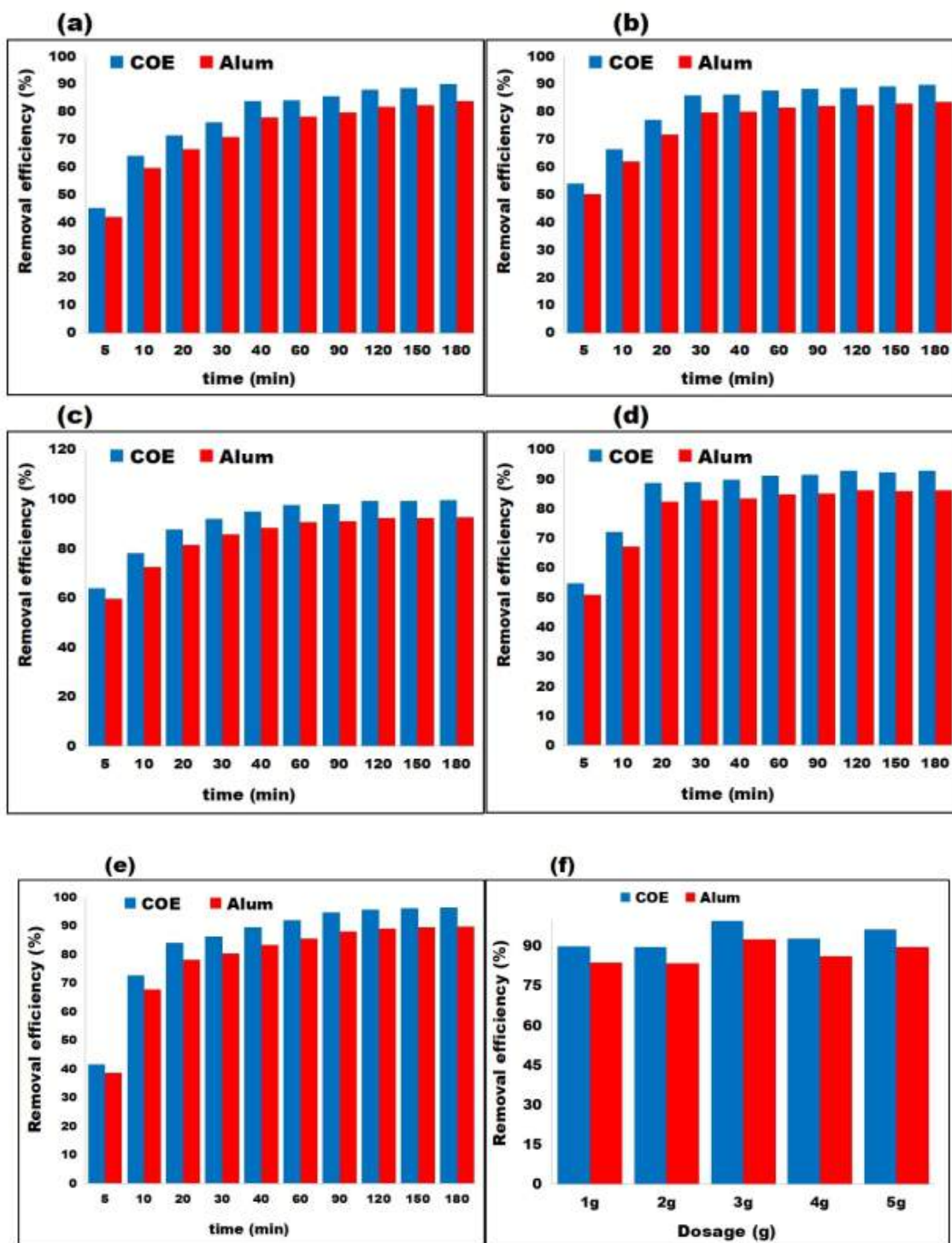


Fig. 7 (a, b, c, d, e, f): Effect of coagulant dosage on turbidity removal using COE and alum

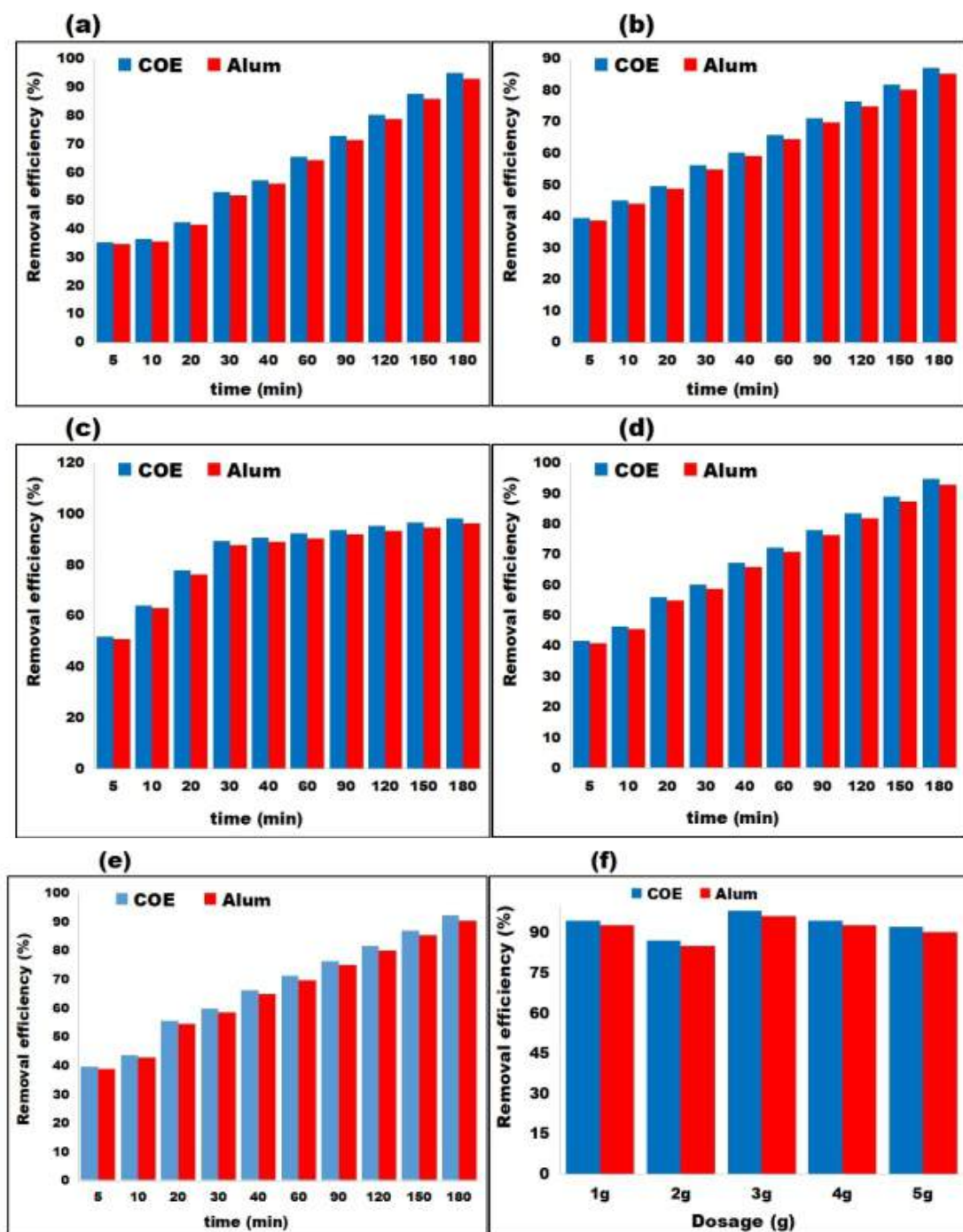


Fig. 8(a, b, c, d, e, f): Effect of Coagulant Dosage on Chromium ion concentration removal using COE and Alum

3.4.3 Polymer coagulation adsorptive kinetics study

Polymer coagulation-adsorption kinetics were analyzed using four kinetic models (pseudo-first order, pseudo-second order and Elovich models) and intra-particle diffusion models. The latter would determine the rate-controlling step. The governing equations for the linear kinetic plots were presented in Table 2.

Table 2: The kinetic model equations

Model	Linear	Nonlinear
Pseudo first order	$\ln(q_e - q_t) = -K_1 t$	
Pseudo second order	$t/q_t = 1/(K_2 q_e^2) + 1/q_e$	$q_t = t/(1/(k q_e^2) + 1/q_e)$
Elovich	$q_t = (1/\beta) \cdot \ln(a/\beta) + (1/\beta) \cdot \ln(t)$	$q_e = 1/\ln(1 + a \beta t)$

The kinetic behaviour of the coagulation process was assessed using four models: pseudo-first-order, pseudo-second-order, Elovich, and intra-particle diffusion. The analysis indicated that the pseudo-second-order model best described the adsorption kinetics, with correlation coefficients (R^2) approaching 1.000 for both coagulants across varying dosages. This suggests that chemisorption was the dominant mechanism governing the rate of contaminant uptake. The Elovich model also provided a good fit, particularly at lower dosages, reflecting a heterogeneous surface interaction. Intra-particle diffusion plots exhibited multilinear characteristics, indicating that multiple steps, such as film diffusion and intra-particle transport, contributed to the overall process. However, since the regression lines did not pass through the origin, intra-particle diffusion was not the sole rate-limiting factor.

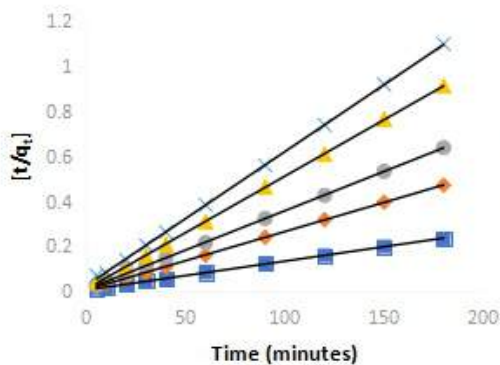


Fig. 10a: A plot of **pseudo-second** order kinetics model for **the** coagulation of PWW using COE

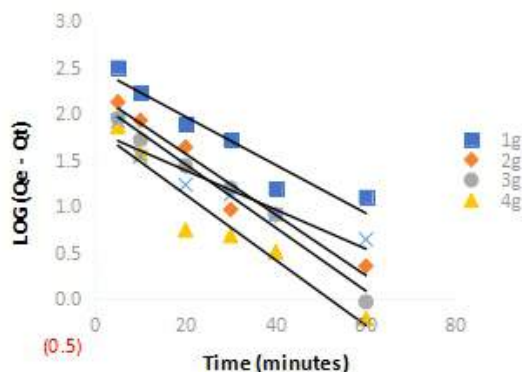


Fig. 10b: A plot of **pseudo-second** order kinetics model for **the** coagulation of PWW using Alum

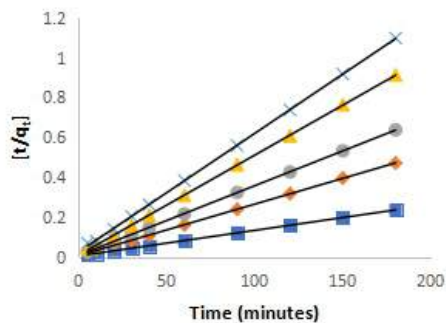


Fig. 10a: A plot of **pseudo-second** order kinetics model for **the** coagulation of PWW using COE

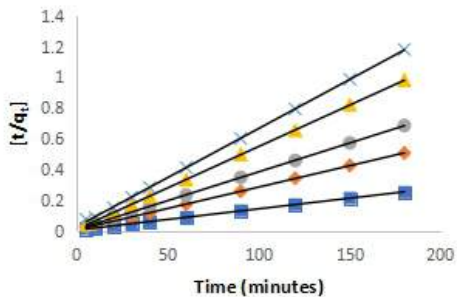


Fig. 10b: A plot of **pseudo-second** order kinetics model for **the** coagulation of PWW using Alum

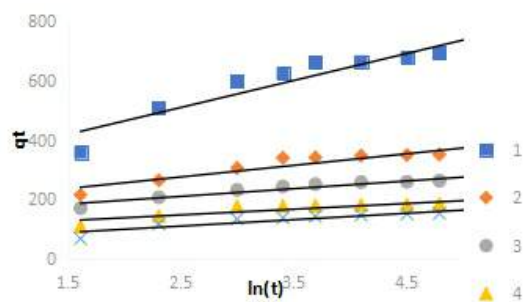


Fig. 11a: A plot of Elovich kinetics model for coagulation of PWW using COE

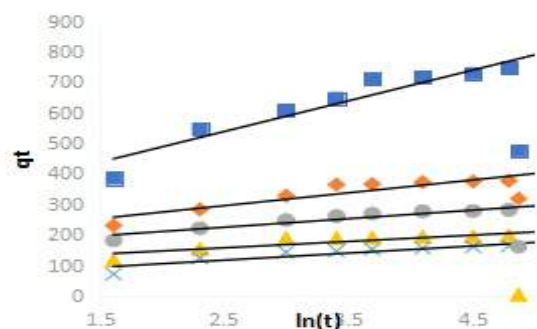


Fig. 11b: A plot of Elovich kinetics model for coagulation of PWW Alum

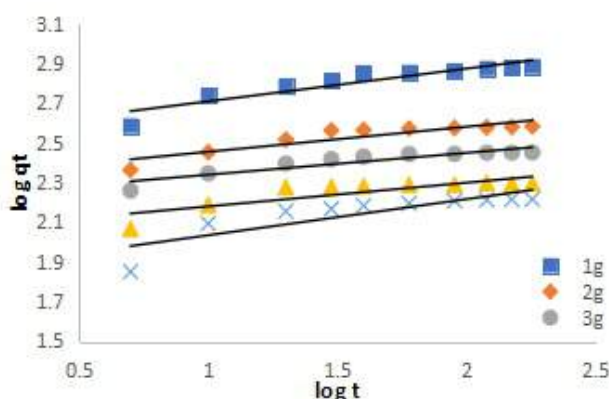


Fig. 12a: An Intra particle distribution plot (rate limiting step) for coagulation of PWW using COE

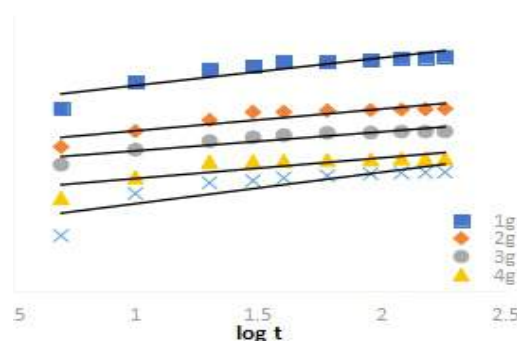


Fig. 12b: An Intra particle distribution plot (rate limiting step) for coagulation of PWW using Alum

3.4.4 Intra-particle diffusion (model rate-limiting step)

Polymer coagulation kinetics could be controlled by several independent factors (bulk diffusion, film diffusion, chemical reaction, intra-particle diffusion, temperature, pH, etc.) that could act individually or interactively as reported by Weber-Morris explained that if the rate-limiting step is the intra-particle diffusion, then the amount of COE adsorbed at any time, t , should be directly proportional to the square root of contact time, t . This can be expressed mathematically as shown in equation 3.1

$$q_{it} = K_{id} t^{0.5} \quad (3.1)$$

Linearizing equation (3.1) gives equation (3.2):

$$\log qt = \log K_{id} + 0.5 \log t \quad (3.2)$$

where qt is the amount of coagulant adsorbed at time, t (min), and K_{id} is the intra-particle rate constant ($\text{mg g}^{-1} \text{min}^{-0.5}$). The plot of $\log qt$ against $0.5 \log t$ gives a straight line with a positive intercept for an intra-particle diffusion-controlled adsorption process.

3.5 Isotherm Analysis

3.5.1 Equilibrium studies using isotherm models

The equilibrium study was carried out using three isotherm models (the Freundlich, Langmuir and Temkin) in order to evaluate the nature of adsorption and the maximal adsorption capacity. The isotherm parameters were estimated using nonlinear forms of the models depicted in Table 3.7.

Table 3: Summary of Isotherm Models

Isotherm	Nonlinear	Linear	Plot
Langmuir	$q_e = \frac{q_m b C_e}{1 + b C_e}$	$\frac{q_e}{C_e} = \frac{1}{b} + \left[\frac{q_m}{b} \right] \frac{1}{C_e}$	$\frac{q_e}{C_e}$ vs $\frac{1}{C_e}$
Freundlich	$q_e = K_f C_e^{1/n}$	$\text{Log } q_e = \text{log } k_f + (1/n) \text{ log } C_e$	$\text{Log } q_e$ vs $\text{log } C_e$
Temkin	$q_e = \left[\frac{bT}{N} \right] \ln (A C_e)$	$\ln q_e = \left[\frac{bT}{N} \right] \ln A + \left[\frac{bT}{N} \right] \ln C_e$	$\ln q_e$ vs $\ln C_e$

where q_e —amount of coagulant uptake per unit mass of the pollutant in the PWW at equilibrium (mgg^{-1}); q_m —Langmuir constant related to monolayer coagulation capacity (mg/g); K_f , K_L , K_T , isotherm constants for Freundlich, Langmuir and Temkin, (mgg^{-1} , Lmg^{-1}); C_e —equilibrium COE concentration in solution (mgL^{-1}); bT —constant in Temkin isotherm (KJmol^{-1}); N —Freundlich constant (dimensionless); T —absolute temperature (K).

The equilibrium behaviour of turbidity and chromium adsorption onto the coagulants was evaluated using three common isotherm models: Langmuir, Freundlich, and Temkin.

The Langmuir isotherm, which assumes monolayer adsorption on a homogeneous surface, exhibited the best fit for turbidity removal using both COE and Alum, with R^2 values exceeding 0.99. The Langmuir separation factor (R_{L}) values ranged between 0 and 1, indicating favourable adsorption across all tested concentrations.

The Freundlich model, suitable for heterogeneous surface adsorption, also fits the data reasonably well. The Freundlich constant n was greater than 1, suggesting a favourable and strong interaction between the coagulants and pollutants.

The Temkin model, which considers interactions between adsorbate and adsorbent, showed moderate agreement with experimental data, highlighting the role of binding energy in influencing adsorption intensity.

The overall findings suggest that both COE and Alum exhibit high affinity for pollutant molecules, with COE slightly outperforming Alum across most conditions due to its polysaccharide-rich surface chemistry and diverse active sites. Also, it could be observed that almost all five isotherm model constants showed a definite trend with temperature variation.

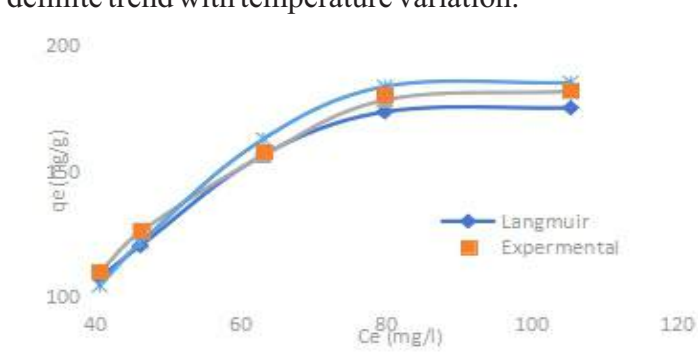


Fig. 13a A plot of q_e (mgg^{-1}) versus C_e (mg l^{-1}) at 35°C for COE

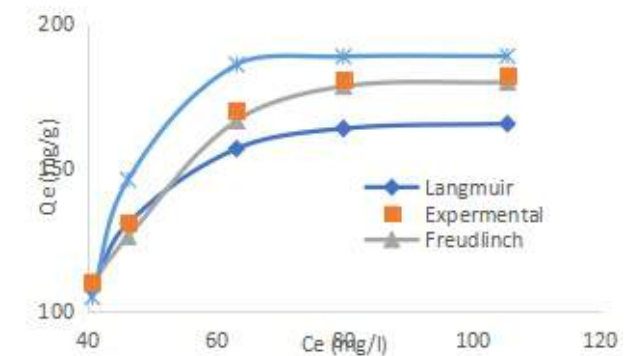


Fig. 13b A plot of q_e (mgg^{-1}) versus C_e (mg l^{-1}) at 35°C for Alum

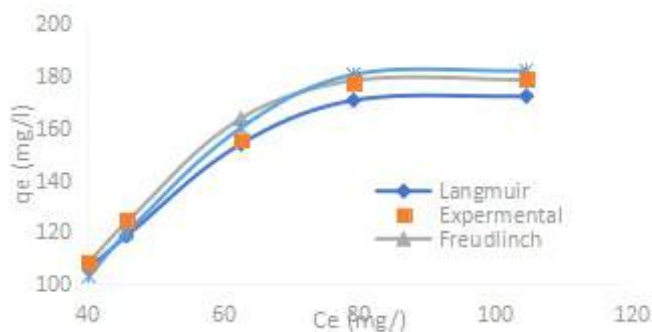


Fig 3.14a A plot of q_e (mgg^{-1}) versus C_e (mg/l) at 4°C for COE

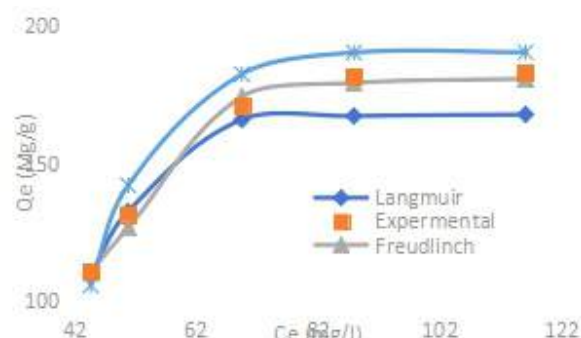


Fig 3.14b A plot of q_e (mgg^{-1}) versus C_e (mg/l) at 45°C for Alum

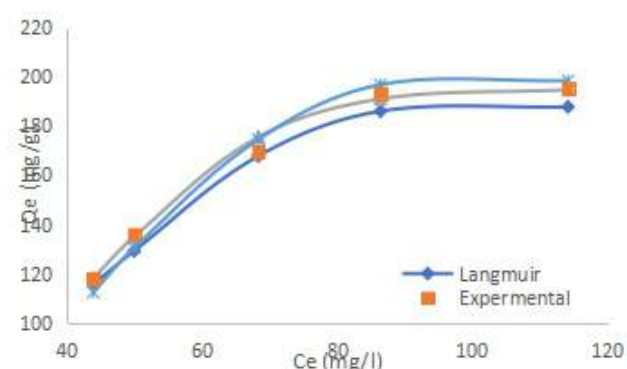


Fig. 15a A plot of q_e (mgg^{-1}) versus C_e (mg/l) at 55°C for COE

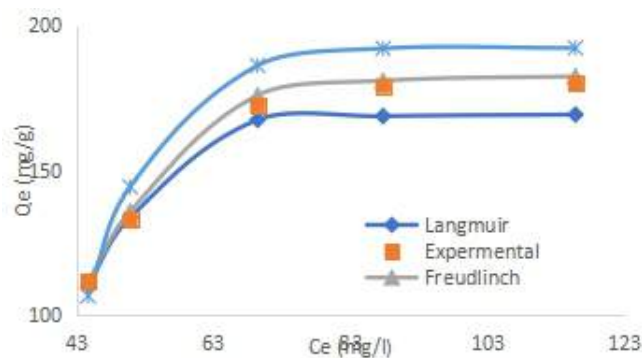


Fig. 15b A plot of q_e (mgg^{-1}) versus C_e (mg/l) at 55°C for Alum

3.5.2 Favorability of the adsorption process

The favorability of the adsorption process was further confirmed using the relationship expressed in Eq. 3.3 to calculate the dimensionless separation factor R_L according to [31]

$$R_L = [1 + (K_L C_o)]^{-1} \quad (3.3)$$

Where K_L is the Langmuir constant (L mg^{-1}) and C_o is the initial PWW concentration (mgL^{-1}). According to [31], the dimensionless separation factor, R_L , was a tool used to indicate the shape of the isotherm as follows: the isotherm is (1) unfavourable when $R_L > 1$, (2) linear when $R_L = 1$, (3) favourable when $R_L < 1$ and (4) irreversible when $R_L = 0$. Based on the parameters presented in Table 3.8 (a and b), R_L values clearly exceeded zero (0) and fell below unity (1), i.e., ($0 > R_L < 1$) for linear Langmuir isotherms. Hence, R_L indicates process favorability for Langmuir, which is the second closest to the Freundlich predominated process. Also, since N -values for the Freundlich model lie between 1.0 and 3.0, the process would be considered favourable, since N -values of 1–3 are within Freundlich threshold range of 1–10.

3.6 Conclusion

This study successfully compared the performance of Cactus-Opuntia ficus-indica Extract (COE) and Alum in the removal of turbidity and hexavalent chromium from simulated paint effluent using coagulation-mass transfer modelling and adsorption studies. Characterization revealed COE to possess favourable morphological and chemical properties, including rough porous surfaces, active functional groups, and phytochemicals that support its flocculation potential.



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Optimal removal efficiencies were achieved at a dosage of 3 g/L and pH 6 for COE and pH 8 for Alum. COE demonstrated superior performance in removing both turbidity (up to 99.6%) and chromium (98.14%) compared to Alum. Adsorption kinetics were best described by the pseudo-second-order model, and equilibrium data aligned well with the Langmuir and the Freundlich isotherms. Conclusively, COE presents a promising, sustainable, and effective alternative to conventional chemical coagulants. Its use in paint effluent treatment offers a cost-effective and environmentally friendly solution that supports wastewater reuse and reduces ecological hazards.

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Optimization of Coagulation-Flocculation Process for Pharmaceutical Wastewater Treatment Using Seed Shells from Melon

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Abstract

This study evaluated the performance of melon seed shell bio-coagulant in treating pharmaceutical wastewater collected from Enugu State, Nigeria. Initial characterization of the wastewater showed pH (7.1), COD (1500 mg/L), TSS (400 mg/L), TDS (1350 mg/L), and turbidity (95 NTU), analyzed using standard methods (SMWW, APHA, AWWA). Melon seed shells obtained from Abakpa market were processed into powder, treated with 3.5% (w/v) NaOH, and applied in a jar test. Proximate analysis revealed moisture (7.85%), ash (4.32%), protein (13.91%), fat (15.31%), crude fiber (10.41%), and carbohydrate (48.20%) contents. FTIR analysis confirmed the presence of functional groups (C=O, O–H, N–H) essential for coagulation, while XRF analysis showed high levels of oxygen (42.476%), silicon (21.319%), and aluminum (7.912%). Process optimization using Response Surface Methodology with a Central Composite Design evaluated coagulant concentration (50–250 mg/L), dosage volume (0.5–2.5 mL), and settling time (3–15 minutes). The quadratic model demonstrated strong predictive accuracy ($R^2 = 0.9433$) and identified optimal treatment conditions of 187.414 mg/L concentration, 1.077 mL dosage volume, and 11.414 minutes settling time, producing a predicted turbidity removal of 36.828% (experimental: 36.911%; error: 0.22%). Post-treatment results showed considerable reductions in COD (130.8 mg/L), TSS (210.5 mg/L), TDS (139.6 mg/L), and turbidity (68.5 NTU). Heavy metal levels were significantly reduced, including copper (from 25.91 to 0.225 mg/L) and nitrate (from 3.18 to 0 mg/L). The findings demonstrate that melon seed shells are a sustainable, efficient, and cost-effective bio-coagulant for pharmaceutical wastewater treatment, offering a promising alternative to conventional chemical coagulants.

Keywords: Melon seed shells, Coagulation, pharmaceutical wastewater, Optimization, Turbidity

1. Introduction

Since it is necessary for many household, agricultural, and industrial processes, water is a valuable and essential resource for all life on Earth (Koul *et al.*, 2022). One of the most important natural resources for maintaining life is water. Households utilize it for a variety of tasks, including cleaning, washing, and drinking. Water is an essential resource in industries that is needed for the majority of manufacturing operations. In industrial processes, it serves as a cooling agent, solvent, raw material, and cleaning agent. Industries require a huge amount of water, and the amount varies according on the industry (Bhagwat, 2019). Water is therefore a basic resource that is necessary for both economic growth and human survival.

However, there is a serious risk to the environment and public health due to the massive amounts of wastewater produced as a result of the fast industrialization and urbanization (Gautam and Saini, 2020). Over 80% of the sewage produced by human activity is dumped untreated into rivers and oceans, polluting the environment and causing over 50 diseases. Poor water quality is linked to 50% of child fatalities and 80% of illnesses globally (Lin *et al.*, 2022). As a result, the pharmaceutical business is thought to be among



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the most polluting industries, generating large amounts of wastewater (Krishnarao *et al.*, 2001). The growing need for industrial output and the subsequent release of contaminants into water bodies have made the treatment of industrial wastewater a critical concern.

The coagulation-flocculation process is one of the most widely utilized techniques for treating industrial wastewater. Chemical precipitation and biological treatment are two examples of traditional wastewater treatment techniques that have drawbacks in terms of cost, effectiveness, and environmental impact. Accordingly, coagulation is crucial to the treatment of water and wastewater (Ejikeme *et al.*, 2020).

Due to its simplicity and cost, the widely utilized coagulation-flocculation process is a crucial stage in the treatment of water and wastewater. Physicochemical processes like flocculation and coagulation can lower pollution and produce clean, reusable water, claim Manhokwe and Zvidzai (2019). It is possible to separate the entire coagulation-flocculation treatment cycle into two separate treatments, which should be administered in that order. Coagulation is the first process that destabilizes a colloidal suspension or solution. The addition of destabilizing particles that clump together, come into contact, and create massive agglomerates that are usually simpler to separate by settling through gravity is the second sub-process, called flocculation (Narmatha *et al.*, 2017). The method is appropriate for treating a variety of industrial wastewater because it effectively removes organic debris, colour, turbidity, and odour from wastewater.

Investigating sustainable and alternative techniques for treating wastewater with natural materials has gained popularity in recent years (Olunusi *et al.*, 2024). Compared to traditional chemicals, using natural materials as coagulants and flocculants provides a number of benefits. First of all, they are easily accessible, renewable resources that is locally available. Second, there is less chance of negative environmental effects because they are non-toxic and biodegradable (Kumar *et al.*, 2019). The treatment of industrial wastewater using a unique natural coagulant (melon seed shells) hitherto regarded as waste came to mind.

The Hausa, of north, Igbo of the east, and the Yoruba of the west in Nigeria, call melon seed shells (*Colocynthis vulgaris* Shrad) "Gushi," "Egusi," and "Elegusi," respectively (Igwilu *et al.*, 2021). It belongs to the Cucurbitaceae family (Essien and Eduok, 2013). Ogbe and George (2012) investigated the proximate composition of melon husks and discovered that, among other things, the husks included notable amounts of crude protein ($19.14\% \pm 0.46\%$) and carbs ($61.01\% \pm 0.35\%$). Proteins and polysaccharides in high concentrations have the ability to coagulate (Amar *et al.*, 2021). Thus, it makes sense to turn this waste into a coagulant for the treatment of industrial wastewater.

Many studies on the seeds of *Colocynthis vulgaris* Shrad have mainly focused on oil extraction from the seeds rather than examining the shells. Some of these studies, like those by Ogunwa *et al.* (2015) and Agu *et al.* (2018), are among the few that have explored this area. Consequently, there is no existing literature on

the utilization of *Colocynthis vulgaris* Shradseed shell(CVSSS) for treating industrial wastewater or effluents. Hence the novelty of the present work. Thus, the research went further to RSM to optimize the coagulation-flocculation process for treating pharmaceutical wastewater using melon seed shells.

2. Materials and Methods

2.1 Materials

A pharmaceutical company in Enugu State, Nigeria, provided the wastewater used in this investigation. To assess its turbidity, pH, COD, and other properties, the wastewater was examined. The bio-coagulant, melonshell, was obtained from Abakpa market in Enugu East L.G.A of Enugu State. All chemicals use were of analytical-grade.

2.2 Methods

2.2.1. Pharmaceutical wastewater characterization

Key initial parameters of the pharmaceutical wastewater were determined using standard methods for the examination of water and wastewater (SMWW), namely methods 2130B (2001), 2320A (2012), the American Public Health Association (APHA) standard method 2540D (1995, APHA, 2005), and the American Water Works Association (AWWA) standard procedure 205 (1985), were followed in determining the turbidity, pH, total suspended solids (TSS), total dissolved solids (TDS), and total solids, both before and after coagulation.

2.2.2. Extraction of bio-coagulant and experimental procedure (jar test)

A commercial grinding machine was used to grind 1,000g of cleaned and sun dried melon seed shells into a fine powder. To guarantee a uniform surface area, the powder was further sieved via a 0.6 mm sieve. The melon seed shells were treated with a 3.5% (w/v) solution of diluted sodium hydroxide (NaOH) to remove the crude coagulant. Using a magnetic stirrer, the powder and NaOH solution were combined in a 500 ml beaker at a 1:10 (w/v) ratio and swirled for two hours at 65°C. While churning, a light foam developed, which eventually evaporated. After the mixture had cooled to room temperature, the crude extract was filtered out of the particles using a filter sack system. To concentrate the bio-coagulant, the filtrate was decanted after being left to settle for half an hour. After being sun-dried to lower its moisture content, the concentrated bio-coagulant was ground into a fine powder with a mortar and pestle and put in an airtight container to be used as a coagulant in a jar test kit. The removal efficiency (% Removal) was calculated from the following formula.

$$\% \text{ Removal} = \frac{C_0 - C}{C_0} \times 100 \quad (1)$$

Where C_0 and C = COD, TSS and colour contents of wastewater (mg/L) before and after coagulation treatment, respectively.



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2.2.3. Coagulation -flocculation process optimization using RSM method

Response surface methodology (RSM) and central composite design (CCD) were used to optimise the coagulation-flocculation process for treating pharmaceutical wastewater. Table 1 lists the process parameters, such as time, coagulant concentration, and coagulant volume, while Table 2 displays the experimental design matrix. Design Expert software (version 8.0.7.1) was used in this work to improve the treatment conditions and build the experimental setup. There were twenty studies in all, using a two-level, three-factor full factorial design as the experimental design. Time, coagulant volume, and coagulant concentration were selected as independent variables. The turbidity reduction attained when treating pharmaceutical wastewater with CVSSS was the reaction. Each variable's actual and coded levels are shown in Table 2. However, it should be noted that the software uses coded values to identify essential elements, meaning that the coded empirical equation is used to look at how the variables affect the response. Equation (2) provides an illustration of the empirical equation.

$$Y = \beta_0 + \sum_{i=1}^4 \beta_i X_i + \sum_{i=1}^4 \beta_{ii} X_i^2 + \sum_{i=1}^4 \sum_{j=i+1}^4 \beta_{ij} X_i X_j \quad (2)$$

Table 1: CCD summary for pharmaceutical waste water treatment by coagulation

Independent variables		Coded variable levels				
			-1	0	+1	+α
Settling time	minute	3	6	9	12	15
Coagulant concentration	Mg/l	50	100	150	200	250
Coagulant volume	ml	0.5	1.0	1.5	2.0	2.5

Table 2: CCD table for pharmaceutical wastewater treatment using melon seed shells in terms of actual process factors

Std	Run Order	Coagulant Conc (mg/l)	Coagulant Volume (mls)	Time (mins)	% Turbidity Removal
4	1	200	2	6	
18	2	150	1.5	9	
9	3	50	1.5	9	
16	4	150	1.5	9	
2	5	200	1	6	
15	6	150	1.5	9	
1	7	100	1	6	
7	8	100	2	12	
17	9	150	1.5	9	
19	10	150	1.5	9	
6	11	200	1	12	
12	12	150	2.5	9	
20	13	150	1.5	9	
10	14	250	1.5	9	
8	15	200	2	12	
14	16	150	1.5	15	
13	17	150	1.5	3	
5	18	100	1	12	
11	19	150	0.5	9	
3	20	100	2	6	

3. Results and Discussion

3.1 Characterization of the Coagulant

A coagulant's ability to neutralize charges on particles, create flocs, and settle or float in the treatment system are some of the features that determine how effective the coagulant is. This section seek to provide information on the potentials of melon seed shells as a coagulant.

3.1.1 Proximate analysis of the natural coagulants

The nutritional and functional characteristics of melon seed shells are revealed by the proximate composition as indicated in Table 3.

Table 3: Proximate composition of the natural coagulant

Parameters (%)	Melon seed shells
Moisture	7.85
Ash	4.32
Protein	13.91
Fat	15.31
Crude fibre	10.41
Carbohydrate	48.20

From the table, melon seed shells have a moisture content of 7.85%. Lower moisture content decreases microbial activity and lengthens the seed's shelf life, hence, produces better coagulant for better coagulation-flocculation performance (Animetu *et al.*, 2017, Ajayi *et al.*, 2014). MSS have an ash level of 4.32%. Ash content represents the amount of inorganic matter in the sample (Animetu *et al.*, 2017). Higher ash content, however, may also result in more turbidity, which could affect the course of treatment negatively.

The protein content in melon seed shells (MSS) is 13.91%, which falls within the range of results ($19.14\% \pm 0.46\%$) of similar studies on melon husks reported by Ogbe and George (2012). The active ingredient responsible for coagulation is protein (Ejikeme *et al.*, 2018; Igwegbe and Onukwuli, 2019). Proteins contribute to the coagulation process by forming complexes with negatively charged particles in the water, leading to the formation of flocs, which finally settles out of the solution (Alfred and Bridgeman, 2015). The crude protein content in *Moringa oleifera* seeds, an established coagulant is 35.97% (Olagbemide and Alikwe, 2015), which is higher value than the ones obtained from the MSS.



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The fat value of melon husks is $1.71\% \pm 0.04\%$, as reported by Ogbe and George (2012), which is different from the 15.31% fat content of MSS. Due to its emulsifying qualities, fats can have a detrimental effect on the coagulation process by increasing turbidity (Animetu *et al.*, 2017). As a result, less fat is usually preferable. The crude fibre value of melon husks is $8.12\% \pm 0.85\%$, which is slightly different from the crude fibre content of MSS (10.41%) as reported by Ogbe and George (2012). By making the water more viscous, crude fibre can aid in the coagulation process and promote the development of flocs. Higher levels of crude fibre, however, can also result in more turbidity. The carbohydrate content (Table 3), suggests that polysaccharides like carbohydrate are potential coagulants for wastewater treatment, according to other researchers (Okuda *et al.*, 2001; Torres *et al.*, 2013). However, the carbohydrate content of melon seed shells (MSS) differs slightly from the work of Ogbe and George (2012), with the carbohydrate value of melon husks being $61.01\% \pm 0.35\%$. Carbohydrate contains oxygen and hydrogen elements as part of its chemical composition, which increases the likelihood of the formation of charges like hydrogen and oxygen ions (Njuguna *et al.*, 2014).

As a result, organic substances like proteins and polysaccharides make up the majority of the active elements in natural coagulants that cause coagulation in wastewater treatment. These substances aid in the neutralization of charges on suspended particles, which promotes their aggregation and facilitates their removal from wastewater.

3.1.2 Fourier transform infrared spectroscopy (FTIR) of the coagulants

FTIR is used to identify the functional groups that are actively taking part in the coagulation-flocculation processes (Nharingo *et al.*, 2015). The spectrum was collected from 3500 to 1000 cm^{-1} . The FTIR spectra of the MSS are shown in Figure 1. The presence of peak at $(1625 - 1640\text{ cm}^{-1})$ indicates the presence of double bond $\text{C}=\text{C}$ of amino compounds. The carboxyl, $\text{C}=\text{O}$ ($1733.2 - 1740.7\text{ cm}^{-1}$), and hydroxyl, $\text{O}-\text{H}$ ($2169.3 - 2322.1, 3697.5, 3265.1\text{ cm}^{-1}$) groups were observed. Other groups including amino or amide ($\text{N}-\text{H}$) are among the preferred groups for the coagulation-flocculation processes (Zhang *et al.*, 2010). The medium alkane group, $\text{C}-\text{H}$ stretch ($2855.1 - 2922.2\text{ cm}^{-1}$) was observed on the coagulant. A strong band of $\text{O}-\text{H}$ stretch of alcohols (3265.1 cm^{-1}), was observed. Strong bonds of $\text{C}=\text{O}$ stretch of aldehyde (1740.7), strong bonds of $\text{N}-\text{O}$ stretch of nitro compound (1535.1 cm^{-1}), and $\text{C}-\text{H}$ weak bend of aromatics (1979.2) were also observed. These strong bands took an active part in the treatment process. Also, the presence of $-\text{H}-\text{C}=\text{O}$ stretch of aldehydes (2832.8 cm^{-1}) was dictated in melon seed shell (Table 4).

Table 4: FTIR of Melon Seed Shells (MSS)

S/no	Peak	Intensity	Functional Group	Class of Compounds
1	3697.5	98.678		
2	3391.9	96.431	O-H stretch	Alcohols
3	3280.1	95.990	=C-H stretch	Alkanes
4	2892.4	98.823	C-H Stretch	Alkanes
5	2832.8	96.670	H-C=O Stretch	Aldelyde
6	2091.0	98.120	C-H Stretching	Aldelyde
7	1934.5	98.106	C=C=C Stretching	Allenenes
8	1733.2	95.598	C=O Stretch	Aldelyde
9	1640.0	93.326	C=C Stretch	Alkane
10	1509.6	93.514	N-H Bend	
11	1420.1	92.270	-C	Acids
12	1367.9	92.609		Alkane
13	1226.3	91.630	C-F Stretch	Alkyl halides
14	1263.6	91.680	=C-o-c Sym. & Asym. Stretch	Ethers
15	1144.3	90.052		
16	1006.4	31.931	C-F Stretch	Alkyl halides

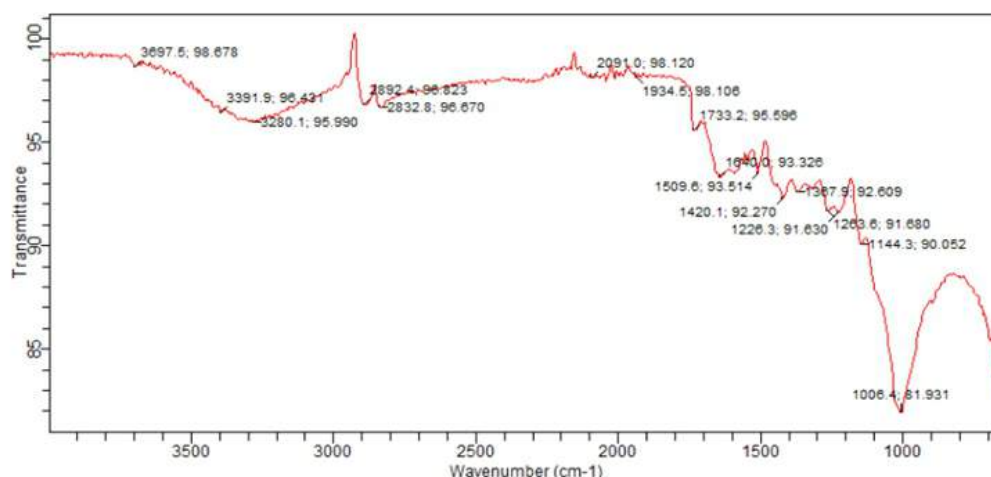


Fig. 1: FTIR spectra on Melon Seed Shells(MSS)

3.1.3 X-ray fluorescence (XRF) analysis of the coagulants

The XRF-mineral analysis was conducted to determine the micro-nutrients composition in the MSS. The result obtained showed remarkable higher concentration of O, Al and Si in Melon seed shells. Moreover, a weaker concentration was obtained for S, Cl, K, Ca and Fe for MSS. However, the concentration of P, S, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Rb, Sr, Zr, Nb, Ta and W appeared as trace elements. Ernest *et al.*, (2017) reported that the mineral elements present in water melon seeds which may have aided its coagulant properties were Al, Ca, Mg and Fe etc.

3.2 Characterization of Wastewater before and after treatment

This section presents the findings from the physicochemical characterization of the pharmaceutical wastewater that was collected both before to and after the coagulation treatment. Understanding



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wastewater's composition, spotting possible health hazards, and creating efficient treatment techniques are all made easier with its characterization. The characteristics of pharmaceutical wastewater are thus shown in Table 5. The table indicated high levels of alkalinity, acidity, hardness, chloride, COD, BOD, TS, conductivity, temperature, and turbidity in the untreated pharmaceutical wastewater. According to Ugonabo *et al.* (2016), the presence of total dissolved solids (TDS) and total suspended solids (TSS), in the pharmaceutical wastewater made the wastewater murky and necessitated their treatment.

The results obtained after treatment were compared to national and international standard for water and wastewater, including pH, total suspended, total dissolved solids, total solids, and turbidity (NESREA, 2009; WHO, 1996). In comparison to the allowable limit of 5 mg/l (NESREA: National Environmental Standards and Regulations Enforcement Agency), 60 mg/L (WHO), and 1500 mg/l (NESREA, WHO) for effluent reuse, the results indicate a total suspended solid (TSS) of 400 mg/l and a total dissolved solid (TDS) content of 1350 mg/l, respectively (Ejimofofor *et al.*, 2021; Aniyikaiye *et al.*, 2019; Act, 2004). As a result, the TDS in the sample was found to be within the WHO and NESREA permissible limits. The high TSS suggests that the wastewater has a high particle load, which would be problematic if it were released into the environment or water bodies. Pharmaceutical wastewater had a pH of 7.1, which was within the WHO and NESREA acceptable ranges of 6.5 to 8.5 and 6 to 9, respectively (Ado *et al.*, 2015; WHO Compendium, 2006).

Therefore, if the pharmaceutical wastewater is released or used for other purposes like irrigation, its pH won't affect aquatic life or the environment. In contrast to the standard values of 1000 mg/l (WHO, Kenneth *et al.*, 2016) and 300 NTU (National Environment Standards for Discharge of Effluent into Water or on Land Regulations, 1999), respectively, the total solid (TS) and the extent of the colloidal matter in nephelometric turbidity unit (NTU) were determined to be 1750 mg/l and 95 NTU (turbidity).

Table 5: Characterization of pharmaceutical wastewater (PW) before and after treatment with the coagulant

Parameters	Unit	Before treatment	After treatment
Alkalinity	(mg/l)	150	110
Acidity	(mg/l)	150	115
Hardness	(mg/l)	300	18.6
Chloride	(mg/l)	1871	125.5
COD	(mg/l)	1500	130.8
BOD	(mg/l)	500	138.2
DO	(mg/l)	312	319.9
TSS		400	210.5
TDS		1350	139.6
TS		1750	350.1
Conductivity	(Ns/cm)	1500	200.6
Temperature	(°C)	280	27.7
Lead	(mg/l)	0.010	NIL
Copper	(mg/l)	25.91	0.225
Iron	(mg/l)	0.532	0.151
pH		7.1	7.0
Phosphorus	(mg/l)	5.391	0.118
Mag/cal	(mg/l)	85.30	21.8
Sulphate	(mg/l)	450.9	80.5
Turbidity	(NTU)	95	68.5
Nitrate	(mg/l)	3.18	NIL

Following wastewater treatment with a MSS coagulant, the pH (7.0) stayed within the normal allowable limit, but the TSS, TS, turbidity, and TDS levels were reduced by 210.5 mg/l, 350.1 mg/l, 68.5 NTU, and 139.6 mg/l, respectively, compared to their initial values (Igwegbe and Onukwuli, 2019; Menkiti *et al.*, 2016; Menkiti and Ejimofor, 2016).

When MSS were added to the untreated wastewater, the alkalinity dropped from 150 mg/l to 110 mg/l (Table 5). Acidity, hardness, chloride, COD, BOD, conductivity, and temperature all decreased following treatment (Table 5). For instance, after applying the coagulant to the untreated wastewater, the chloride level dropped from 1871 mg/l to 125.5 mg/l.

Significant levels of lead, copper, iron, and phosphorus were found in the untreated wastewater in terms of heavy metals (Table 5). Nevertheless, these heavy metals were greatly decreased or entirely removed after treatment (Table 5). For example, once the coagulant was added, the copper content in the untreated wastewater dropped from 25.91 mg/l to 0.225 mg/l. The treated pharmaceutical wastewater had negligible nitrate levels, demonstrating how well the treatment removed the nitrate pollutant.

3.3 Optimization of the Process Factors for the Treatment of Pharmaceutical Waste (PW) Using Coagulation

The experimental and predicted values for the central composite design (CCD) for treating pharmaceutical wastewater using MSS are shown in Table 6. Three experimental components and a total of 20 experimental runs were utilized.

Table 6: Experimental design with response for the treatment of wastewater from pharmaceutical industry using melon seed shells.

Run Order	Coagulant Conc (mg/l)	Coagulant Volume (mls)	Time (mins)	PW-MS Turbidity Removal (%) Exp	PW-MS Turbidity Removal (%) Prd
1	200	2	6	33.54	33.95
2	150	1.5	9	35.30	34.94
3	50	1.5	9	27.87	28.53
4	150	1.5	9	35.49	34.94
5	200	1	6	31.61	32.15
6	150	1.5	9	34.02	34.94
7	100	1	6	27.70	27.90
8	100	2	12	34.0	33.58
9	150	1.5	9	35.52	34.94
10	150	1.5	9	35.50	34.94
11	200	1	12	36.83	37.27
12	150	2.5	9	34.63	36.12
13	150	1.5	9	35.13	34.94
14	250	1.5	9	34.82	34.40
15	200	2	12	36.0	35.20
16	150	1.5	15	34.14	34.55
17	150	1.5	3	28.36	28.18
18	100	1	12	33.30	33.02
19	150	0.5	9	33.65	33.76
20	100	2	6	33.38	32.33



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3.3.1 Statistical analysis (PW-MSS turbidity removal)

To evaluate the adequacy of the model showing the elimination of turbidity by treating pharmaceutical wastewater with MSS, two separate tests were conducted: the lack of fit tests and the model summary statistics. The highest order polynomial that is not aliased and has a non-significant p-value would typically be selected from the lack of fit tests. The 2FI, linear, and cubic model (aliased) did not adequately describe the experimental data, according to the findings of the lack of fit tests.

The R-squared number indicates how well the experimental variables and their interactions can account for the variability in the actual response values. Typically, the model with the highest adjusted and predicted R-squared is chosen, and the difference between the adjusted and predicted R-squared should typically not exceed 0.2. There might be an issue with the data or the model if the predicted and adjusted R-squared values are too far apart (by more than 0.2) (Taran and Aghaie, 2015). The quadratic model's R-squared, adjusted R-squared, and forecasted R-squared values are 0.9433, 0.9102, and 0.8065, respectively, according to the model summary statistics. The afore-mentioned results demonstrate that the quadratic model gave an excellent explanation for the link between the independent variables and the related response. The quadratic model was used to assess each parameter's impact in relation to these findings.

The results, which are displayed in Table 7, were examined using the analysis of variance (ANOVA) to ascertain how appropriate is the experimental design. The quadratic regression model's ANOVA showed that it is a significant model. The ratio of the regression's adjusted mean square to the residual's adjusted mean square was used to get the model's F-value. It is the ratio of the amount of variation that the model has been able to explain to the amount of variance that remains unexplained. The model's F-Value of 28.51 suggested that it was significant, and noise had a 0.01% probability of producing an F-value this high. The test used to compare the variance associated with a term with the residual variance is called the F-Value. The F-value of the independent variables A, B and C were estimated at 54.48, 8.81, and 64.11 respectively.

The significance of the model is demonstrated by its extremely low model P-value (Prob. >F). The model terms are considered significant when the P-value is less than 0.05. The tested variables utilized in the design are significant model terms, according to the values of P for the estimated coefficients. A, B, C, AB, BC, A², and C² are hence important model terms (Table 7). The "Lack of Fit F-value" of 2.55 suggests that, in comparison to the pure error, the Lack of Fit is not significant. Noise has a 16.02% chance of producing a "Lack of Fit F-value" this high. Since it shows that the model is well fitted, a non-significant lack of fit is advantageous. As a result, the model may be used to accurately forecast how the percentage of turbidity removed from pharmaceutical wastewater using MSS will respond. Equation (3) displays the final model equation in terms of coded factors.

$$\text{PW-MS Turbidity removal} = +34.94 + 1.47A + 0.5905B + 1.59C - 0.6587AB - 0.9666BC - 0.8688A^2 - 0.8926C^2 \quad (3)$$

In terms of the actual factors, the final model equation (Equation 4) is as follows:

$$\text{PW-MSS Turbidity removal} = -6.49637 + 0.173142 \text{ Coagulant Conc.} + 10.93288 \text{ Coagulant Volume} + 3.28260 \text{ Time} - 0.026350 \text{ Coagulant Conc.} * \text{Volume} - 0.644375 \text{ Coagulant Volume} * \text{Time} - 0.000348 \text{ Coagulant Conc.}^2 - 0.099174 \text{ Time}^2 \quad (4)$$

In Equations (3) and (4) all the linear factors (coagulant conc. (A), coagulant volume (B) and time (C)) were significant (p-values < 0.05). The effect of the linear interactions AB and BC are also significant (p-values < 0.05). While the negative sign suggests an antagonistic influence of the factor on the response, the positive sign in front of the terms indicates a synergistic effect.

Table 7 ANOVA for response surface quadratic model (PW-MS turbidity removal)

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	126.35	7	18.05	28.51	< 0.0001	significant
A- Coagulant Conc.	34.49	1	34.49	54.48	< 0.0001	
B- Coagulant Volume	5.58	1	5.58	8.81	0.0117	
C-Time	40.59	1	40.59	64.11	< 0.0001	
AB	3.47	1	3.47	5.48	0.0373	
BC	7.47	1	7.47	11.81	0.0049	
A ²	19.89	1	19.89	31.42	0.0001	
C ²	20.99	1	20.99	33.16	< 0.0001	
Residual	7.60	12	0.6331			
Lack of Fit	5.93	7	0.8477	2.55	0.1602	not significant
Pure Error	1.66	5	0.3326			
Cor Total	133.94	19				

The ratio of the estimate's standard deviation to the actual response's mean value is known as the coefficient of variation, or CV. It also serves as a gauge for the models' repeatability and reproducibility (Chen *et al.*, 2012). The model can be regarded as reasonably replicable, according to the results, which showed a CV value of 2.37% (Chen *et al.*, 2012). According to Table 8, the signal to noise ratio, which is used to determine the value of sufficient precision, is 18.6248. This suggests that there is a sufficient signal to noise ratio relationship. The outcome demonstrates that navigating the design space is possible using the model.

Table 8: Summary of regression values (PW-MSS Turbidity removal)



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Std. dev.	0.7956	R-squared	0.9433
Mean	33.53	Adj. R-squared	0.9102
C.V. %	2.37	Pred. R-Squared	0.8065
Adeq. Precision	18.6248		

As seen in Figure 2, the data were also examined to determine whether the experimental and anticipated turbidity removal (%) correlated. The projected values were computed from the quadratic equation, whereas the experimental values were the measured response data for the runs created by the CCD model. Figure 2 shows that there was a good correlation between the experimental and anticipated values of the response, with the data points on the plot being fairly dispersed close to the straight line. This demonstrates that the central composite design (CCD) may be utilized to carry out the process optimization operation and that the selected model is suitable.

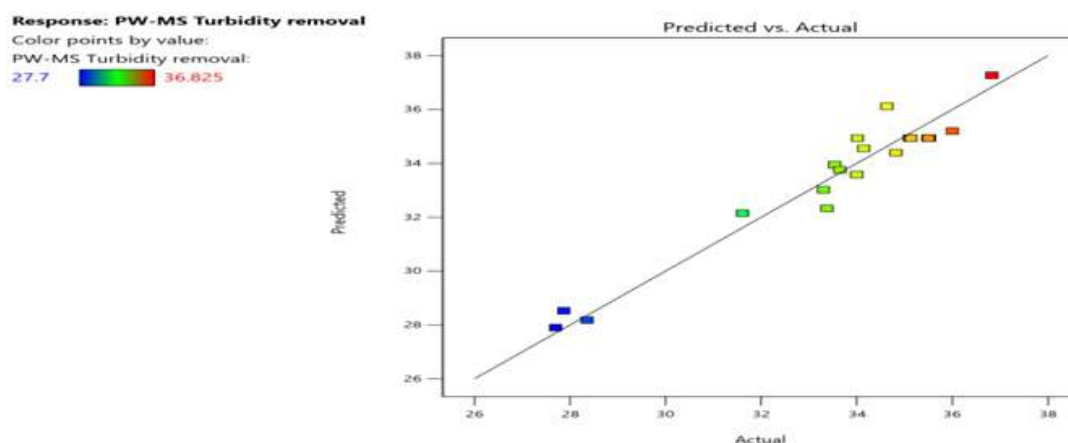


Fig. 2: Plot of predicted values versus experimental values (PW-MSS Turbidity removal)

In order to identify the ideal conditions, the turbidity removal from pharmaceutical wastewater was optimized for varying coagulant concentration, coagulant volume, and time. The response, or the removal of turbidity, was plotted against two factors while keeping other factors at their central level. The effect of process parameters on turbidity removal was represented by 3D response surface plots and contour plots, as shown in Figures 3 to 4, which show the influence of coagulant concentration (A), coagulant volume (B), and time (C) on turbidity removal, with the significance of interactive variables expressed in terms of response surface plots and contour plots. The three input variables examined were found to have an impact on the turbidity removal with $p < 0.05$ each.

Using a 3D response surface methodology, Figures 3–4 illustrate the effects of the three variables on coagulation-flocculation efficiency under the optimal coagulation condition and complex interaction between the two condition variables, which implies that the effect produced by changing one variable depends on the level of other variables (Mirazimi *et al.*, 2013). The treatment method for removal of

turbidity from pharmaceutical wastewater was investigated in order to determine how the process factors affected the removal of turbidity, and RSM's flexibility in exploring the design area was a plus. With the assumption that all other factors were set to their mean coded value of zero, only the relationship between two components was considered at any given time when solving the model equations for the various interacting effects on turbidity removal. The combined interactive impacts of changing the process parameters inside the design space were observed using 3D surface plots.

The coagulant concentration used has a significant impact on the efficacy of the coagulation-flocculation process; the maximum turbidity removal was recorded at a coagulant concentration of 187.414 (mg/l) and a coagulant volume of 1.077ml, as indicated by the quadratic interactive effect (Figure 3). The turbidity removal was found to be linearly related to the coagulant concentration, increasing with the coagulant concentration, with the optimum occurring at 187.414 (mg/l). Table 8 shows that the concentration of the coagulant had a significant impact on the removal of turbidity. As a result, coagulant concentration and coagulant volume effectively interact; this interaction was noteworthy (Table 8). The 3D plot of coagulant concentration with coagulant volume (Figure 3) is concave sloping both from back to front and left to right with the pick at the middle and concentric contour lines. This demonstrates that both adjustments in the parameters have approximately identical impact on turbidity removal.

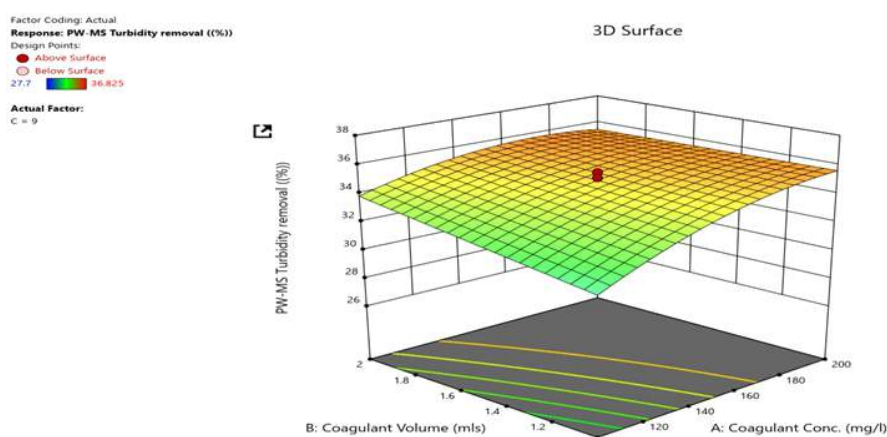


Fig. 3: 3D plot of the effect of coagulant volume and coagulant concentration on % removal of turbidity from pharmaceutical wastewater treatment with MSS

Figure 4's contour and three-dimensional plot demonstrate how the coagulant volume and solution duration had a major impact on the percentage of turbidity removed during coagulation. Table 8 makes this clear, and the impact of coagulant amount is substantial. Along with time and coagulant concentration, the coagulant volume factor had substantial combined effects. The P-values were less than 0.05, as shown in Table 6. On contour graphs, where the contour plots are curves, this is also understandable. 1.077 millilitres was the wastewater treatment's ideal coagulant volume. As the coagulant volume rises, the turbidity values fall, suggesting that the coagulant is successful in eliminating suspended particles and lowering the wastewater's turbidity.

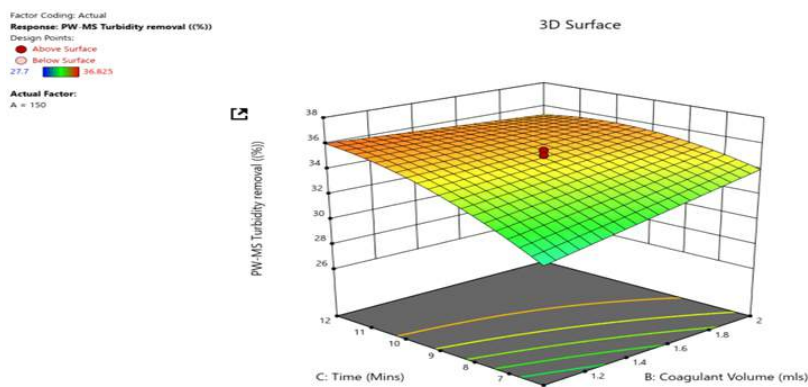


Fig. 4: 3D plot of the effect of time and coagulant volume on %turbidity removal from pharmaceutical wastewater treatment with MSS

3.3.2 Verification of optimum numerical solution for coagulation-flocculation process

Optimization focuses on identifying the best option from a comprehensive set using effective quantitative techniques. The primary objective of optimization is to determine the variable values within the process that will provide the optimal performance criterion (Igwilu *et al.*, 2021). The model identified the process parameters that resulted in the highest turbidity removal. The selected optimal solution consisted of a coagulant concentration of 187.414 mg/l, a coagulant volume of 1.077 ml, and a duration of 11.414 minutes (Table 9). Under these ideal conditions, the model predicted a maximum turbidity removal of 36.828%. To validate these predicted outcomes, an experiment was conducted under the same optimal conditions, yielding a maximum turbidity removal of 36.911%. This experimental result was only 0.22% lower than the predicted maximum, indicating that the model is reliable.

Table 9: Numerical optimum values for coagulation-flocculation process (PW-M5Turbidity removal)

Time (mins)	Coagulant conc. (mg/l)	Coagulant volume (ml)	Turbidity removal (predicted) (%)	Turbidity removal (experimental)(%)	Error(%)
11.414	187.414	1.077	36.828	36.911	0.22

The graph of the predicted versus the actual values, as shown in Fig. 2, also established the nearness of the predicted and actual values. The diagonal positions of the optimisation data on the squared graph showed the nearness of the predicted and the actual points, and as a result, the quadratic model fits the data.

4. Conclusion

This study highlights the efficacy of melon seed shells (MSS) as a sustainable, eco-friendly coagulant for pharmaceutical wastewater treatment. MSS was characterized through proximate analysis, FTIR spectroscopy, and XRF, revealing key components like proteins (13.91%), polysaccharides (48.20%), and



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functional groups (O-H, C=O, N-H) that enable charge neutralization and floc formation, enhanced by minerals such as Al, Si, and Fe. Physicochemical analysis demonstrated significant reductions in critical wastewater parameters, including TSS (400 to 210.5 mg/L), COD (1500 to 130.8 mg/L), BOD (500 to 138.2 mg/L), turbidity (95 to 68.5 NTU), and heavy metals like copper (25.91 to 0.225 mg/L) and lead (0.010 to NIL), aligning treated effluent with NESREA and WHO standards. Optimization using response surface methodology and central composite design identified ideal conditions (coagulant concentration: 187.414 mg/L, volume: 1.077 mL, time: 11.414 minutes), achieving 36.911% turbidity removal, closely matching the predicted 36.828% (error: 0.22%), with a reliable quadratic model ($R^2 = 0.9433$, adjusted $R^2 = 0.9102$). Melon seed shells thus offer a cost-effective, green alternative to synthetic coagulants, promoting agricultural waste valorization, with potential for scalability and enhanced efficiency through future research into long-term stability and material combinations for broader environmental remediation applications.



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D. Food Security for Sustainable Development, Quality Management and Support to SMEs, The Role of AI in Process Industry

Unlocking Sustainable Lithium Mining in Nasarawa State, Nigeria: Opportunities for Chemical Engineers and Conflict Resolution Strategies

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Abstract:

Nasarawa State, Nigeria's "Home of Solid Minerals," sits atop significant lithium deposits crucial for the global energy transition. This study examines the socio-environmental challenges and economic opportunities of lithium mining in Nasarawa Local Government Area (LGA), where conflicts over land in communities like Mararaba Udege, Agatu Onda, and Udege Mbeki threaten sustainable development. Through field surveys, GIS mapping, and stakeholder analysis, the study documents how illegal mining operations have contaminated water sources, displaced farmers, and triggered violent clashes. The authors recognized the potentially pivotal role of chemical engineers in implementing value-addition technologies and sustainable mining practices that could transform Nigeria's mineral sector. Findings reveal that establishing local processing plants could increase regional GDP by 30% while reducing environmental degradation by 50%. The study proposes a community-centred framework for mineral development that prioritizes conflict resolution, technical training, and circular economy principles. With lithium prices projected to grow 200% by 2030, Nigeria must act decisively to harness this resource wealth responsibly.

Keywords: Lithium mining, Nasarawa State, artisanal mining conflict, value addition, chemical engineering solutions, sustainable mineral policy

1. Introduction

The global energy transition has driven lithium prices from £4,600/ton in 2020 to over £61,000/ton by 2022 (CAPPA, 2024), positioning Nasarawa State—with its 44 mineral types, including high-grade spodumene—as a key player in this surge (Tyessi, 2022; Ogbuigwe, 2024). Major investments like Avatar Energy's \$100 million processing plant in Endo highlight its economic potential (CAPPA, 2024). However, illegal mining and escalating land-related conflicts, as seen in Mararaba Udege, Agatu Onda, and Udege Mbeki, risk repeating the Niger Delta's "resource curse" (Oguntona & Bolaji, 2021). This study explores how chemical engineers, through sustainable mining and value-chain integration, can turn lithium from a source of conflict into a tool for development. Drawing on field data, we assess pollution, analyze conflict triggers, and propose technical solutions aligned with Nigeria's Mineral Value Chain Regulations (Alake, 2023; FurtherAfrica, 2025), addressing the urgent need to balance economic gains with community rights and environmental protection.

2. Mineral Resource Mapping and Strategic Potentials in Nasarawa

Nasarawa State, known as “The Home of Solid Minerals,” lies in Nigeria's middle belt and is rich in pegmatitic and sedimentary formations bearing high-demand industrial and energy minerals. The Nigerian Geological Survey Agency (NGSA, 2023) and local exploration reports confirm significant lithium-bearing deposits—particularly spodumene and lepidolite—in Udege Mbeki, Mararaba Udege, and Agatu Onda, all within Nasarawa LGA. Beyond lithium, the state also holds commercial quantities of tantalite, columbite, gold, limestone, coal, clay, and glass sand. These resources are unevenly distributed, offering region-specific opportunities for SMEs and localized value addition. Accurate knowledge of mineral locations and volumes is essential for strategic planning by investors, engineers, and entrepreneurs

(see Fig. 1).

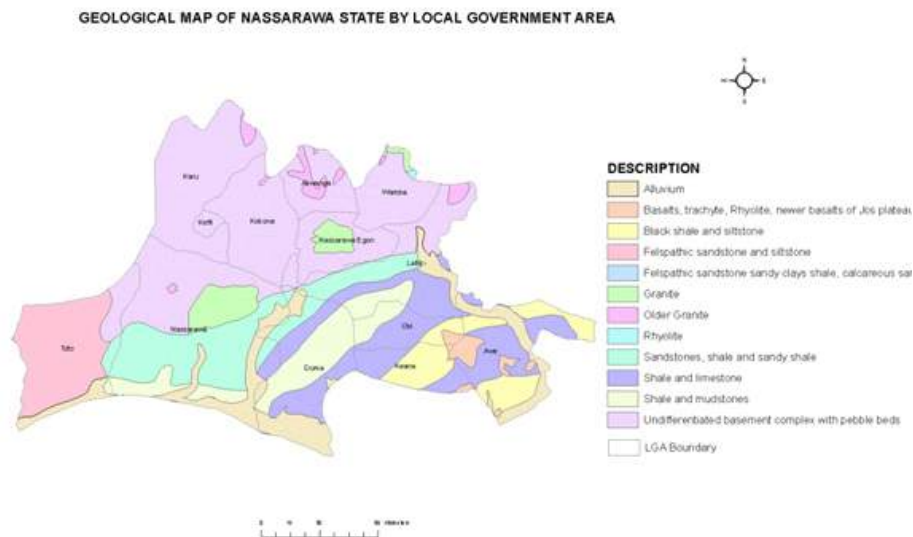


Table 1: Key Mineral Occurrences in Nasarawa State

Mineral	Main LGAs/Communities	Estimated Resource	Industrial Value
Lithium (Li O)	Udege, Mararaba Udege, Agatu Onda	~1,200–3,000 tonnes	EV batteries, storage devices, green energy
Tantalite/Columbite	Akwanga, Udege Mbeki, Wamba	~5,000–8,000 tonnes	Electronics, specialty alloys
Gold	Kokona, Nasarawa Eggon, Agatu Onda, Wamba	~200–500 kg	Investment, jewelry, foreign exchange
Limestone	Adudu, Obi, Jangwa	~5 million tonnes	Cement, building material
Coal	Obi, Shankodi, Jangwa	~3 million tonnes	Energy, local power generation
Salt/Glass Sand	Keana (salt), Lafia, Doma (sand, clay)	Variable industrial deposits	Sodium compounds, bottles, ceramic

Source: NGSA (2023); REAN Bulletin (2024); State Mineral Development Review

The confirmed lithium reserves (~2,000+ tonnes) in Nasarawa present a strategic opportunity for the state to become Nigeria's lithium processing hub, enabling SMEs to provide micro-scale services such as crushing, pre-concentration, and packaging. Chemical engineers and technical graduates can support the sector through ore beneficiation, pilot plant development, environmental impact assessments, effluent control, and the design of lithium separation systems. Artisanal and semi-industrial operators in Wamba and Udege can tap into new technologies for tantalite extraction, while industrial minerals in Adudu, Jangwa, and Obi LGAs create low-cost opportunities for SMEs in cement brick making, coal briquette production, and glass component manufacturing.

2.1 Lithium Mining and the Rise of SME Potential in Nasarawa

Lithium mining in Nasarawa LGA presents a pivotal opportunity to expand Nigeria's industrial base and stimulate local economies through SME participation. Globally recognized as a strategic mineral, lithium is critical to the clean energy transition, particularly for lithium-ion batteries used in electric vehicles, electronics, and renewable systems (Ogunleye, 2021). With rising global demand, Nasarawa's pegmatite-hosted lithium deposits, especially in Udege and Mararaba offer significant potential, currently underexploited by artisanal miners (see Table 2). Despite growing interest from foreign firms, local SME involvement remains limited due to challenges such as inadequate geological data, poor infrastructure, and a lack of processing capacity (Eze & Alabi, 2021). However, SMEs can participate across the value chain through mineral sorting, crushing, gravity concentration, and supporting services like surveying, drilling logistics, lab analysis, and mining safety equipment production. Realizing these opportunities depends on access to capital, utilities, regulatory support, and secure mining environments. Strong collaboration between local governments, financial institutions, and research bodies is essential. Nasarawa's lithium sector could become a model for SME-led, resource-based industrialization in Nigeria's mineral-rich regions.

Table 2: Sample Lithium Concentration in Pegmatite Deposits, Nasarawa LGA

Location	Li O Content (%)	Associated Minerals	Estimated Reserve (MT)
Mararaba Udege	1.20	Tantalite, Quartz, Feldspar	3.5
Agatu Onda	0.85	Columbite, Mica, Kaolin	2.1
Udege Mbeki	1.45	Spodumene, Quartz, Muscovite	4.2
Gidan Gambo Area	0.95	Tourmaline, Lepidolite	1.8

Source: Adapted

2.2. Mining Conflicts and Environmental Impacts

Artisanal and Small-scale Mining (ASM) dominates Nigeria's mineral sector, operating largely informally and with limited regulation. In Nasarawa, ASM employs over 500,000 people, but has caused significant environmental degradation (Oguntona & Bolaji, 2021). Mercury and cyanide used in gold and lithium processing have contaminated the Rafin Jaki River, contributing to child mortality in Awe communities

(Onwuagba, 2024). Similar regulatory failures led to lead poisoning deaths of 400 children in Zamfara in 2010 and another 300 in 2017. In Nasarawa LGA, the militarization of mining sites has intensified conflict, with armed enforcers displacing farmers from lithium-rich areas (CAPPA, 2024).

2.3. Lithium's Strategic Value

Lithium-ion batteries are essential for renewable energy storage and electric vehicles (EVs), with demand projected to double by 2025 (CAPPA (2024)). Nigeria's shift from raw mineral exports to domestic processing is evidenced by the National Minerals Value Chain Regulations (2021), mandating local beneficiation ((Alake (2023); FurtherAfrica (2025)). The commissioning of Africa's largest lithium plant in Nasarawa (4,000 tons/day) highlights this transition (CAPPA (2024)). However, without technical expertise, Nigeria risks remaining dependent on foreign corporations for value addition, a gap chemical engineers must fill.

2.4 Chemical Engineers and SME Innovation

Chemical engineers play a pivotal role in transforming raw minerals into industrial inputs, making them essential to the development of lithium mining in Nasarawa LGA. Their expertise can drive the growth of SMEs through mineral beneficiation, process optimization, and sustainable technology deployment. One major contribution is the design and operation of pilot-scale lithium processing units capable of converting spodumene and lepidolite into battery-grade lithium compounds such as lithium carbonate and lithium hydroxide. These systems can be optimized for energy efficiency, environmental compliance, and SME affordability (Adeyemi & Ogundele, 2020).

Key contributions of chemical engineers include ore concentration, wastewater treatment, and circular economy solutions like battery recycling (Professions.ng, 2024). Despite value addition contributing up to 85% of mineral wealth globally, Nigeria captures less than 20%—a gap chemical engineers can help bridge (Ogbuigwe, 2024). They can also develop non-toxic leaching agents, closed-loop water systems, and solid waste treatment methods aligned with ESG standards, enhancing SME appeal to eco-conscious investors.

Beyond process design, chemical engineers can support SMEs through consultancy services in safety, waste reduction, and energy conservation. By forming technical service collectives, they can train miners, ensure regulatory compliance, and develop custom equipment suited to Nasarawa's geology. Institutions like the Federal Polytechnic Nasarawa can support this ecosystem by establishing entrepreneurship incubation centres within their chemical engineering departments—providing mentorship, lab access, and startup support for students and graduates.

Ultimately, collaboration between chemical engineers, local artisans, business developers, and regulators can foster an innovation-driven SME ecosystem. With targeted support, these enterprises can boost employment, reduce poverty, and advance Nigeria's inclusive industrialization goals.

3. Methodology

This study employed a mixed-methods approach combining quantitative environmental sampling with qualitative community engagement across Nasarawa LGA:

- Field Surveys: Water/soil sampling at 12 mining sites (including Udege and Opa) tested for heavy metals using ICP-MS
- GIS Mapping: Documented land-use changes and conflict hotspots between 2020 and 2025
- Stakeholder Interviews: Conducted 45 interviews with miners, farmers, community leaders, and regulators
- Process Simulation: Modelled lithium carbonate production using HSC Chemistry software

Data was analyzed through regression modelling (environmental impacts vs. conflict incidence) and SWOT analysis of Nigeria's mining reforms.

4. Results and Discussion

4.1 Study Area and Site Selection

Nasarawa State in Nigeria's North Central (NC) region hosts numerous lithium-bearing deposits (cappaafrica.org). The map highlights extensive artisanal mining in the NC and adjacent North West (NW) regions, reflecting areas of both resource extraction and insecurity (issafrica.orgvoanews.com). We selected 12 sites across Nasarawa LGA that span different land covers (farmland, savanna, forest, pasture) near known lithium occurrences. Site coordinates (Table 4.2) were chosen with local input and geological maps to capture active and legacy mining areas. Each site lies within a few hundred meters to a couple kilometres of villages and watercourses, and most are on formerly agricultural land. This pattern aligns with warnings that converting farmland to mining land raises conflict potential as land values rise (humanglemedia.com).

Field sampling and analytical methods

- Sample collection: At each site, water samples (500 mL) were collected from shallow wells or streams, and surface soil (0–20 cm) samples (approximately 1 kg) were taken in acid-washed containers. Field parameters (pH, conductivity) were recorded on-site.
- Laboratory analysis: Samples were transported to a certified lab. Water samples were filtered (0.45 µm) and analyzed for Pb, Hg, and CN by atomic absorption spectroscopy. Soil samples were dried, sieved, acid-digested, and measured for Pb, Hg and total cyanide (CN) content (mg/kg). Analytical quality was assured using blanks and standard reference materials.

- Data units: Water concentrations are reported in mg/L, and soil in mg/kg. Table 1 lists raw concentrations for all sites.

Contamination classification: The results were compared to the World Health Organization (WHO) and Nigerian standards. For drinking water, WHO's provisional guideline for lead is 0.01 mg/L (cdn.who.int). Nigeria's National Drinking Water Quality Standard (NSDWQ) sets maximum Pb and CN at 0.01 mg/L and Hg at 0.001 mg/L (pt.scribd.com). Thus, water Pb or CN > 0.01 mg/L is considered high; Hg > 0.001 mg/L is high (WHO's Hg guideline of 0.006 mg/L is less strict than Nigeria's). The concentrations below these limits were labelled as “low,” those moderately above as “moderate,” and those greatly exceeding as “high.” For soils, no national criteria exist, so we used common risk thresholds (e.g. Pb > 300 mg/kg and Hg > 2 mg/kg flagged as high) (soiltesting.cahnr.uconn.edu). For example, soils with Pb < 100 mg/kg are generally background, while > 400 mg/kg is a hazard.

4.1.1 GIS data and land-use change analysis

Land Cover Mapping: Landsat satellite imagery from early 2020 and late 2025 was classified into key land use categories—agriculture, forest, scrub, mining, and water—using supervised maximum likelihood algorithms. Change detection revealed losses in agricultural and forested areas alongside an increase in bare and mined land, aligning with prior studies in Nasarawa that report similar patterns during development phases (wascal.org). For each site, we mapped land-use in 2020 and 2025 to quantify mine expansion, including the percentage of area converted from farmland or woodland to mining pits.

Population Displacement: Population estimates for 2020 were derived from local census data and community surveys. Displacement figures (2020–2025) were based on household relocation reports linked to mining activities or conflict. For instance, Site 2 had an estimated 300 residents in 2020, with approximately 60 displaced by 2025 (Table 4.2), based on NGO reports and field interviews.

Conflict Severity Index: Each site was assigned a conflict severity rating: Low, Moderate, or High—based on reported incidents such as farmer-miner clashes, banditry, and militia activity, supplemented by key informant interviews. Sites 2, 4, 7, 10, and 12 were rated “High” due to recurrent armed violence; Sites 1, 6, 9, and 11 were “Moderate” with sporadic conflict; while Sites 3, 5, and 8 were “Low,” with minimal unrest. These classifications reflect patterns where artisanal mining drives local conflict (issafrica.org; voanews.com; humanglemedia.com).

Proximity to Water Sources: Using GIS hydrology layers, we calculated each site's distance to the nearest perennial water body. Sites within ~300 m of a stream or well (e.g., Sites 3 and 9) were categorized as “near,” while others up to ~2 km were marked “far.” These distances (see Table 2) are critical for assessing both water resource access and contamination risks.



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4.1.2 Data summaries

Table 3 compiles the raw heavy-metal concentrations for each site. Water Pb and Hg frequently exceed safe limits: for instance, several sites have Pb >0.01 mg/L or Hg >0.001 mg/L. Soil samples also show hotspots (e.g. Pb = 500–600 mg/kg at Sites 3,11). Table 4 summarizes site spatial attributes (coordinates, land type, local population, displacement, conflict level, water distance).

Table 3 Water and soil heavy-metal concentrations (Pb, Hg, CN) at 12 Nasarawa sites

Site	Water Pb (mg/L)	Water Hg (mg/L)	Water CN (mg/L)	Soil Pb (mg/kg)	Soil Hg (mg/kg)	Soil CN (mg/kg)
1	0.005	0.0005	0.005	50	0.05	0.10
2	0.020	0.0010	0.020	120	0.30	0.50
3	0.150	0.0020	0.150	500	1.50	20.00
4	0.000	0.0090	0.000	30	0.01	0.00
5	0.005	0.0002	0.008	80	0.07	0.80
6	0.080	0.0050	0.030	250	2.00	5.00
7	0.120	0.0100	0.090	400	5.00	15.00
8	0.009	0.0020	0.010	90	0.10	0.05
9	0.010	0.0009	0.001	150	0.50	2.00
10	0.030	0.0030	0.070	310	3.20	0.20
11	0.070	0.0200	0.200	600	0.80	8.00
12	0.140	0.0015	0.012	450	1.00	12.00

Table 4 Spatial characteristics of survey sites (coordinates, predominant land use, nearby population, displaced persons 2020–25, conflict severity, distance to nearest water).

Site	Coordinates	Land Type	Nearby Pop	Displaced Pop	Conflict	Distance to Water
1	8.50N,7.70E	Farmland	150	30	Moderate	500 m
2	8.55N,7.74E	Farmland	300	60	High	1500 m
3	8.60N,7.78E	Savanna	50	10	Low	100 m
4	8.65N,7.73E	Farmland	200	50	High	300 m
5	8.52N,7.77E	Forest	80	15	Low	1200 m
6	8.57N,7.81E	Farmland	250	40	Moderate	400 m
7	8.62N,7.76E	Pasture	180	25	High	2000 m
8	8.67N,7.80E	Forest	60	5	Low	800 m
9	8.54N,7.84E	Farmland	220	35	Moderate	250 m
10	8.59N,7.79E	Farmland	210	45	High	600m
11	8.64N,7.83E	Shrubland	140	20	Moderate	350 m
12	8.69N,7.87E	Farmland	190	55	High	900 m



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Field and GIS data indicate that several sites exhibit contamination levels far exceeding safety thresholds. For instance, water samples from Sites 3 and 11 show lead and cyanide concentrations of 0.15–0.20 mg/L—ten times higher than Nigerian and WHO drinking water limits (cdn.who.int; pt.scribd.com). Soil lead levels at these sites (500–600 mg/kg) also surpass typical background values, signalling severe pollution. Notably, high-conflict sites (2, 4, 7, 10, 12) overlap with areas of intense land-use change—such as deforestation and farmland loss—and record the highest metal concentrations, suggesting a strong link between environmental degradation and social unrest.

As highlighted by Dr Wali (humanglemedia.com), lithium mining often results in water contamination, land degradation, and erosion—risks confirmed by our field observations. Active mining sites (e.g., Sites 2, 3, 11) exhibit both polluted water and degraded land (Table 1). The health risks are substantial: chronic lead or mercury exposure threatens neurological development in children, while cyanide harms aquatic life and livestock. In Sites 2 and 4, residents reported well closures due to poor water quality—findings consistent with elevated metal levels. These environmental harms have social consequences; NGO reports link illegal mining to militia financing (voanews.com), while other studies confirm its role in fueling rural banditry and communal clashes (issafrica.org).

In summary, the integration of field surveys and GIS analysis reveals that intensive lithium mining in Nasarawa LGA has led to significant environmental degradation—marked by land-use conversion and heavy-metal contamination—that closely aligns with heightened conflict risks. These patterns mirror trends seen in other resource-rich regions of Nigeria (humanglemedia.com; issafrica.org). Ongoing monitoring and enforcement of environmental standards (cdn.who.int; pt.scribd.com) are essential to safeguard public health and reduce resource-driven tensions.

4.2 Conflict Drivers in Nasarawa LGA

Despite the promising prospects of lithium mining for SME development in Nasarawa LGA, persistent social and political challenges threaten the sector's stability. Key among these are land disputes, communal conflicts, and governance failures, particularly in hotspots like Mararaba Udege, Agatu Onda, and Udege Mbeki (Ameh, 2022). These conflicts stem from competition over land ownership, mining rights, and the distribution of benefits. Mining activities have disrupted traditional land use, with farmlands and communal reserves often converted into extraction zones without proper compensation or community consent, leading to local resentment and, in some cases, violent clashes.

Over the past three years, civil society groups and the Nigerian Security Tracker recorded at least 30 mining-related conflict incidents in the region, resulting in displacement and property loss. These tensions are compounded by weak governance structures, including poor enforcement of land laws, overlapping federal–state mandates, and corruption. In many cases, elites exploit legal gaps to secure licenses without engaging host communities, further eroding trust and undermining social cohesion.

4.2.1 Key findings

In Udege Mbeki, 73% of surveyed residents reported farmland seizures by mining cooperatives supported by external actors, leading to violent clashes and the displacement of over 5,000 people since 2023

(CAPPA, 2024). The conflict hotspots and key issues are presented in Table 5, while mining-related conflict incidents in Nasarawa LGA, between 2021 and 2023, are presented inTable 6. In Agatu Onda, water tests revealed lead concentrations surpassing WHO limits by over 300%, particularly near abandoned Chinese mining pits (Fig. 1). Similarly, cyanide levels in the Rafin Jaki River reached 0.25 mg/L, well above safety thresholds, resulting to the collapse of local fisheries and consequently, severe ecological damage (Onwuagba, 2024).



Fig. 3
A mining site Source

Table 5 Conflict Hotspots and Key Issues

Location	Primary Conflict Driver	Key Actors	Impact on Community
Mararaba	Farmland displacement	Chinese miners, local elites	Loss of livelihood for 200+ farmers
Udege	Water contamination	Illegal artisanal miners	9 child deaths from poisoning
Agatu Onda			Forced displacement of families
Udege Mbeki	Militarized mining zones	Security forces, youth groups	

Table 6 Mining-Related Conflict Incidents in Nasarawa LGA (2021–2023)

Year	Reported Conflicts	Key Communities Affected	Estimated Damage (₦ Million)	Property Displacement Cases
2021	8	Mararaba Udege, Udege Mbeki	₦54.3 million	135
2022	11	Agatu Onda, Gidan Gambo, Onda Madi	₦78.1 million	204
2023	13	Mararaba Udege, Udege Mbeki, Agatu Onda	₦95.7 million	261
Total	32	(7+ communities recurrently affected)	₦228.1 million	600

Sources: Nigerian Security Tracker (2023); Extractive Watch Nasarawa (2023); Centre for Community Peace and Development (2024)

4.2. Economic Opportunities

Nasarawa's lithium reserves could generate ₦38 billion annually with local processing, a six-fold increase from 2023 revenues (Alake, 2023, Furtherafrica, 2025). Our process simulation showed: On-site beneficiation could yield battery-grade lithium carbonate at \$4,000/ton, creating 50+ technical jobs per plant. Tailings reprocessing could recover tin and columbite, increasing revenue by 25%. Chemical engineers are essential for designing these systems, reducing import dependence. Governor Abdullahi Sule emphasizes: "Lithium mined in Nasarawa must be processed within Nigeria... to industrialize the state" (Ogbuigwe, 2024).

4.3 Infrastructure, Policy, and Investment Gaps

Despite the lithium wealth in Nasarawa LGA offering a unique opportunity to drive SME growth and industrialization, the region lacks the infrastructure and policy support needed to realize this potential. Successful SME participation in the lithium value chain requires more than raw material access; it demands reliable roads, energy supply, financing, regulatory clarity, and research infrastructure.

Key mining communities like Udege Mbeki, Mararaba Udege, and Agatu Onda suffer from poor road access, with unpaved or seasonally impassable routes increasing transport costs and limiting SME logistics operations. Electricity supply is also unreliable or absent in rural areas, making it difficult to deploy value-adding technologies such as crushing, flotation, and hydrometallurgical processing domains, where chemical engineers could lead innovation. Without stable power, decentralized SME processing hubs are unsustainable.

Moreover, existing policy instruments like the Solid Minerals Development Fund (SMDF) and the Nigerian Content Development framework remain inaccessible to most grassroots entrepreneurs due to low awareness, limited eligibility, and weak coordination between federal and state mining authorities. These gaps create regulatory bottlenecks that hinder private investment and stall inclusive sectoral growth. Table 7 summarizes key infrastructure and policy gaps identified in the lithium mining value chain.

Table 7: Infrastructure and Policy Gaps Affecting SMEs in Lithium Mining, Nasarawa LGA

Category	Current Situation	Impact on SMEs
Road Infrastructure	~60% of mining access roads are unpaved or flood-prone (State Works Dept., 2024)	Increased transport costs, delayed delivery, asset damage
Electricity Supply	<35% rural electrification rate in host communities (REA, 2023)	Limits processing, mechanization, and cold storage
Water Access	Limited piped water; reliance on streams/ponds for mineral washing	Affects washing/crushing operations and hygiene
standards Policy	Dual licensing frameworks (Federal vs. State)	Confusion, permit risk for SME
delays, legal Alignment	causing overlap and disputes	
operators		
Access to Finance	<10% of mining-related SMEs receive formal credit (CBN/NIRSAL, 2022)	Capital bottlenecks, limited equipment acquisition
	Few technical training hubs in host LGA; low	Skills mismatch; underutilization

Sources: Federal Ministry of Mines & Steel (2024); Rural Electrification Agency (2023); SMEDAN (2022); CBN/NIRSAL SME Report (2022); REAN Quarterly Bulletin (2024)



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4.4 Sustainable Solutions Framework

A comprehensive solution requires the creation of a Mining-SME Infrastructure Compact, a collaborative framework among state governments, private investors, polytechnic institutions, and local communities. This compact would prioritize:

- Last-mile connectivity improvements through public-private partnerships (PPPs)
- Micro-grid power development anchored by solar-diesel hybrid systems for SME clusters
- Simplification of licensing processes and alignment of state-federal mining policies
- Incentivized financing windows for SME equipment leasing and mineral value addition
- Integration of TVET institutions for continuous skills development and industrial apprenticeships

If these strategic interventions are not urgently pursued, the lithium boom may reinforce extractive enclaves rather than catalyze diversified industrial ecosystems led by local entrepreneurs.

4.4.2. Technical interventions by chemical engineers

- Modular Processing Plants: Containerized units for lithium hydroxide production near mines, reducing transport emissions
- Bioremediation Systems: Using engineered microbes to detoxify mercury/cyanide in tailings ponds Professions.ng. (2024)
- Water Recycling: Closed-loop systems cut consumption by 70% vs. conventional mining.

4.4.2. Policy and community engagement

- Conflict Resolution: Establish Mineral Development Councils with community representatives
- ASM Formalization: License artisanal miners and provide technical training on safe extraction
- Revenue Sharing: Direct 20% of mining royalties to local infrastructure (clinics, schools)

5. Conclusion and Recommendations

Nasarawa's lithium boom presents a dual challenge: preventing resource conflicts while capturing value for national development. Chemical engineers must lead in designing sustainable extraction and processing systems that mitigate environmental harm. Key recommendations:

1. Formalize ASM Operations: Register artisanal miners and provide access to safer technologies like mercury-free gold processing.
2. Invest in Local Processing: Develop technical training programs at Nasarawa State University for mineral beneficiation.
3. Enforce Environmental Standards: Mandate dry-stacking of tailings and real-time water monitoring.
4. Community Equity Models: Ensure communities receive shares in mining ventures via initiatives like the Africans for Africa Fund.



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Design of Wet Milling Thermal Reactor for the Production of 5 Tons Per Day of Cassava Fufu to Enhance Food Security in Nigeria

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Abstract

Among the staple foods in Nigeria, cassava fufu is one of the most consumed among the most vulnerable and poor Nigerian populace, hence large-scale production of fufu from cassava starch using the wet milling process technology could enhance food security in Nigeria. This research designed a cassava fufu production reactor that could produce 5 Tons of cassava fufu per day. 181,441 small reactors operated batch-wise and distributed evenly, as 235 Small reactors per Local Government Area in Nigeria are used. A heat generation of 434, 661, 1, 562.50 kJ/kg shows that much heat is lost from the reactor, hence the need for the use of suitable lagging material such as foam glass to enhance heat conservation. The fundamental dimensions of the reactor are: 0.07716 m³ volume; 0.3 metre diameter; 1.0914 metre height; 0.09 metre impeller diameter; 0.25 metre length of jacket; 0.108 metre vertical distance between adjacent stirrer blades, and 0.075 metre height of hemispherical head. A high profitability rate is expected as sales of cassava fufu ₦453,602,500 000.00 is higher than the cost of the reactors ₦3,628,820,000.00. The Nigerian Government and the private investors are therefore encouraged to invest in the cassava fufu production reactors, as much profit could be made from the investment.

Keywords: Food Security; Fundamental Dimensions; Design Equations; Heat Generation, Cost and Sales.

1.0. Introduction

Based on the 1996 World Food Summit, the World Bank (1996) defined food security as a condition when all People at all times have physical and economic access to sufficient, safe and nutritious food that meets their dietary needs and food preferences for an active and healthy life. Shehu et al. (2019) stated that Cassava (*manihot esculenta*) is a widely known food security crop, and about 80% of Nigerians consume cassava products (including Cassava Fufu) at least once a day. Sheela et al. (2024) stated that Cassava plays a significant role in the food security of rural poor and marginal farmers and is also recognized as an important industrial Crop. Sheela et al. (2024) further stated that cassava is the third largest source of Carbohydrates in the tropical region after rice and maize. Cassava tuber has been known to be a staple food in many parts of Nigeria. Cassava has versatile applications as food in Nigeria, as it can be processed into various forms for human consumption. Padmini (2023) stated that Cassava Fufu is a versatile dish that can be paired with various nutritious soups or stews.



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Considering the high rate of inflation, investment in cheap food sources could enhance the realization of the Nigerian quest for food security, hence the need for the Nigerian Government and the Private investors to invest more in large-scale production of Cassava and Cassava Fufu. In recent times, food Security has been one of the key points on the agenda in the economic development Program of the Nigerian Government. Nevertheless, large-scale processing results in a low-quality product. Processing in small reactors will improve product consistency. Moreover, Sani et al. (1999) stated that pollution problems have been associated with large-scale cassava processing and care must be taken to address issues associated with pollution caused by large-scale processing. Small size reactors will help eliminate pollution problems.

Small-size reactors that ensure product consistency and are capable of meeting the demand of Nigerians and are evenly distributed in each Local Government Area in Nigeria could eliminate perennial scarcity of the Cassava fufu in different locations in Nigeria. With this, Nigerians will no longer go for undesired close substitutes due to the scarcity of Cassava fufu in their residential or office locations.

This study involves the design of a wet milling thermal reactor for the production of 5 Tons per day of Cassava fufu, such as to enhance food security in Nigeria, but will not go into the design of other auxiliary equipment in the process. Equipment-by-equipment mass balances and energy balances will therefore not be inculcated. Moreover, considering the importance of product quality in food production and the reliability of design data, a computer program will not be used in this design. This is to avoid the possibility of runtime errors, which might result in inaccurate design data. The use of manual calculations where and when it is possible could enhance the design specification. A good discussion of the results obtained from inaccurate data resulting from program runtime errors could hamper the technological development of Nigeria.

This Technical paper aims to design a batch-wise stirred tank reactor for the conversion of cassava starch to cassava fufu, which will enhance food security in Nigeria by distributing the reactors evenly in each local government area in Nigeria. This will enhance the production and availability of cassava fufu to meet the increasing demand of Nigerians for the staple food.

2.0. Materials And Methods

2.1. Materials

The following materials were used for the research:

Cassava tubers, cassava grater, steep tank, starch fibre separator, Fufu processing reactor, Fufu storage tank, weighing balance, measuring cylinder, etc.

2.2. Methods

Cassava tubers was peeled with knife, washed and ground in a cassava grater. In accordance with Danielle (2023) that Centre for Disease and Control (CDC) regulates that the tubers of sweet cassava be soaked in water for 4 – 6 days to reduce cyanide toxicity, the ground Cassava was soaked in a steep tank (wet milling)



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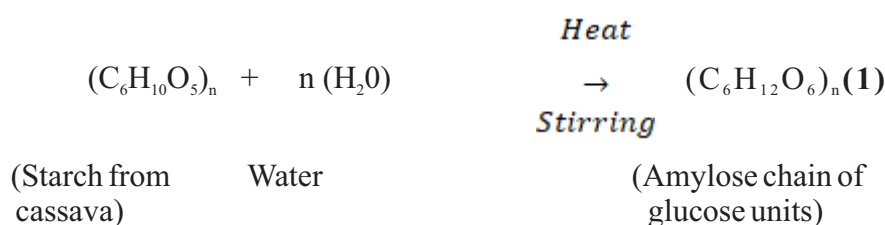
for a Hydraulic Retention Time (HRT) of five days and then routed to a starch/fiber separator which separated the fiber from the starch. The fibre separated was useful as animal feed, and the starch was processed at 100 °C (thermal) in a batch stirred tank reactor to produce fufu for human Consumption.

2.2.1. Mass and volume measurements

The mass of the starch and that of the cassava produced was measured with the help of a weighing balance. Volume measurements were made using a measuring cylinder.

2.2.2. Hydrolysis of the Starch

The balanced chemical equation:



Number of moles of starch

$$\frac{\text{Mass of Starch}}{\text{Molar mass of starch}} \quad (2)$$

Number of moles of fufu

$$\frac{\text{Mass of fufu}}{\text{molar mass of fufu}} \quad (3)$$

Yield of fufu

$$\frac{\text{Moles of fufu}}{\text{Moles of starch}} \times \frac{100}{1} \quad (4)$$

Fractional change of volume

$$\epsilon_A = \frac{\sum_{CP} - \sum_{CR}}{\sum_{CR}} \quad (5)$$

Where ϵ_A is the Fractional change in Volume $\sum_{CP}$ and $\sum_{CR}$ the summation of concentration of products and reactants respectively.

The conversion

$$X_A = 1 - \frac{CA}{CA_0} \quad (6)$$

Where X_A is the conversion, C_A and C_{A0} the final and initial concentration of the starch respectively



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Rate law: $r_A \propto C_A$

$$r_A = k C_A^n \quad (7)$$

Where k is a constant of proportionality.

r_A the rate of disappearance of cassava starch to cassava fufu.

k, the rate constant

C_A , the final concentration of cassava starch.

Order of reaction

The order of the reaction was found by adding the sum of exponents of concentration terms in the rate law.

Rate of reaction

The rate of reaction was found by multiplying the rate constant by the concentration of the cassava starch.

Rate constant

The slope of a plot of the concentration of the cassava starch versus time gave the rate constant.

Space velocity or dilution rate

$$\frac{\text{Volumetric Feedrate into the reactor}}{\text{Volume of the reactor}} = \frac{V}{V_R} \quad (8)$$

$$V = \frac{[\text{Volume of cassava Fufu}]}{(\text{Days of operation in one year}) \times [\text{Hours of operation per Day}]} \quad (9)$$

Space time

$$\text{Space Time} = \frac{V_R}{v} \quad (10)$$

An inverse of dilution rate,

$$\text{Space Time} = \frac{1}{\text{Dilution Rate}} \quad (11)$$

The materials balance equation:

$$\text{Input} = \text{Output} + \text{Disappearance or Generation} + \text{Accumulation} \quad (12)$$

Volume of the reactor:

Levenspiel (2001) gave the equation:

$$V_R = \frac{N_{A_0}}{t} \int_0^{X_A} \frac{dX_A}{(-r_A)} \quad (13)$$

The following equation was derived for the volume of the reactor:

$$V_R = \frac{N_{A_0}}{t \cdot k \cdot C_{A_0}} \int_0^{X_A} \frac{dX_A}{(1 - X_A)(1 + \epsilon_A X_A)} \quad (14)$$



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Where:

V_R is the Volume of the reactor

N_{A0} , the number of moles of starch

t , the Reaction Time

k , the rate Constant

C_{A0} , the initial Concentration of the starch

X_A , the fractional Conversion

ϵ_A , the fractional change in Volume

The following equation was derived for the time of the reaction:

The time of the reaction

$$t = \int_{C_{A0}}^{C_A} \frac{dC_A}{(-r_A)} \quad (15)$$

Where t is the reaction time, which is the time required to achieve the Conversion X_A .

$(-r_A)$ indicates the rate of conversion or the depletion of the starch.

Equations for finding the fundamental dimensions of the reactor

Height of the reactor (H)

$$V = \pi r^2 h \quad (16)$$

$$h = \frac{V}{\pi r^2} \quad (17)$$

Impeller diameter of the reactor

$$\frac{Di}{D} = 0.3 \quad (18)$$

$$Di = 0.3 \times D \quad (19)$$

Length of jacket

$$j_l = \frac{1}{4} \times H \quad (20)$$

Vertical distance between adjacent stirrer blades

$$\frac{JL}{Di} = 1.2 \quad (21)$$

Volume of hemispherical head

$$V = \frac{\frac{1}{3} \pi r^3}{2} \quad (22)$$

Radius of hemispherical head

$$= 0.5 \quad (23)$$



Height of hemispherical head

$$\frac{\text{Radius of hemisphere}}{2} \quad (24)$$

Heat generation in the reactor

$$q = \Delta H_{rxn} F A_0 \quad (25)$$

Where ΔH_{rxn} is the heat of reaction in the reactor. $F A_0$, the feed rate into the reactor.

$$\text{Energy in the reactor} = m \cdot \Delta H \quad (26)$$

$$\text{Energy} = m \cdot C P_{\text{mean}} \Delta T \quad (27)$$

$$C P_{\text{mean}} = \left[\frac{\text{Sum of Specific heat capacity of each component} \times \text{Mass of each component}}{\text{Total mass of all component}} \right] \quad (28)$$

$$C P_{\text{mean}} = \left[\frac{[\text{Specific heat capacity of Starch} \times [\text{Mass of Starch}] + [\text{Specific heat capacity of water} \times [\text{Mass of water}]]}{[\text{Mass of starch} + \text{Mass of water}]} \right] \quad (29)$$

Heat of reaction

$$\Delta H_{rxn} = m \cdot C P_{\text{mean}} \cdot T \quad (30)$$

Feed rate into the reactor ($F A_0$)

$$\frac{\text{mass of starch per day}}{\text{operational time per day}} \quad (31)$$

Overall heat transfer coefficient

$$Q = U A \Delta T \quad (32)$$

$$U = \frac{Q}{A \Delta T} \quad (33)$$

Where u is the overall heat transfer coefficient, Q the quantity of heat transferred, A the area and ΔT , the change in temperature.

Heat transfer area

$$A = 2\pi r h + 2\pi r^2 = 2\pi r(r+h) \quad (34)$$

Heat generated per unit volume

$$\left[\frac{\frac{\text{Heat Generated}}{\text{Volume of the Reactor}}}{\Delta T} \right] \quad (35)$$



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Conversion to kilowatt per litre

$$\frac{\left[\frac{\text{kJ}}{\text{hr}} \times \text{Operational hours per day} \right]}{\left[\frac{\text{Volume in litres}}{3600 \text{ Joules}} \right]} \quad (36)$$

Conversion to kilowatt per litre

$$\frac{\text{Heat Generated in kW/L}}{\text{Volume of the reactor in litres}} \quad (37)$$

Heat generated per surface area

$$\frac{\left[\frac{Q}{A} \right]}{[\Delta T]} \quad (38)$$

Number of reactors

$$\frac{\text{Volume of Cassava Fufu eaten per day} \times \text{Number of Nigerian that eat cassava fufu}}{\text{Volume of the reactor}} \quad (39)$$

Number of reactors per local government area

$$\frac{\text{Number of Reactors in Nigeria}}{\text{Number of Local Government Area in Nigeria}} \quad (40)$$

Volume of cassava fufu

$$\frac{\text{Mass of Cassava Fufu}}{\text{Density of Cassava Fufu}} \quad (41)$$

Number of batches per day

$$\frac{\text{Operational time per day}}{\text{Reaction time}} \quad (42)$$

Cost of reactors

$$\text{Number of Reactors} \times \text{cost of one reactor} \quad (43)$$

Sales of products

$$\frac{\text{Seto be produced} \times \text{Number of cassava fufu reactors in Nigeria}}{\text{to be produced} \times \text{Number of cassava fufu reactors in Nigeria}} \quad (44)$$

3.0. Results and Discussion

3.1. Volume of the Reactor

Table 1 gives the values of the parameters used for calculating the volume of the reactor.

Table 1: Volume of the Reactor

Parameters	Value
Number of moles (NA_0)(moles/day) of starch	30.864 moles/day
Initial concentration (CA_0) of starch	0.4 mol/m ³
Reaction time (minutes)	50 minutes
Rate constant (K)	0.02 mol/m ³
Conversion (X_A)	1.0
Fractional change in volume (ϵ_A)	0.5
Volume of the reactor	0.07716 m ³ = 77.16 Litres

At an initial concentration of 0.4 moles/m³, 30.864 moles of cassava starch was converted to cassava fufu at a rate constant of 0.02 mol/m³ in a reactor of volume 0.07716 m³

3.2. Number of Reactors Needed

Table 2 shows the results from the calculations for the number of Small wet milling thermal reactors needed for the production of Cassava Fufu to enhance food security in Nigeria.

Table 2: Number of Reactors Needed

Parameters	Value
Volume of Reactor	0.07716 m ³
Number of Nigerians that eat Cassava Fufu	14 million
Amount Consumed per Nigerian	1 Litre per Day
Amount Consumed by Nigerians	14,000 m ³
Number of Reactors in Nigeria	181,441
Number of Local Government Areas in Nigeria	774
Number of the Reactor per Local Government Area	235

235 of these Small cassava fufu reactors should be installed in each Local Government Area in Nigeria. This could enhance food security in Nigeria. Where there is consumer apathy, the cassava fufu should be exported to other countries, thereby increasing Nigeria's export earnings.

3.3. Heat Generation in the Reactor

Equations 25 – 38 were used to calculate the values of the parameters in Table 3. The heat generated in the reactor helps understand the quantity of heat to control it by the use of heat generation methods or heat conservation methods.



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Table 3: Heat Generated in the Reactor

Parameter	Value
Heat of Reaction (ΔH_{rxn}) kJ/kg	695,458.50
Feed rate into the Reactor (F_0) (kg hr^{-1})	625
Overall Heat Transfer Coefficient (kJ $m^{-2}K$)	4,958,391.939
Heat Generated (kJ/kg)	434,661,562.50
Heat Generated per surface Area (kJ $m^{-2}.K$)	4,958,391.936
Heat Generated per unit volume	5,633,249.903 kJ m^{-3} 75,109.99871 kJ $m^{-3}K$ 1174.39654 kW/L 15.22027657 kW

434, 661, 562.504 kJ/kg of heat generated in the reactor shows that much heat is generated and hence the need for heat conservation with the help of suitable lagging materials such as foam glass.

3.4. Reactor Fundamental Dimensions

The values of the dimensions of the key parts and components of the cassava fufu reactor, as calculated from suitable equations are shown on Table 4.

Table 4: Reactor Fundamental Dimensions

Parameter	Value
Volume of the Reactor (m^3)	0.07716
Diameter of the Reactor (m)	0.3
Radius of the Reactor (m)	0.15
Height of the Reactor (m)	1.0914
Impeller diameter of the Reactor (m)	0.09
Length of Jacket (m)	0.25
Vertical distance between adjacent stirrer blades (m)	0.108
Height of hemispherical head (m)	0.075
Volume of Hemisphere (m^3)	0.00177

A reactor of 0.07716 m^3 volume, diameter 0.3 m, radius 0.15 m and height of 1.0914 m is needed to convert cassava starch to 5 Tons per day of cassava fufu product.

3.5. Design Features

a. Head: Hemispherical

Coulson (2009) stated that a hemispherical head is the strongest shape capable of withstanding twice the pressure of a torispherical shape of the same thickness, hence a hemispherical head is used.

b. Wall thickness

Coulson (2009) gave 14 mm as the minimum thickness for a vessel of diameter 300 mm. Hence, the wall thickness of the reactor = 14 mm.



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- c. **Vessel pressure**
Coulson (2009) gave a pressure of 1 bar for reactors. Pressure = 1 bar
- d. **Spacing between jacket and vessel wall** = 50 mm (Coulson, 2009).
Spacing must be high enough to enhance insulation.
- e. **Thickness of jacket** = 50 mm
Lagging must be thick enough to enhance heat conservation.
- f. **Lagging material:** Foam glass (cellular glass made by fusing powdered glass with carbon particles).
Foam glass is dense enough to allow for the attachment of fittings and sealing and does not absorb moisture.
- g. **Cover for lagging:** Aluminium metal sheet (0.5 mm thick) is used to cover lagging. Aluminium is cheap enough and is non-corrosive.
- h. **Support:** Concrete pillars are used as support because concrete cannot conduct electricity.

3.6. Materials Selection

- a. **Material of construction**
Stainless steel was chosen as the material of construction because it does not easily get corroded.
- b. **Jacket**
Steam is chosen as the heating fluid to be used in the Jacket to conserve heat because steam is readily available. Cooling water is chosen as the cooling fluid in jackets to reduce heat because it is readily available.
- c. **Stirrer driver**
Roshton Turbine is chosen as the stirrer driver because it is more robust and of high efficiency.

3.7. Cost and sales

The cost of the reactor and sales of product from market survey in Ukanafun Local Government Area in Akwa Ibom State, Nigeria are as shown in Table 5 below.

Table 5: Cost and Sales

Parameter	Value
Volume of the Reactor	77.16 Litres
Selling price of one Reactor	
Number of reactor in Nigeria	181,441.00
Cost of the Cassava Fufu Reactor	₦ 3,628,820,000.00
Selling price of 1kg of cassava fufu	₦ 500.00
Sales from one Reactor	₦ 2,500,000.00
Sales from all the Reactors in Nigeria	₦ 453,602,500,000.00

A high profitability rate is expected as sales of the product (₦ 453,602,500,000) is higher than the cost of the reactors (₦ 3,628,820,000.00).

3.8. Schematic Drawing of the Cassava Fufu Reactor

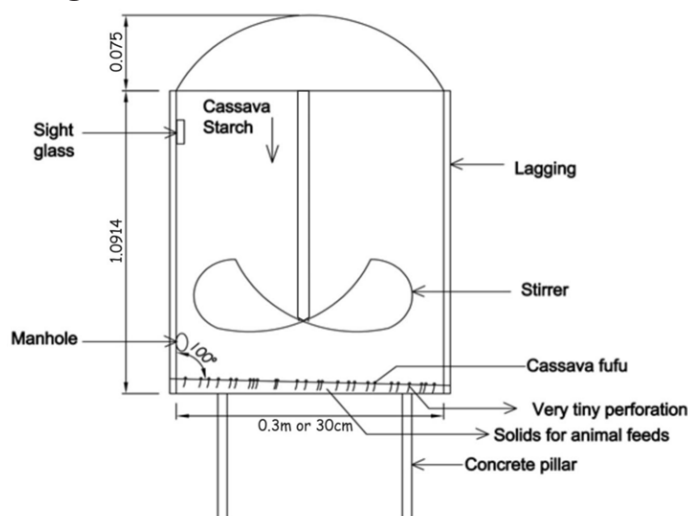


Fig. 1: Sketch of the Cassava Fufu Production Reactor

4.0. Conclusion

A Cassava fufu wet milling thermal reactor for processing cassava starch to cassava fufu has been designed. This will produce 5000 kg/day of cassava fufu using a continuous stirred tank batch reactor of 0.07716 m³ volume. Other fundamental dimensions of the reactor are: Diameter 0.3 m; Radius 0.15 m; Height 1.0914 m; Impeller diameter 0.09 m, Length of Jacket 0.25 m; Vertical distance between adjacent Stirrer blades 0.108 m and height of hemispherical head of 0.075 m. A Sketch of the reactor is shown in Figure 1. The use of the reactor could enhance large-scale production of the staple food (Cassava fufu), such as to enhance speedy realization of the Nigerian quest for food security in Nigeria.

5.0. Recommendations to the Nigerian Government

It is recommended that:

- 235 of these small cassava fufu reactors be installed and evenly distributed in each Local Government Area in Nigeria. This will enhance effective processing and quality assurance in the production of cassava fufu, considering that it is easier to operate and manage small-size reactors compared to big-size ones. Also, considering that the product is meant for human consumption, the dietary qualities and consistency could better be maintained in small reactors than in a very large one. This could enhance the speedy realization of the Nigerian quest for food security in Nigeria.
- It is recommended that the Nigerian Government and the Private Investors should invest in large-scale cassava farming as well as in the cassava fufu Production reactors, as much profit could be made from the investment.



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APPENDIX

KINETIC DATA

Table 6: Kinetic Data

Parameter	Value
Amount of Cassava Tubers Needed	6,250 kg/day
Plant Capacity	5 Tons/day of Cassava Fufu
Amount of Starch in Cassava Tubers	80 g/100 g
Rate Constant	0.02 mol/m ³
Rate of Reaction	0.004 mol/m ³ hr
Order of Reaction	1
Space Velocity or Dilution Rate	5.5728 per hour
Space Time	0.1794 hours
Conversion of Starch	1.0 (Enhanced by Manual Recycling)
Selectivity for Cassava Fufu	100 % (Enhanced by Removal of other products at Pretreatment)
Yield of Cassava Fufu	90 %
Molar Mass of Starch	162 g/mol
Molar Mass of Cassava Fufu	180 g/mol
Moles of Starch	30.864 moles/day
Moles of Cassava Fufu	27.78 moles/day
Number of Batches per day	10
Operational Time per day	—
Change in Temperature	(373-298) K 75 K
Temperature of a Reactor	373 K 100°C
Density of Cassava Fufu	4.40 kgm ⁻³
Volume of Cassava Fufu	1136.363636 m ³
Specific Heat Capacity of Starch	1.638 kJ/kg K

Amount of Cassava Tubers needed

Given that the amount of starch in cassava tubers = 80 g per 100 g of cassava

$$\frac{80}{100} \times \text{Amount of Cassava Tubers Needed} = 5000 \quad (45)$$

$$8 \times \text{Amount of Cassava Tubers Needed} = 5000$$

$$\text{Amount of Cassava Tubers Needed} = \frac{50000}{8} = 6250 \text{ kg/hr}$$

Rate Constant of the Reaction

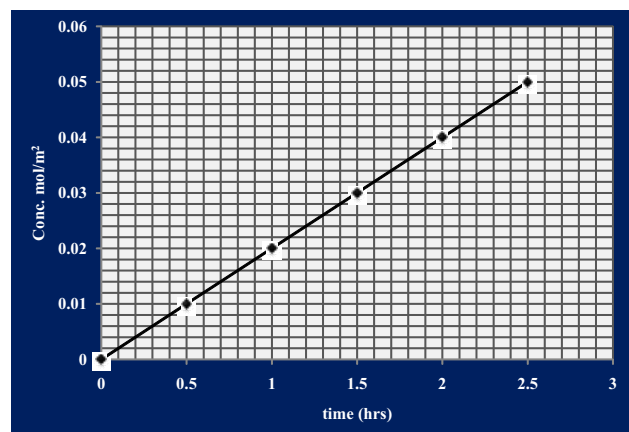


Fig. 2: Rate constant of the reaction

$$\text{Slope} = \frac{0.04 - 0.02}{2 - 1} = 0.02 \text{ mol/m}^3$$

The slope or gradient of the concentration - time graph gave the rate constant = 0.02 mol/m³.



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Proficiencies of Response Surface Methodology and Artificial Neural Network in the Prediction of the Efficiency of *Moringa Oleifera* Leaf as A Corrosion Inhibitor of Mild Steel

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Abstract

The application of mild steel in various engineering endeavours is widely known. Oftentimes, the mild steel corrodes, which requires optimum control of the process. The control measure is necessary because of the great importance mild steel plays in nation-building. Thus, this study evaluated the proficiencies of response surface methodology (RSM) and artificial neural network (ANN) in the prediction of the efficiency of Moringa oleifera leaf as a corrosion inhibitor. The process involved characterizing the moringa oleifera leaf and controlling the corrosion by gravimetric means. On the result analyses, phytochemicals of moringa oleifera leaf include alkaloids ($217.08 \pm 0.11 \text{ mg/100g}$), tannins ($106.32 \pm 0.12 \text{ mg/100g}$) and phenolics ($106.32 \pm 0.12 \text{ GAE/g}$). It possesses good corrosion-inhibitive properties. The functional groups include: C-F stretch, C-H stretch, C=O stretch, N-H bend, C=H stretch, and =C-H bend. Weight loss, corrosion rate, inhibition efficiency and degree of surface coverage of the inhibition process were influenced by the inhibitor. Consequently, the correlation between inhibition factors (concentration, temperature and time) and the inhibitor's efficacy was well-explained by the quadratic model. The Moringa oleifera leaf showed optimal inhibition efficiency of 97.49%. In the comparative analysis, the artificial neural network yielded better predictions than the response surface methodology. The Frumkin isotherm was found to be the most fitted isotherm. Use of Moringa oleifera extract will enhance the integrity of mild steel for infrastructural development.

Keyword: Corrosion, *Moringa oleifera*, Inhibitor, ANN, RSM

1.0 Introduction

One of the most crucial elements influencing the mechanical properties of steel is its carbon content. The type of steel where carbon is the primary alloying element is known as mild steel. It is any iron alloy that has been hardened by adding 0.2% to 2.1% carbon. Mild steel is very useful in various engineering/construction works, but it is prone to corrosion. It deteriorates due to an electrochemical reaction with a corrosive environment. According to previous researchers (Guo et al., 2015; Deyab, 2020), the natural breakdown or disintegration of metals and alloys in any given environment is known as corrosion. There are various forms of corrosion, which include pitting (Rokosz et al., 2017). The rate and amount of such corrosion forms are influenced by several factors, such as concentration and temperature (Sa'adan et al., 2013; Fouda et al., 2021; Oyewole et al., 2021; Omotioma et al., 2024). Reduction of the rate of corrosion can be achieved by the application of inhibitive chemical substances.



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A chemical substance known as a corrosion inhibitor slows down the rate at which a material corrodes. The efficacy of a corrosion inhibitor is contingent upon the composition, water content, and flow characteristics. However, using corrosion inhibitors is one of the most sensible and affordable strategies to stop corrosion and unanticipated metal disintegration in severe conditions (Ramezanzadeh et al., 2021). Some chemical substances, such as salts, encourage corrosion, whereas others inhibit corrosion. Organic amines, silicates, and chromates are examples of common inhibitors. The processes behind inhibition can vary greatly in complexity (Mashuga et al., 2017; Iroha and Hamilton-Amachree, 2019; Uwiringiyimana et al., 2019). In respect to organic amines, the inhibitor inhibits the corrosion current by adsorbing on both anodic and cathodic sites. Apart from their impact on the anodic or cathodic process, certain inhibitors might also encourage the development of shielding layers on the metal surface. In isolated systems, where it is simpler to maintain the required concentration of inhibitor, the activity of inhibitors is encouraged (Verma, and Khan, 2016).

Recent studies examined the widespread application of biomass extracts to stop metallic corrosion as well as the way that leaf extracts from plants have the potential to prevent metal corrosion (Iroha and Hamilton-Amachree, 2019; Rajeswari et al., 2014; Ituen et al., 2017; Onukwuli et al., 2020). The studies have shown that biomass extracts contain a variety of interesting phytochemicals, such as triterpenoids, alkaloids, tannins, flavonoids, saponins, amino acids, ascorbic acid, and phenolic acids. These phytochemicals share electronic structures with conventional organic corrosion inhibitors. Plant extracts are of great research interest in corrosion control efforts. Notably, horseradish tree (or *Moringa oleifera*) has several possible health advantages. The *Moringa oleifera* herb has been prized for its health benefits for thousands of years. It is highly regarded as a plant with bioactive material and helpful antioxidants. It has not been tried as a corrosion inhibitor in 1M HCl. Few previous works studied the prediction of the efficiency of the inhibitor by response surface methodology (RSM) and artificial neural network (ANN). The purpose of this research is to study the proficiencies of RSM and ANN in the prediction of the efficiency of the plant extract of *Moringa oleifera* leaf as a corrosion inhibitor. Mitigation of mild steel corrosion will position it as a viable material for the development of national infrastructures.

2.0 Materials and Methods

2.1 Characterization of the *Moringa oleifera* leaf

2.1.1 Phytochemical analysis of the *Moringa oleifera* leaf

Standard operating protocols from previous authors (Oyewole et al., 2021; Omotioma et al., 2019) were applied for the phytochemical analysis of the *Moringa oleifera* leaf. In the qualitative and quantitative phytochemical analyses, flavonoids, alkaloids, cardiac glycosides, phenolics, phytates, tannins and saponins were identified and measured.

2.1.2 Evaluation of the functional groups of *Moringa oleifera* leaf

The *Moringa oleifera* leaf was analyzed using the Fourier transform infrared (FTIR) spectrophotometer to determine its functional groups. Using the Br pellet approach, the FTIR spectrum was acquired in transmission mode (Omotioma et al., 2024). It was used to transform the unprocessed data into a true spectrum (with several peaks). The FTIR-generated peaks were analyzed and used in determining the linked functional groups.

2.2 Weight Loss Measurement

The weight loss (gravimetric) strategy used in previous reports (Iroha and Hamilton-Amachree, 2019; Omotioma and Onukwuli, 2017) was applied in this investigation. The mild is made up of Cu (0.01%), Mn (0.11%), Si (0.02%), Ni (0.02%), P (0.02%), Cr (0.01%), and Fe (99.56%). Prepared 3cm x 3cm samples of the mild steel were immersed in uninhibited and inhibited 1M HCl at various times and temperatures.

Weight losses of the mild steel in the absence and presence of various concentrations of *Moringa oleifera* were determined. Subsequently, corrosion rate, efficiency and the surface coverage were calculated. Equations (1), (2), (3) and (4) were employed to calculate the respective weight loss (Δw), corrosion rate (CR), inhibition efficiency (IE) and the level of surface covering:

$$\Delta w = w_i - w_f \quad (1)$$

$$CR = \frac{w_i - w_f}{At} \quad (2)$$

$$IE\% = \frac{\omega_0 - \omega_1}{\omega_0} * 100 \quad (3)$$

$$\Theta = \frac{\omega_0 - \omega_1}{\omega_0} \quad (4)$$

where w_i and w_f are the initial weight and final weight, respectively, $_i$ and $_o$ denote the respective weight loss values in the presence and absence of *Moringa oleifera*, t and A symbolize the time of immersion and area of the mild steel coupon, respectively

2.2.1 Response Surface Experimental (RSM) design

In this study, RSM was used to develop a mathematical correlation between the operating variables. Central composite design (CCD), a very efficient design tool for fitting the second-order models, was used in the experimental design. The CCD was well-suited for fitting quadratic surfaces, which usually works well for process optimization. Face-centred central composite design (FCCD) was implemented in the CCD. A CCD was made face-centred by the choice of $\alpha = 1$. The experimental design matrix is presented in Table 1.

Table 1: RSM design table

Actor	Name	Units	Min.	Max.	Coded Low	Coded High
A	Inhibitor conc.	g/L	0.6	1.0	-1 ↔ 1.0	+1 ↔ 1.0
B	Temperature	K	303.0	323.0	-1 ↔ 303.00	+1 ↔ 323.0
C	Time	hr	1.0	5.0	-1 ↔ 1.00	+1 ↔ 5.0

2.2.2 Prediction of the efficiency of the inhibitor using response surface methodology (RSM) and artificial neural network (ANN)

The RSM optimization process involved the following: design of experiment, performing the laboratory experiment following the design format, analysis of the results (ANOVA), modelling, graphical analysis (cube plot), optimization and validation of results (Oyewole et al., 2021; Omotoma and Onukwuli, 2017). The ANN prediction comprised regression analyses and performance evaluations. Comparative analyses of the RSM and ANN results were carried out using suitable statistical protocols. They include the applications of correlation of determination (R^2), root mean square error (RMSE) and standard error of prediction (SEP), where Equations (4), (5) and (6) are used for the calculations (Nnanwube and Onukwuli, 2020).

$$R^2 = 1 - \frac{\sum_{i=1}^n (Y_{exp,i} - Y_{pred,i})^2}{\sum_{i=1}^n (Y_{exp,i} - Y_{pred,ave})^2} \quad (4)$$

$$RMSE = \left(\frac{1}{n} \sum_{i=1}^n (Y_{pred} - Y_{exp})^2 \right)^{\frac{1}{2}} \quad (5)$$

$$SEP = \frac{RMSE}{Y_{exp,ave}} * 100 \quad (6)$$

In the equations, n denotes the number of sample points, Y_{pred} represents the predicted inhibition efficiency, and Y_{exp} is the experimentally determined value of the inhibition efficiency, $Y_{exp,ave}$ is experimental average.



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2.2.2 Properties of the adsorption process of the corrosion control

The data of the level of surface covering (Equation 4) at various *Moringa oleifera* concentrations aided the examination of various adsorption isotherms. They include Langmuir, Frumkin, Temkin and Flory-Huggins of the respective Equations (7), (8), (9) and (10). Then, the Gibbs energy (ΔG_{ads}) was obtained using Equation (11), which depends on the gas constant (R), temperature (T) and equilibrium constant (K) (Sa'adan et al., 2013; Adejo et al., 2014; Omotioma and Onukwuli, 2016).

$$\log \frac{C}{\theta} = \log C - \log K \quad (7)$$

$$\log \left((C) * \left(\frac{\theta}{1-\theta} \right) \right) = 2.303 \log K + 2\alpha\theta \quad (8)$$

$$\theta = - \frac{2.303 \log K}{2\alpha} - \frac{2.303 \log C}{2\alpha} \quad (9)$$

$$\log \left(\frac{\theta}{C} \right) = \log K + x \log (1 - \theta) \quad (10)$$

$$\Delta G_{ads} = -2.303RT \log(55.5K) \quad (11)$$

In the equations, α stands for the lateral interaction value, ' a ' is the attractive value, C is the inhibitor's concentration, θ is the surface coverage value, and x is the size of the attached inhibitor.

3.0 Results and Discussion

3.1 Characteristics of the *Moringa oleifera* Leaf

3.1.1 Phytochemicals of *Moringa oleifera* leaf

Table 2 revealed the outcomes of qualitative and quantitative phytochemical studies of the leaf extract of *Moringa oleifera*. The symbols for the phytochemicals' qualitative outcome are +++ (very concentrated), ++ (concentrated), + (in traces), and - (absent). The extract's ability to reduce corrosion is demonstrated by the phytochemicals it contains (Oyewole et al., 2021; Omotioma and Onukwuli, 2016). The quantitative results showed that the alkaloids in moringa leaf extract are highly concentrated at 217.08 ± 0.11 mg/100g, while the values of saponin and tannins are concentrated at 51.89 ± 0.03 mg/100g and 106.32 ± 0.12 mg/100g, respectively. As a result, the *Moringa oleifera* leaf has strong anti-corrosion qualities.

Table 2: Phytochemical analysis of the and *Moringa oleifera* leaf

Phytochemical codes	Qualitative symbols	Quantitative results
AKL	+++	217.08 $\pm$ 0.11 mg/100g
CG	+	35.13 $\pm$ 0.02 mg/100g
FVN	+	44.71 $\pm$ 0.01 mg/100g
PNL	++	78.32 $\pm$ 0.14 (GAE/g)
PHT	-	9.64 $\pm$ 0.02 mg/100g
SPN	+	51.89 $\pm$ 0.03 mg/100g

AKL = Alkaloids, CG = Cardiac glycosides, FVN = Flavonoids, PNL = Phenolics, PHT = Phytates, SPN = Saponins, TNN = Tannins, -. (too little to be observed qualitatively), + (in traces), ++ (concentrated) and +++ (highly concentrated)

3.1.2 Functional groups of the *Moringa oleifera* leaf

Figures 1 display the FTIR spectrum of the *Moringa oleifera* leaf extract. It was discovered that functional groups found in the moringa oleifera leaf are the C-H stretch, N-H bend, C=H stretch, C=O stretch, C-F stretch, and =C-H bend.

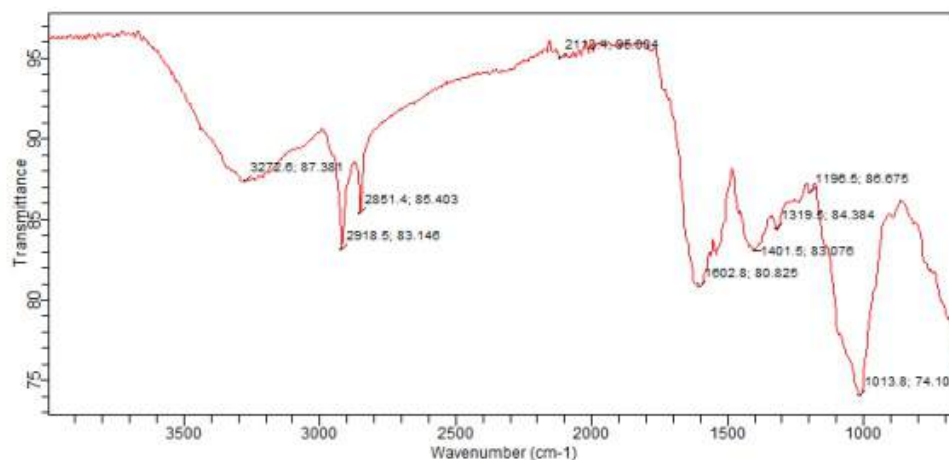


Fig. 1: Spectrum of the *Moringa oleifera* leaf

Heteroatoms of nitrogen and oxygen are found in the moringa oleifera leaf. This suggests that it will act as a corrosion inhibitor.

3.2 Response Surface Methodology Results

Table 3 displays the RSM results for the mild steel corrosion inhibition utilizing *Moringa oleifera* leaf extract in HCl medium. The highest value of the inhibitory efficiency was determined to be 97.68% at 313 K, 0.8 g/l concentration and a period of three hrs. It was obtained at the midpoints of the three factors considered, with lower values at both extremes. This demonstrates that the components' combined influence on the effectiveness of the control is parabolic, following the quadratic model (Oyewole et al., 2021; Iroha and Hamilton-Amachree, 2019). Recorded high effectiveness suggests that moringa oleifera leaf is a viable inhibitor.

Table 3: RSM result of corrosion control with *Moringa oleifera* leaf

S	A (g/L)	B (K)	C (hr)	IE (%)
4	1.0	323	1	65.62
13	0.8	313	1	88.83
12	0.8	323	3	82.51
17	0.8	313	3	97.68
18	0.8	313	3	97.68
11	0.8	303	3	91.29
1	0.6	303	1	64.75
10	1.0	313	3	91.86
14	0.8	313	5	95.46
20	0.8	313	3	97.68
3	0.6	323	1	51.51
7	0.6	323	5	57.54
19	0.8	313	3	97.68
9	0.6	313	3	82.43
15	0.8	313	3	97.68
16	0.8	313	3	97.68
5	0.6	303	5	67.71
2	1.0	303	1	73.78
6	1.0	303	5	82.64
8	1.0	323	5	80.62

S = standard number, *A* = inhibitor conc., *B* = inh. conc., *C* = time, *IE* = inhibition efficiency,



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3.2.1 Model fit summaries

Table 4 provides a fit summary of the model for the inhibitory efficiency of *Moringa oleifera*. Four models of quadratic, cubic, two-factor interaction (2FI) and linear were tested. The numbers and correlation between the adjusted and forecasted R^2 values led to the suggestion that the quadratic model was the best-fitting model. For the quadratic model, the corrected/adjusted R^2 of 0.9913 shows a divergence of less than 0.2 from the expected R^2 of 0.9630.

Table 4: Fit summary of the model for efficiency of *Moringa oleifera* leaf

Considered model	p-value; sequential	Corrected (adjusted) R^2	Expected (predicted), R^2	Comment
LM	0.3059	0.0465	-0.4678	NR
2FI	0.9707	-0.1527	-5.1334	NR
QM	< 0.0001	0.9913	0.9630	S
CM	0.0194	0.9974	-0.0001	Aliased

LM = linear model, 2FI = two factor interaction, QM = quadratic model, CM = cubic model, NR = not recommended, S = suggested, ALS = aliased.

3.2.2 Model ANOVA (analysis of variance) of the *Moringa oleifera* leaf efficiency

Tables 5 provide the ANOVA data of the quadratic equation of the efficiency of the moringa oleifera leaf. The model's F-value of 241.05 in Table 4 suggests that the model is significant. It is based on the fact that the likelihood of noise producing a significant F-value of this magnitude is about 0.01% (Omotioma and Onukwuli, 2017). Model terms are considered significant when P-values are less than 0.0500. So, A, B, C, AB, AC, BC, A^2 , B^2 , and C^2 are important model terms in this instance. The appropriate precision is used to measure the signal-to-noise ratio. Since a ratio greater than 4 is favoured, the recorded number is a preferred precision. There is a sufficient signal when the ratio is 46.805. The design space can be driven by using this paradigm. The model (quadratic) is expressed in Equation 12.

Table 5: ANOVA for quadratic equation of the efficiency of *Moringa oleifera* leaf

S	SS	D-f	MS	FV	PV	Comment
M	4209.84	9	467.76	241.05	< 0.0001	Significant
A	498.15	1	498.15	256.71	< 0.0001	
B	179.52	1	179.52	92.51	< 0.0001	
C	155.87	1	155.87	80.32	< 0.0001	
A.B	21.88	1	21.88	11.27	0.0073	
A.C	27.64	1	27.64	14.24	0.0036	
B.C	10.60	1	10.60	5.46	0.0415	
(A) ²	367.26	1	367.26	189.26	< 0.0001	
(B) ²	383.00	1	383.00	197.37	< 0.0001	
(C) ²	118.21	1	118.21	60.92	< 0.0001	
Residual	19.40	10	1.94			
Lack-of-fit	19.40	5	3.88			
Pure-error	0.0000	5	0.0000			
Cor-total	4229.24	19				
Std-dev.	1.39		R^2		0.9954	
Mean	83.13		Adj. R^2		0.9913	
CV %	1.68		Prtd. R^2		0.9630	
			Adeq. Precision		46.8048	

M = model, A = inhibitor conc., B = inh. conc., C = time, MS = Mean Square, SS = Sum-of-Squares, S = source, D-f = degree of freedom. FV = F-value, PV = Probability value

$$IE = + 98.09 + 7.06A - 4.24B + 3.95C + 1.65AB + 1.86AC + 1.15BC - 11.56A^2 - 11.80B^2 - 6.56C^2 \quad (12)$$



3.2.3 Model coefficients

Model coefficients of the efficiency of *Moringa oleifera* leaf are shown in Table 6. It shows the data of CE (coefficient estimate), which are the estimated change in response for each unit change in factor value (when all other factors are held constant). The overall average reaction across all runs is the intercept in an orthogonal design. The coefficients show the adjustments performed with respect to the average given in the selected parameters. When the factors are orthogonal, the VIFs equal 1. Multicollinearity is indicated by VIFs larger than one.

Table 6: Model coefficients of the efficiency of *Moringa oleifera* leaf

Factor	CE	D-f	S-E	95% CI Low	95% CI High	VIF
I	98.09	1	0.4789	97.02	99.16	
A	7.06	1	0.4405	6.08	8.04	1.00
B	-4.24	1	0.4405	-5.22	-3.26	1.00
C	3.95	1	0.4405	2.97	4.93	1.00
A.B	1.65	1	0.4925	0.5564	2.75	1.00
A.C	1.86	1	0.4925	0.7614	2.96	1.00
B.C	1.15	1	0.4925	0.0539	2.25	1.00
(A) ²	-11.56	1	0.8400	-13.43	-9.68	1.82
(B) ²	-11.80	1	0.8400	-13.67	-9.93	1.82
(C) ²	-6.56	1	0.8400	-8.43	-4.68	1.82

F = factor, *I* = Intercept, *CE* = Coefficient Estimate, *D-F* (degree of freedom), *confidence interval (CI)*, *variance inflation factor (VIF)*, *S-E* (Standard Error)

3.2.4 Representation of the efficiency in a cube plot

Figure 2 displays the cub plot of the RSM result. Interactive impacts of the independent factors on the dependent variable revealed 97.49% as the predicted efficiency of the *Moringa oleifera*.

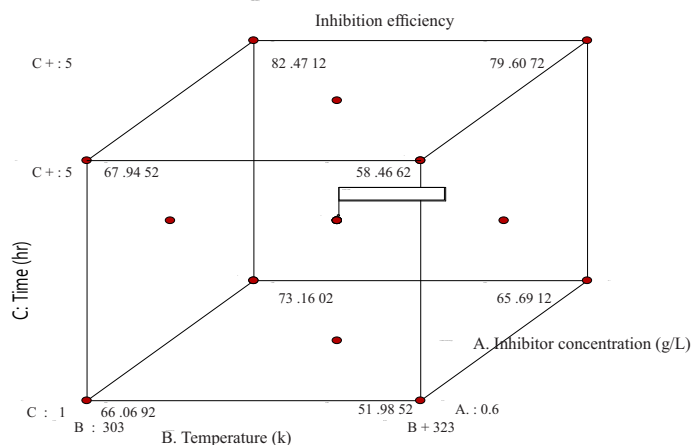


Fig. 2: Cube plot of the inhibition efficiency of moringa oleifera leaf

3.2.5 Optimum values and validation of the RSM result of the study

Table 7 displays the optimum result and its validation. *Moringa oleifera* has an efficiency of 97.49%. Projected and experimental values of the inhibitory efficiency were compared under ideal circumstances using the statistical approach of percentage deviation (error). The percentage deviation values for the *Moringa oleifera* leaves were found to be 0.44%.

Table 7: Validation of the RSM result

Conc. (g/L)	T. (K)	t (hr)	Optimum or predicted IE (%)	Exp. IE (%)	Error (%)
0.78	313.49	3.16	97.49	97.06	0.44

3.3.6 ANN result of the study

Performance assessment graph (Figure 3) and regression plot (Figure 4) are the ANN results of the corrosion control. Graphical outcomes of the testing, validation, and training were shown in both situations. In the performance plot, 6 epochs were revealed. Notably, too, a linear graph was revealed in the regression plot, which indicates that ANN is suitable for the prediction of the efficacy of *Moringa oleifera* leaf.

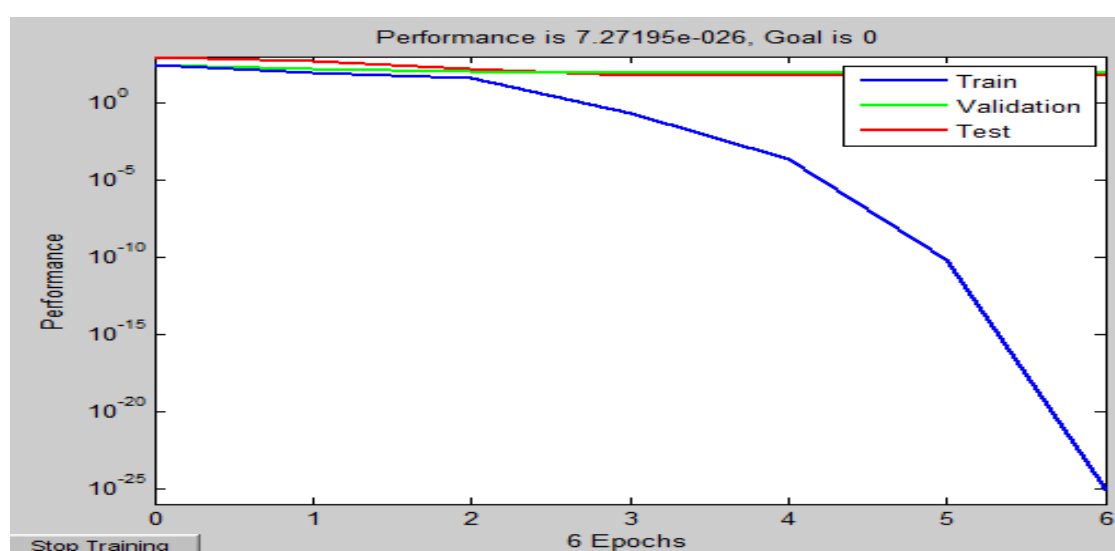


Fig. 3: Performace assessment of ANN result

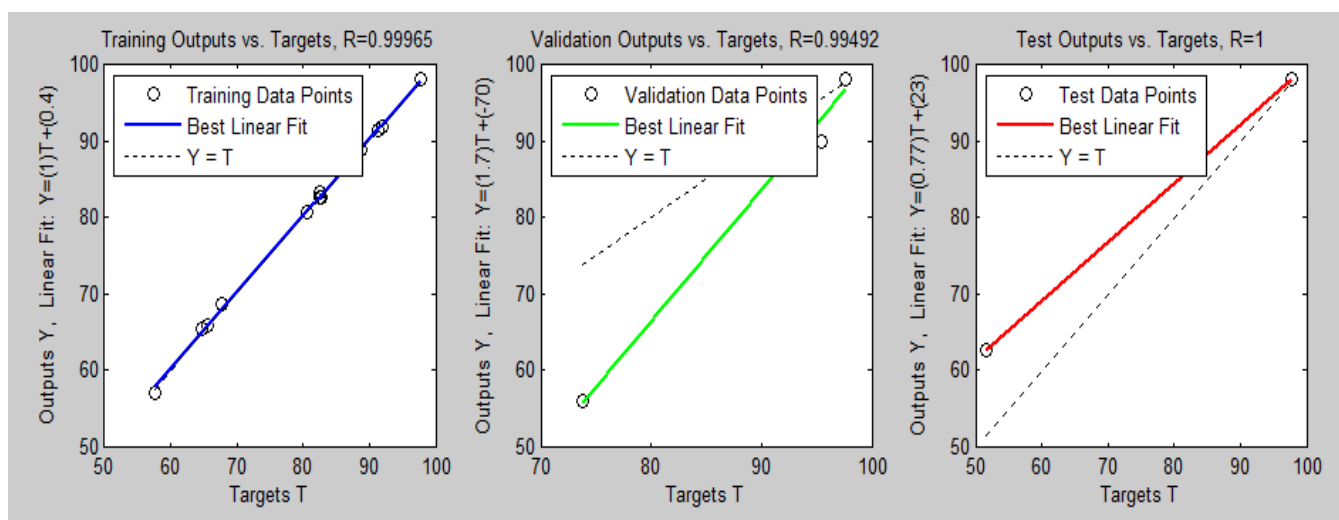


Fig. 4: ANN regressional diagram of the efficacy of *Moringa oleifera* leaf

3.2.7 RSM and ANN Results of Corrosion Control

Table 8 provides the RSM and ANN results of corrosion control utilizing moringa oleifera leaf. The experimental or real inhibitory efficiency (IE), the RSM predicted IE, and the ANN predicted IE were presented as functions of time, temperature, and concentration.



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Table 8: RSM and ANN results of the effectiveness of *Moringa oleifera* leaf

F 1 A: Inh. conc. g/L	F 2 B: Temp. K	F 3 C: Time Hr	Actual IE (%)	RSM predicted IE (%)	ANN predicted IE (%)
1	323	1	65.62	65.69	66.02
0.8	313	1	88.83	87.58	89.23
0.8	323	3	82.51	82.05	82.91
0.8	313	3	97.68	98.09	98.08
0.8	313	3	97.68	98.09	98.08
0.8	303	3	91.29	90.52	91.69
0.6	303	1	64.75	66.07	65.15
1	313	3	91.86	93.59	92.26
0.8	313	5	95.46	95.48	95.86
0.8	313	3	97.68	98.09	98.08
0.6	323	1	51.51	51.99	51.91
0.6	323	5	57.54	58.47	57.94
0.8	313	3	97.68	98.09	98.08
0.6	313	3	82.43	79.47	82.83
0.8	313	3	97.68	98.09	98.08
0.8	313	3	97.68	98.09	98.08
0.6	303	5	67.71	67.95	68.11
1	303	1	73.78	73.16	74.18
1	303	5	82.64	82.47	83.04
1	323	5	80.62	79.61	81.02

3.2.8 ANN and RSM results comparison

Table 9 presents the comparison of the results obtained by the ANN and RSM. It shows lower values for the ANN's root mean square error (RMSE) and standard error of prediction. This finding demonstrates that ANN provided a more accurate prediction than RSM. This discovery is in line with the findings of previous studies (Nnanwube et al., 2020; Pilkington et al., 2014), which noted ANN's superiority over RSM. ANN additionally has a higher rating based on the correlation of determination (R^2). Consequently, ANN outperformed RSM in the prediction of the *Moringa oleifera* efficiency.

Table 9: Comparison of the ANN and RSM results

Root mean square error, RMSE	
RSM	ANN
0.986512	0.4
Standard error of prediction, SEP	
RSM	ANN
1.186688	0.481165
Correlation of determination, R^2	
RSM	ANN
0.987677	0.997974



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3.2.9 Adsorption parameters for the corrosion control

Results of the adsorption parameters are shown in Table 10. It revealed the Frumkin isotherm as the best-fitted isotherm. This assertion was based on the recorded highest values of the coefficient of determination (R^2) (0.999 and 0.9863 at 313 K and 323 K, respectively) (Sa'adan et al., 2013; Ituen et al., 2017; Adejo et al., 2014). The value is the closest to the critical value of 1 (one) compared to the R^2 values of other isotherms (Langmuir, Temkin and Flory-Huggins). Lateral interactive term (α) of 3.3954 and 2.4348 at 313 K and 323 K, respectively, are positive. It means that there was appreciable attraction between the molecules of the *Moringa oleifera* and the mild steel surface. On Temkin results, the attractive parameter (a) values are negative (-2.8651 and -3.0641 at temperatures of 313 K and 323 K, respectively). It shows that there was no chemical reaction between the mild steel and the inhibitor. Similarly, positive values (0.3609 and 1.0262) of the size property (x) were revealed by the analysis of the Flory-Huggins isotherm. This is an indication that there was a reasonable layer of the *Moringa oleifera* attached to the mild steel. Recorded Gibb's free energy is lower than -40.00 kJ/mol. Thus, the adsorption of moringa oleifera's molecules is a physical one (not chemisorption).

Table 10: Adsorption parameters for the corrosion control

AI	T (k)	R^2	K	ΔG_{ads} (J/mol)	IP
LI	313.00	0.9672	0.9672	-10294.2	
	323.00	0.8680	0.8680	-10322.6	
TI	313.00	0.8916	250.38	-10366.8	a -2.8651
	323.00	0.9359	197.65	-10407.3	-3.0641
FI	313.00	0.9990	5.9170	-10294.2	3.3954
	323.00	0.9863	0.0320	-10322.6	2.4348
FHI	313.00	0.6488	3.7154	-10366.8	x 0.3609
	323.00	0.85	6.6481	-10407.3	1.0262

AI = adsorption isotherm, LI = Langmuir Isotherm, TI = Temkim isotherm, FI = Frumkin isotherm, FH Flory-Huggins isotherm, IP = isotherm property, K = equilibrium constant.

4.0 Conclusion

From the analyses of the experimental results, the following conclusions were drawn: Phytochemical results revealed that predominant phytochemicals of moringa oleifera extract include alkaloids (217.08 $\pm$ 0.11 mg/100g), tannins 106.32 $\pm$ 0.12mg/100g) and phenolics (106.32 $\pm$ 0.12 GAE/g). The extract has good corrosion-inhibitive properties. Its functional groups include: C-F stretch, C-H stretch, C=O stretch, N-H bend, C=H stretch and =C-H bend. It contains heteroatoms of nitrogen and oxygen, which shows that the extract is a potential corrosion inhibitor. The quadratic model adequately described the relationship between efficiency and the factors of inhibitor concentration, temperature, and time. The optimum efficiency of 97.49% was attained by *Moringa oleifera* leaf extract. On the predictive ability, the artificial neural network (ANN) gave better predictive results than the response surface methodology (RSM) because the ANN has a higher value of R^2 and lower values of RMSE and SEP. Frumkin isotherm is the best-fitted isotherm. This assertion was based on the recorded highest values of the coefficient of determination (R^2) (0.999 and 0.9863 at 313 K and 323 K, respectively).



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55TH INTERNATIONAL CONFERENCE “COAL CITY 2025”



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55TH INTERNATIONAL CONFERENCE “COAL CITY 2025”



Investigating the Effects and Benefits of Building Information Modelling Deployment in Nigerian Construction Industry

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Abstract

This research examines the effects and benefits of Building Information Modelling (BIM) implementation within the Nigerian construction industry. The study begins by outlining the current state of BIM adoption, noting its limited implementation despite global recognition of its advantages. A qualitative and applied methodology, grounded in a comprehensive literature review, explored key challenges such as financial barriers, lack of skilled labour, and resistance to change. The findings indicate that, while BIM has not yet gained widespread use, its potential benefits, including cost savings, efficiency improvements, and enhanced project delivery, make it a vital tool for the future of construction in Nigeria. Recommendations are directed towards government support, industry collaboration, education, and research investment to encourage the broader adoption of BIM across the sector.

Keywords: Building, Information, Modelling, Construction, Nigeria.

1. Introduction

Building Information Modelling (BIM) has developed as a disruptive technology in the worldwide construction industry, offering a digital representation of a facility's physical and functional properties. BIM is a shared knowledge resource about a facility that is utilized throughout its lifecycle, from design to demolition, to improve project stakeholders' collaboration and decision-making (Azhar et al., 2012). Globally, BIM has demonstrated the potential to reduce construction inefficiencies by lowering rework, enhancing communication, and optimizing workflows (Eastman et al., 2011). In the UK, for example, BIM adoption has resulted in significant cost savings and improved project execution (NBS, 2019).

However, the Nigerian construction industry confronts substantial obstacles that can be addressed through BIM adoption. These difficulties include ineffective project management, cost overruns, schedule delays, and inadequate stakeholder collaboration (McAuley et al., 2017). Despite its benefits, BIM adoption in Nigeria remains low, owing to constraints such as high implementation costs, insufficient training, and low awareness among construction professionals (Succar, 2009; Kassem et al., 2013). BIM adoption is thus viewed as a viable solution to the inefficiencies that plague Nigeria's construction industry, although its implementation is far from ubiquitous.

Although the benefits of BIM are extensively recognized globally, its adoption in the Nigerian construction industry has been limited (Barlish and Sullivan, 2012). Many construction projects continue to rely on traditional design and project management techniques, which are prone to errors and inefficiencies. This unwillingness to embrace current technology like BIM has led to considerable losses in project delays, cost overruns, and subpar project outcomes (Wong and Fan, 2013).

Furthermore, limited studies have been conducted on the specific consequences of BIM implementation in Nigeria. While studies from other countries show that BIM has a favourable influence on minimizing rework, promoting collaboration, and improving overall project outcomes, the Nigerian industry lacks empirical evidence to support these claims (Aouad et al., 2013). A comprehensive evaluation of the constraints impeding widespread BIM implementation in Nigeria is also required to provide actionable insights for enhancing industry performance. This study intends to close this gap by looking into the consequences and benefits of BIM implementation in Nigerian construction projects.

The study aims to provide insight into the current state of BIM in Nigerian Construction projects and how it can be more effectively integrated to enhance productivity, collaboration and overall project outcomes. The study will be carried out by achieving the following objectives to achieve the above aim:

1. *To assess the current level of BIM adoption in Nigerian construction projects*
2. *To identify the key challenges hindering the widespread adoption of BIM in Nigeria*
3. *To evaluate the potential benefits of integrating BIM into Nigerian construction projects*

This research will be of significant importance to various stakeholders in the Nigerian construction industry. First, it will provide valuable insights into the current state of BIM adoption, identifying both the benefits and barriers to its use (Musa and Bello, 2018). For construction firms, the findings will highlight how BIM can improve project management processes, reduce risks, and enhance cost efficiency (Abubakar et al., 2014). Policymakers and regulators will benefit from the study's recommendations on how to create an enabling environment for BIM adoption through training programs, policy development, and incentives. In addition, the study will contribute to academic knowledge on BIM implementation in developing countries, particularly Nigeria, where research has been scarce in this area (Olugboyega et al., 2016). Clients, including government agencies and private developers, will be better informed about the potential for improved project delivery, higher-quality outputs, and more effective cost management through BIM implementation (Oyewobi et al., 2017). Overall, the findings will have far-reaching implications for improving productivity and collaboration in the Nigerian construction industry.

This study will focus on the deployment of BIM in the Nigerian construction industry, specifically analyzing its impact on project performance, cost management, collaboration among stakeholders, and quality control (Laryea and Leiringer, 2020). Data will be collected from professionals in large- and small-scale construction projects across major Nigerian cities, including Lagos, Abuja, and Port Harcourt. The research will also explore the challenges that hinder widespread BIM adoption, such as the lack of technical expertise, high costs of implementation, and resistance to change (Olatunji, 2011). Existing policies and regulations related to BIM in Nigeria will be examined to provide a comprehensive understanding of the regulatory framework governing its deployment [16].

2. Study Area

Nigeria is in West Africa, surrounded by the Atlantic Ocean to the south and lying between latitudes 4°N and 14°N and longitudes 3°E and 15°E. It is Africa's most populous country, with over 200 million people and a diverse range of cultures, languages, and ethnic groupings. Nigeria's economy is primarily reliant on the oil, agriculture, and construction sectors. The building industry, in particular, is critical to the country's infrastructure development and contributes significantly to its GDP, providing millions of jobs.



Fig. 1: Map of Africa showing Nigeria



Fig. 2: Map of Nigeria



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Despite its rapid growth, the Nigerian construction industry confronts a number of issues, including inefficient project execution, cost overruns, delays, and inadequate stakeholder coordination. These issues have hampered the sector's ability to address the needs of an expanding population and urbanization.

3. Literature Review

3.1 Overview of Building Information Modelling (BIM)

In the construction sector, Building Information Modelling (BIM) has emerged as a revolutionary approach that is transforming the way projects are planned, designed, and executed. Defined as a digital representation of a building's physical and functional characteristics, BIM serves as a comprehensive resource for all participants involved in the construction process. By integrating data into a dynamic 3D model, it enables seamless collaboration among architects, engineers, contractors, and other stakeholders, facilitating efficient communication and coordination as the project advances through its various stages (Azhar et al., 2012; Eastman et al., 2011). Eastman et al. (2011) highlight that BIM has dramatically changed how building projects are delivered, particularly in developed countries, where its adoption has resulted in shorter construction timelines, enhanced cost control, and improved overall project efficiency. Unlike traditional design methods that rely heavily on two-dimensional drawings, BIM introduces a multi-dimensional framework that accounts for various aspects of construction, such as time (4D), cost (5D), sustainability (6D), and facility management (7D). Since its inception, BIM has been heralded as a game-changer in terms of improving project accuracy, reducing human errors, and facilitating real-time data sharing between project teams.

Globally, BIM adoption is becoming increasingly common, with several nations mandating its use for both public and private construction projects. In the UK, for instance, the government introduced a mandate in 2016 requiring the use of BIM Level 2 for all publicly funded projects. This mandate has led to significant cost reductions and enhanced efficiency in project delivery, making the UK one of the leaders in BIM implementation (McAuley et al., 2017; Succar, 2009). The US and Australia have also made substantial progress in implementing BIM by establishing national standards and guidelines to support its use in both the public and private sectors (Kassem et al., 2013). The global shift towards BIM adoption reflects its effectiveness in streamlining processes, improving communication, and reducing errors during project execution (Barlish and Sullivan, 2012). Despite the widespread recognition of BIM's advantages, developing countries like Nigeria still face numerous challenges in fully integrating the technology into their construction practices. The disparity in adoption rates highlights the need for tailored strategies to overcome the unique obstacles that impede BIM's full deployment in these regions (Wong and Fan, 2013).

3.2 Current Use of BIM in Nigeria

In Nigeria, the construction industry is gradually acknowledging the potential benefits of BIM; however, its adoption remains limited to specific projects, particularly those undertaken by multinational corporations or those involving significant technological advancements. Research conducted in the Nigerian context indicates that while the importance of digital construction processes is being recognized globally, BIM usage in the country is far from widespread. Musa and Bello (2018) reveal that the majority of Nigerian construction firms have yet to integrate BIM into their daily operations, with its use largely restricted to the design and pre-construction phases. A comprehensive study by Abubakar et al. (2014) found that only 22% of Nigerian construction firms have adopted BIM to some extent, with even fewer having fully integrated it across the entire project lifecycle. The study highlights that BIM adoption is primarily concentrated in major urban centres like Lagos and Abuja, where large-scale developments and international collaborations



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necessitate its use. In contrast, smaller projects and firms continue to rely on traditional methods of construction that often lag in terms of efficiency and precision. According to Olugboyega et al. (2016), the sluggish adoption of BIM in Nigeria can be attributed to the industry's deep-rooted dependence on outdated design processes, which, though familiar, are often time-consuming and less efficient. Another significant factor contributing to the slow uptake of BIM is the absence of government-mandated regulations or guidelines that would require its use in public sector projects. Unlike countries such as the UK or Singapore, where BIM is compulsory for public construction projects, Nigeria lacks a similar legal framework, leaving its adoption largely at the discretion of private enterprises (Oyewobi et al., 2017). This regulatory gap has resulted in a fragmented construction industry that remains heavily reliant on manual, two-dimensional designs, further hampering the widespread use of BIM (Laryea and Leiringer, (2020).

Additionally, the Nigerian construction sector is characterized by a large number of small and medium-sized enterprises (SMEs) that often lack the financial and technical resources to adopt BIM. This fragmentation has created a challenging environment for the technology's broader deployment, as many firms struggle to keep pace with international standards (Olatunji et al., 2011).

3.3 Benefits of BIM in the Nigerian Construction Industry

Despite its slow adoption, numerous studies have demonstrated that BIM could significantly benefit the Nigerian construction industry by addressing some of the sector's most persistent challenges. One of the most prominent advantages of BIM is its ability to reduce errors and minimize rework by providing all project stakeholders with a single, unified platform for sharing and managing project information. This centralized approach improves project planning and coordination, enabling more accurate design and construction processes (Oyewobi et al., 2016). The integration of multiple design models into a coherent system also reduces the risk of miscommunication between design and construction teams, resulting in more efficient project execution (Aibinu and Papadonikolaki, 2020). BIM's ability to enhance cost estimation and control is another critical advantage. Arayici et al. (2011) found that BIM has the potential to reduce construction costs by 5–10%, primarily through improved resource management, waste reduction, and optimized procurement strategies. In a country like Nigeria, where construction projects are frequently plagued by delays and cost overruns, the cost-saving potential of BIM could be a game-changer. Musa and Bello (2018) corroborate this finding, noting that BIM could play a crucial role in mitigating the financial risks associated with large-scale infrastructure projects.

Moreover, BIM has the potential to accelerate project delivery timelines by up to 30%, as noted by Aibinu and Papadonikolaki (2020). This is especially valuable in Nigeria's rapidly urbanizing areas, where there is an urgent need to meet the growing demand for housing and infrastructure. The ability to streamline construction processes and complete projects faster could significantly boost the country's capacity to address its infrastructure deficit.

In addition to improving project timelines and costs, BIM also enhances construction safety by enabling the simulation of various construction sequences and identifying potential hazards before they arise. The predictive modelling capabilities of BIM allow safety protocols to be integrated into the design phase, helping to reduce the risk of accidents and injuries on construction sites. As Abubakar et al. (2014) point out, this proactive approach to safety could have a significant impact on improving the overall safety record of the Nigerian construction industry.

3.4 Challenges of BIM Adoption in Nigeria

Despite its numerous benefits, BIM adoption in Nigeria faces several significant challenges that hinder its widespread implementation. One of the most notable obstacles is the high cost associated with deploying BIM technology. For many construction firms, particularly SMEs, the expense of purchasing BIM software, training personnel, and integrating the technology into existing workflows is prohibitively high. According to Musa and Bello (2018), the cost of acquiring BIM software remains a major barrier, with limited access to affordable alternatives further complicating the situation (Nwakpa and Oke, 2020).

In addition to financial constraints, the Nigerian construction industry also grapples with a lack of technical expertise in BIM. While awareness of BIM is gradually increasing, there is still a significant skills gap in the workforce, with many professionals lacking the necessary training to effectively use the technology. This shortage of BIM experts is exacerbated by the fact that few Nigerian universities or training institutions offer formal education programs focused on BIM. As Oyewobi et al. (2016) and Abubakar et al. (2014) report, even those professionals who are aware of BIM are often hesitant to adopt it due to the steep learning curve involved in mastering the technology.

Cultural resistance to change is another significant hurdle. Nigeria's construction sector, like many in developing countries, is deeply rooted in traditional practices, making it resistant to technological innovation. Laryea and Leiringer (2020) argue that many construction professionals are sceptical of the long-term benefits of BIM, preferring to stick with familiar methods such as two-dimensional drawings and manual project management tools (Sacks and Pikas, 2013). This reluctance to embrace change is further compounded by the absence of regulatory frameworks or government-backed initiatives to promote BIM adoption.

Table 1: Barriers to BIM Implementation in Nigeria

Barriers	Description
Lack of Knowledge and Awareness	Limited understanding of BIM and its benefits among construction professionals.
High Cost of Implementation	Financial constraints associated with adopting new technologies and software.
Inadequate Government Policies	Absence of supportive legislation and policies to promote BIM adoption at a national level.
Lack of Demand for BIM	Insufficient market demand for BIM services from clients and stakeholders in the construction sector.
Inadequate Training and Education	Insufficient training programs and educational resources for professionals to learn BIM effectively.
Technological Barriers	Issues related to software compatibility and the technological readiness of firms in the industry.
Cultural Resistance to Change	Preference for traditional methods of construction and reluctance to adopt new practices.
Inadequate Infrastructure	Poor technological infrastructure to support BIM implementation and data management.
Interoperability Issues	Challenges in integrating BIM with existing systems and processes.
Reluctance from Stakeholders	Resistance from various stakeholders, including contractors and clients, to embrace BIM.

3.5 Potential Effects of Further BIM Deployment in Nigeria

The potential benefits of increasing BIM adoption in Nigeria's construction industry are profound. By facilitating improved project coordination and communication among stakeholders, BIM could significantly enhance the overall quality of construction projects. Abubakar et al. (2014) assert that BIM's real-time data capabilities enable continuous monitoring of project progress, ensuring that projects are delivered on time and within budget. This is particularly important in Nigeria, where project delays and cost overruns are prevalent, often resulting in unfinished or substandard projects (McPartland, (2020). BIM also offers a unique opportunity to promote sustainability in the Nigerian construction sector. By optimizing resource management and minimizing material waste, BIM can contribute to more environmentally friendly construction practices. Oyewobi et al. (2016) highlight that BIM's ability to simulate energy consumption and carbon emissions during the design phase can assist architects and engineers in developing more sustainable buildings. As global emphasis on sustainability continues to grow, BIM could help Nigeria align with international standards for green construction, making it a key tool in the country's efforts to reduce its environmental footprint (Udom, 2020).

In the context of infrastructure development, BIM has the potential to address some of Nigeria's most pressing construction challenges. With the country's urban population expected to surge in the coming decades, the demand for high-quality infrastructure will become increasingly urgent. BIM's ability to shorten project timelines, reduce costs, and ensure that projects meet the highest standards could play a crucial role in addressing this demand. Additionally, by enabling the simulation of different construction scenarios, BIM can help identify potential safety risks before construction begins, reducing the frequency of accidents and fatalities on Nigerian construction sites (BCA, 2016).

Table 2: Potential Effects of Further BIM Deployment in Nigeria

Potential Effects	Description	Reference
Improved Project Delivery	Enhanced project coordination and reduced errors lead to better adherence to timelines and budgets.	[Abubakar et al., 2014; McPartland, 2020]
Reduction in Construction Costs	Better planning, resource management, and error minimization contribute to cost savings.	[Musa and Belo, 2018; Arayici et al., 2011]
Enhanced Sustainability	Integration of sustainable building techniques through energy consumption modeling.	[Oyewobi et al., 2016; Udom, 2020]
Better Infrastructure Development	Facilitates the delivery of high-quality infrastructure to meet urban demands.	[Agboola, 2021]
Improved Safety	Simulation of construction sequences to reduce accidents and ensure worker safety.	[BCA, 2016]



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3.6 Global Comparisons and Lessons for Nigeria

While Nigeria's BIM adoption is still in its early stages, learning from other countries can provide significant insights into how to utilize the technology more efficiently. The United Kingdom, for example, has achieved major increases in construction efficiency after adopting BIM for all public sector projects in 2016 (McAuley et al., 2017). The government's dedication to BIM, as seen by the creation of standards, training, and regulatory frameworks, has propelled the United Kingdom to the forefront of BIM implementation.

Singapore's example also has important lessons for Nigeria. The Singaporean government has played an important role in fostering BIM adoption by providing financial incentives to construction companies and mandating the use of BIM in public projects (Succar, 2015). The government's assistance has been critical in encouraging BIM adoption throughout the country, making Singapore one of the most advanced BIM marketplaces in the world. Nigeria could benefit from taking a similar strategy and implementing rules that encourage the use of BIM in both public and commercial construction projects. This might involve providing financial incentives to enterprises that use BIM, as well as developing a national BIM strategy that establishes clear criteria for its use across the industry (Kiviniemi and Codinhoto, 2014).

4. Research Methodology

This study employs a comprehensive literature review as its primary research methodology, emphasizing a qualitative and applied approach. This method is particularly suited for exploring the deployment of Building Information Modelling (BIM) within the Nigerian construction industry, as it facilitates a thorough analysis of existing research, theories, and practices. A literature review allows for the synthesis of diverse perspectives and findings, helping to identify significant trends, challenges, and gaps in the current understanding of BIM adoption. In qualitative research, the focus is on understanding the nuances and complexities of human experiences and social phenomena. Therefore, a literature review becomes an essential tool for gaining insights into the perceptions and attitudes of stakeholders within the construction sector. By examining a broad spectrum of scholarly articles, industry reports, and case studies, this methodology provides a rich contextual framework for assessing how BIM is utilized in practice and the various barriers that may hinder its widespread implementation. Such an approach is critical in understanding the cultural, economic, and technological factors influencing BIM adoption, particularly in a developing country like Nigeria, where traditional methods often dominate the construction landscape. Moreover, the applied nature of this research underscores its relevance to practitioners in the field. By investigating the real-world implications of BIM deployment, the study aims to provide actionable insights and recommendations that can enhance integration strategies within the Nigerian construction industry. The findings from the literature review will be instrumental in informing industry stakeholders about best practices, potential pitfalls, and the overall impact of BIM on project delivery and collaboration among construction professionals. A literature review not only contributes to academic discourse but also serves as a bridge between theory and practice. It helps to illuminate how theoretical concepts are manifested in real-world scenarios, thereby guiding future research directions and practical applications. This methodological choice also allows for the identification of gaps in the existing literature, paving the way for further studies that can explore uncharted areas related to BIM in Nigeria.

Overall, the comprehensive literature review approach adopted in this study aligns with the qualitative and applied research goals, ensuring that the findings are not only relevant to academia but also beneficial to the construction industry. By focusing on the existing body of knowledge, this research aspires to foster a deeper understanding of the potential benefits and challenges associated with BIM adoption, ultimately contributing to the advancement of the construction sector in Nigeria.



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5. Findings

The investigation into the deployment of Building Information Modelling (BIM) within the Nigerian construction industry reveals a complex landscape of opportunities and challenges that reflect the current state of technological adoption. This analysis yields several important insights pertinent to the three research objectives: assessing the current level of BIM adoption, identifying key challenges to its widespread implementation, and evaluating the potential benefits of integrating BIM into construction projects.

1. Current Level of BIM Adoption in Nigerian Construction Project:

The findings suggest that the current level of BIM adoption in Nigeria is relatively low, although it is gradually increasing as awareness grows among industry stakeholders. While larger firms and those involved in high-profile infrastructure projects have begun to embrace BIM, the overall integration across the industry remains limited, particularly among small and medium-sized enterprises (SMEs). Many construction professionals still rely heavily on traditional methods due to a lack of understanding of BIM's functionalities and the tangible benefits it offers. This gap in awareness contributes to a prevailing perception that BIM is an advanced, optional tool rather than a necessary evolution in construction practices.

Additionally, many industry stakeholders lack access to comprehensive educational resources that would facilitate a clearer understanding of BIM's capabilities. The limited exposure to successful case studies showcasing local BIM implementations further exacerbates this issue, perpetuating skepticism and hesitation among potential adopters. Furthermore, while the interest in BIM is evident, particularly in progressive firms, a significant portion of the industry remains largely untouched by these advancements. This disparity underscores the need for increased outreach and education about the transformative potential of BIM within the Nigerian construction landscape.

2. Key Challenges Hindering Widespread Adoption of BIM in Nigeria:

Several critical barriers have been identified that hinder the widespread adoption of BIM in Nigeria. Financial constraints rank among the most significant challenges, as many firms struggle to allocate sufficient resources for the necessary investments in BIM software, hardware, and training. The high costs associated with acquiring and maintaining BIM technology can be particularly daunting for SMEs operating on tight budgets, which often lack the financial flexibility to adopt new technologies. Additionally, the existing workforce's lack of skills in BIM poses a substantial challenge; many professionals in the construction sector have not received formal training in these advanced technologies, resulting in a workforce that is largely unprepared to leverage the capabilities of BIM effectively. Cultural resistance to change is another considerable obstacle to BIM adoption. Many stakeholders in the construction industry are deeply entrenched in traditional practices and may view BIM as an unnecessary complication rather than an improvement. This cultural inertia is often exacerbated by the fragmented nature of the Nigerian construction industry, which is characterized by limited collaboration and communication between various stakeholders. Such fragmentation complicates the effective implementation of BIM, as firms may be uncertain about how to integrate BIM into their existing workflows without standardization and collective effort. Furthermore, the lack of unified standards and practices further complicates matters, as firms may be unsure of how to align their processes with those of their peers.

3. Potential Benefits of Integrating BIM into Nigerian Construction Projects:

Despite the myriad challenges, the literature reveals numerous potential benefits associated with integrating BIM into construction practices in Nigeria. One of the most significant advantages of BIM



55TH INTERNATIONAL CONFERENCE “COAL CITY 2025”



is its capacity to enhance collaboration among stakeholders involved in the construction process. By fostering better communication and coordination between architects, engineers, contractors, and clients, BIM can help significantly reduce conflicts, minimize errors, and streamline project delivery. This collaborative environment is essential for improving overall project performance and ensuring that projects are completed on time and within budget. Furthermore, the advanced visualization capabilities of BIM empower stakeholders to gain a clearer understanding of project designs before construction begins. This improved visualization facilitates better decision-making and enhances client satisfaction, as clients can visualize the final product and provide valuable feedback during the design phase. The ability to explore virtual representations of projects allows for more effective planning and design adjustments, reducing the likelihood of costly changes during construction.

In addition to fostering collaboration and improving visualization, BIM can lead to enhanced project performance and quality. The integration of real-time data and analytics enables stakeholders to monitor project progress closely, identify potential issues early on, and make informed adjustments as necessary. This proactive approach to project management is crucial in addressing unexpected challenges and ensuring that projects meet their established objectives. Moreover, BIM can significantly reduce costs through more accurate project estimations, minimizing rework, and improving resource allocation. The efficiencies gained through BIM adoption can ultimately contribute to higher profit margins for firms that are willing to invest in this technology.

Moreover, the integration of BIM can lead to enhanced safety standards within the construction industry. By facilitating better planning and coordination, BIM can help identify potential safety hazards before construction begins, enabling firms to implement appropriate measures to mitigate risks. This proactive approach to safety can contribute to a reduction in workplace accidents and injuries, fostering a safer working environment for all personnel involved in construction projects. The ability to simulate construction processes also allows for better safety training and preparation, further emphasizing the value of BIM in improving on-site safety. Finally, the literature underscores the importance of a supportive policy framework in fostering BIM adoption in Nigeria. Government incentives, industry standards, and educational initiatives are crucial for encouraging stakeholders to embrace BIM. By creating a conducive environment for BIM integration, the government can help elevate the Nigerian construction industry, making it more competitive on a global scale. The establishment of clear guidelines and standards for BIM use can also facilitate greater collaboration and interoperability among different stakeholders, driving a more cohesive approach to project delivery.

In conclusion, the findings of this research indicate that while BIM adoption in Nigeria faces several significant challenges, the potential benefits of integrating this technology into construction projects are substantial. By addressing the barriers to adoption and fostering a culture of innovation, the Nigerian construction industry can enhance its efficiency, reduce costs, and improve the overall quality of its projects. The successful implementation of BIM has the potential to revolutionize construction practices in Nigeria, leading to a more robust and sustainable sector that is better equipped to meet the demands of the future. The insights gained from this research provide a valuable foundation for further exploration of BIM's role in shaping the future of construction in Nigeria, paving the way for a more integrated and technologically advanced industry.

In light of these findings, it is essential for stakeholders, including government agencies, educational institutions, and industry leaders, to collaborate in creating an environment that encourages the adoption of

BIM technologies. Such collaboration can lead to the development of comprehensive training programs, the establishment of incentives for early adopters, and the promotion of best practices that highlight the advantages of BIM. By fostering a culture of innovation and adaptability, the Nigerian construction industry can not only improve its own practices but also contribute to the overall advancement of the sector on a global scale.

6. Conclusions and Recommendations

The research on the deployment of Building Information Modelling (BIM) in the Nigerian construction industry has highlighted both significant challenges and transformative potential. While BIM adoption remains limited across the sector, particularly among smaller firms, there is increasing recognition of its benefits, including enhanced collaboration, improved project visualization, greater efficiency, and increased safety standards. The findings of this study indicate that for Nigeria to harness the full potential of BIM, a concerted effort is required from all stakeholders involved in the construction process.

The barriers to BIM adoption, including financial constraints, lack of skilled professionals, cultural resistance, and insufficient policy frameworks, must be addressed to enable widespread implementation. The advantages of BIM, such as cost savings, enhanced project delivery, and improved quality, are too substantial to ignore. Thus, the Nigerian construction industry must embrace this technology not just as an option but as an essential component for future competitiveness.

1. Government Support and Policy Framework:

The government should take an active role in promoting BIM adoption by developing supportive policies and frameworks. This could include tax incentives for companies investing in BIM technologies, funding for educational initiatives aimed at enhancing the workforce's skills, and establishing standards for BIM implementation across the construction sector. By creating a regulatory environment conducive to BIM integration, the government can encourage firms to adopt these practices more readily.

2. Industry Collaboration and Networking:

Stakeholders in the construction industry—including architects, engineers, contractors, and clients—should collaborate to foster an environment of knowledge sharing and mutual support. Establishing industry networks or forums where experiences and best practices regarding BIM adoption can be discussed will encourage firms to share insights and lessons learned. This collaborative approach can help to demystify BIM and reduce cultural resistance by showcasing successful implementations and the tangible benefits realized by early adopters.

3. Education and Training Programs:

Investing in education and training programs is essential to developing a workforce proficient in BIM technologies. Educational institutions, in collaboration with industry players, should integrate BIM training into their curricula, ensuring that the next generation of construction professionals is equipped with the skills necessary to utilize BIM effectively. Additionally, firms should invest in continuous professional development for their employees, offering workshops, online courses, and certifications in BIM-related competencies.



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4. Promoting Case Studies and Success Stories:

Highlighting successful case studies of BIM implementation within Nigeria can serve as a powerful motivator for firms hesitant to adopt the technology. Stakeholders should actively document and share success stories that illustrate the benefits of BIM, including improved efficiency, cost savings, and enhanced project outcomes. By showcasing local examples of BIM in action, stakeholders can build confidence in its applicability and effectiveness within the Nigerian context.

5. Encouraging Research and Development:

To foster innovation in the construction sector, stakeholders should prioritize research and development initiatives focused on BIM technologies. Collaborative projects involving academia, industry professionals, and government entities can help drive advancements in BIM applications, tailoring solutions to meet the specific needs of the Nigerian construction landscape. This research can inform the development of new tools, methodologies, and best practices, further facilitating BIM adoption.

6. Investment in Infrastructure and Technology:

Construction firms should prioritize investment in the necessary infrastructure and technology to support BIM adoption. This includes procuring the right software and hardware, ensuring that teams have access to up-to-date tools, and creating an environment conducive to collaboration. By making these investments, firms can facilitate a smoother transition to BIM practices and enhance their operational efficiency.

The deployment of Building Information Modelling in the Nigerian construction industry presents both significant challenges and substantial opportunities. By addressing the barriers to adoption and fostering a culture of innovation, the sector can enhance its efficiency, reduce costs, and improve overall project quality. The recommendations provided here aim to guide stakeholders in their efforts to embrace BIM as a transformative tool that can significantly elevate the construction industry in Nigeria. As the global construction landscape continues to evolve, Nigeria must seize the opportunity to integrate advanced technologies like BIM, ensuring its position in the competitive international market and driving sustainable development in the construction sector.



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Comparative Study of Drying Characteristics of Cocoyam (*Xanthosoma sagittifolium*) Slices Using Convection and Microwave-Assisted Drying Techniques

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Abstract

*This study explores the drying behaviour of cocoyam (*Xanthosoma sagittifolium*) slices using both convective and microwave-assisted drying methods. Freshly harvested cocoyam with an initial moisture content of 66.93% (wet basis) was subjected to convective drying at 50°C to 80°C and microwave drying at power levels ranging from 280W to 700W. The drying process was characterized by a non-linear falling rate period, with a secondary falling rate phase evident at elevated temperatures and microwave powers. Microwave drying reached the critical moisture point more rapidly and achieved a lower final moisture content (2.43% wb at 700W) compared to convection drying (7.70% wb at 80°C). The effective moisture diffusivity values ranged from 4.90×10^{-11} to 1.89×10^{-10} m²/s for convective drying and from 1.69×10^{-11} to 6.00×10^{-11} m²/s for microwave drying. In terms of energy use, microwave drying demonstrated considerably lower specific energy consumption (0.22–0.32 J/g) than convection drying (7.46–8.34 J/g). Among the models evaluated, the Midili model best described the drying kinetics in both methods. Microwave-assisted drying was found to be a more energy-efficient and time-saving approach for preserving cocoyam slices.*

Keywords: Cocoyam drying; Microwave-assisted drying; Convection drying; Thin-layer drying kinetics; Specific energy consumption; Drying models.

1. Introduction

Cocoyam (*Xanthosoma sagittifolium*) is an important tropical root crop cultivated extensively in parts of Africa, Asia, and Latin America. Its adaptability to a wide range of agro-ecological conditions and its nutritional content have positioned it as a valuable food security crop in many developing regions (Onyeka, 2014; Ukwu *et al.*, 2022; Siqueira *et al.*, 2023). Beyond its dietary significance, cocoyam is also a source of livelihood for small-scale farmers. However, its high postharvest spoilage, largely due to its high moisture content (typically up to 80% wet basis, depending on variety), is a major challenge to farmers (Afrifa, 2013). Drying has long been one of the most reliable ways to preserve perishable crops, mainly because reducing their moisture content slows down the very processes that cause produce deterioration, such as microbial growth, enzymatic reactions, and biochemical changes. For cocoyam and other root or tuber crops, this step is not merely about extending shelf life; it also helps to keep much of the crop's original flavour, colour, and nutrient value intact. From a physical standpoint, drying is a coupled heat–mass transfer operation, and the rate at which it proceeds is shaped by several controllable factors: temperature, air velocity, surrounding humidity, and the total drying time (Feng *et al.*, 2012; Soltanbeik and Jayas, 2020). Thin-layer drying models are often used to capture this behaviour in a manageable mathematical form, allowing researchers to predict moisture loss patterns and design systems that make better use of energy (Onwude *et al.*, 2016;



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Inyang *et al.*, 2018).

Researchers have studied these principles in a wide range of crops such as eggplant (Doymaz and Göl, 2011), tomato (Akanbi *et al.*, 2006; Agarry, 2016), red chili (Ajuebor *et al.*, 2022; Handayani *et al.*, 2022), okra (Afolabi and Agarry, 2014), taro (Aregbesola *et al.*, 2022), basil leaves (Altay *et al.*, 2019), and yam (Kamal *et al.*, 2020), among others with these works collectively covering technologies from the most basic (open-sun drying) to advanced systems such as controlled hot-air, microwave heating, and infrared. Although sun drying still finds use in many rural and small-scale operations because it costs almost nothing to run, the trade-off, such as loss of quality due to dust, pests, and microbial attack (Lamidi *et al.*, 2019; Onwude *et al.*, 2016), is evident. More modern approaches, particularly hot-air convection and microwave-assisted drying, give operators far greater control over the process.

In convection drying, heated air is circulated in a regulated manner to remove moisture steadily and evenly, with heat transfer occurring primarily from the surface inward (Akanbi *et al.*, 2006; Doymaz and Göl, 2011). In contrast, microwave systems rely on volumetric heating, whereby water molecules within the material are directly energised, generating internal vapour pressure gradients that accelerate outward moisture migration and sharply reduce drying time (Feng *et al.*, 2012; Zhang *et al.*, 2010). Both methods are widely applied in food processing; however, their differences in mechanism and performance make **head-to-head comparisons not only useful but also necessary** for identifying the most efficient and context-appropriate option for a given produce (Onwude *et al.*, 2016; Lamidi *et al.*, 2019).

In view of this, the present study focuses on *Xanthosoma sagittifolium* (cocoyam) slices, subjected to both hot-air and microwave-assisted drying. Drying behaviour was evaluated in terms of overall drying time, effective moisture diffusivity, and specific energy consumption, while six thin-layer kinetic models were applied to identify the most suitable descriptor of the drying process. The overarching aim was to compare the efficiency of the two methods and provide mechanistic insights into moisture migration and energy use during cocoyam drying, thereby contributing to improved postharvest processing strategies for root and tuber crops.

2. Materials and Methods

2.1. Materials

Fresh cocoyam (*Xanthosoma* spp.) corms were sourced from a local market in Ile-Ife, Nigeria. The corms were washed thoroughly to remove adhering soil and debris, manually peeled with a stainless-steel knife, and cut into uniform rectangular strips measuring approximately 10 cm in length, 2 cm in width, and 5 mm in thickness.

The initial moisture content (wet basis) was determined gravimetrically. Fresh slices (10.00 ± 0.01 g) were weighed into pre-dried and pre-weighed porcelain crucibles and oven-dried at 105 ± 2 °C for 24 h in a laboratory hot-air oven (MRC DFO-80, Essex, UK). At the end of the drying period, samples were cooled in a desiccator to ambient temperature and reweighed. The drying-cooling-weighing sequence was repeated until a constant mass was recorded. Moisture content was computed according to the equation

$$MC_{wb} = \frac{M_i - M_f}{M_i} \times 100 \quad (1)$$

where MC_{wb} is the wet basis moisture content. In addition, M_i and M_f are the initial and final masses of the sample (g), respectively

2.2 Drying Methods

2.2.1 Hot air convection drying

Drying experiments were performed in a laboratory-scale cabinet dryer (Gallenkamp Hot Box Oven, UK) fitted with an 800 W heating element, a centrifugal fan for air recirculation, and a digital temperature controller. For each run, approximately 50 g of uniformly cut cocoyam slices were arranged in a single layer on the central tray of the preheated drying chamber. Drying was conducted at set air temperatures of 50, 60, 70, and 80 °C. Mass measurements were recorded at 5 min intervals during the first 30 min, at 10 min intervals for the subsequent 2 h, and at 20 min intervals thereafter, until the total drying time reached 500 min. All trials were performed in triplicate to ensure experimental repeatability and data reliability.

2.2.2 Microwave-assisted convective drying

Microwave-assisted convective drying was carried out using a domestic microwave oven (Cookworks, Model EM 7, UK) with a maximum power output of 700 W at a frequency of 2.45 GHz. A centrifugal blower, mounted externally, supplied hot air to the drying chamber to facilitate convective heat transfer (Figure 1). For each experiment, about 50 g of cocoyam slices were evenly spread in a single layer on the middle tray and subjected to microwave power levels ranging from 280 to 700 W. Sample mass was recorded at 1-minute intervals until a constant weight was achieved. Each treatment was conducted in triplicate to confirm reproducibility.

2.2.3 Moisture ratio determination

The moisture ratio (MR) of the cocoyam slices during drying was calculated following the method of Afolabi and Agarry (2014):

$$MR = \frac{M_t - M_e}{M_o - M_e} \quad (2)$$

where M_t is the dry-basis moisture content at a given drying time (g water/g dry matter), M_o is the initial dry-basis moisture content, and M_e is the equilibrium dry-basis moisture content corresponding to the mean drying-air conditions. Since the relative humidity and temperature of the drying air fluctuated during experiments, M_e was assumed negligible, allowing Equation (2) to be simplified as:

$$MR = \frac{M_t}{M_o} \quad (3)$$

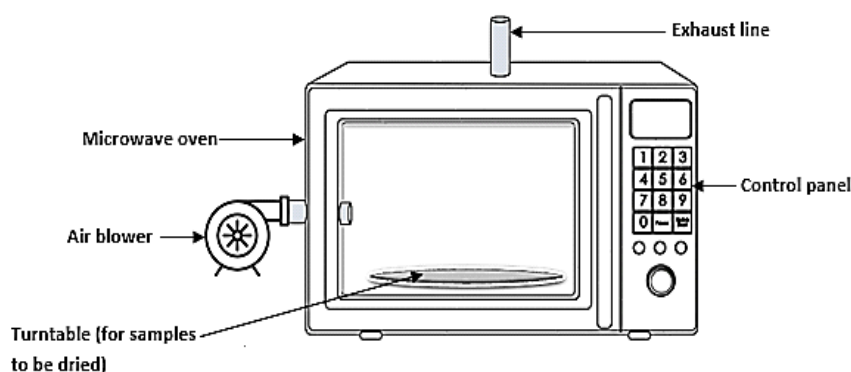


Fig. 1: Schematic diagram of the microwave drying unit

2.3. Modelling of Drying Kinetics

To describe the drying kinetics of cocoyam slices, experimental moisture ratio (MR) data were fitted to widely adopted semi-theoretical thin-layer drying models. The mathematical forms and references of the six models assessed (Lewis, Page, Henderson and Pabis, Logarithmic, Two-Term Exponential, and Midilli–Kucuk) are presented in Table 1. These models have been extensively employed in previous studies for predicting moisture migration in a variety of agricultural materials.

Nonlinear regression analysis was performed in Microsoft Excel (2016) to estimate model parameters for each drying condition. The adequacy of model fit was assessed using three statistical indicators: coefficient of determination (R^2), reduced chi-square (χ^2), and root mean square error (RMSE). The R^2 values were obtained directly from the regression analysis, whereas χ^2 and RMSE were computed according to the following expressions (Morakinyo *et al.*, 2020):

$$\chi^2 = \frac{\sum_{i=1}^N (MR_{exp,i} - MR_{pred,i})^2}{N - z} \quad (4)$$

$$RMSE = \left[\frac{\sum_{i=1}^N (MR_{exp,i} - MR_{pred,i})^2}{N} \right]^{0.5} \quad (5)$$

where

$MR_{exp,i}$ = moisture ratio obtained from experiment i ;

$MR_{pred,i}$ = model predicted moisture ratio for experiment i ;

N = number of observations, and

z = number of model parameters.

Table 1. Thin-layer drying models evaluated for cocoyam slices.

Model	Equation	Reference
Lewis	$MR = \exp(-kt^n)$	Roberts <i>et al.</i> (2008)
Page	$MR = \exp(-kt^n)$	Doymaz <i>et al.</i> (2023)
Henderson and Pabis	$MR = a \cdot \exp(-kt) + c$	Isa and Jimoh (2021)
Logarithmic	$MR = a \cdot \exp(-kt) + c$	Handayani <i>et al.</i> (2022)
Two-Term Exponential	$MR = a \cdot \exp(-kt) + b \cdot \exp(-kt^n)$	Jeevarathinam <i>et al.</i> (2022)
Midilli–Kucuk	$MR = a \cdot \exp(-kt^n) + bt$	Küçük <i>et al.</i> (2022)

2.4. Determination of Effective Moisture Diffusivity

Effective moisture diffusivity (D_e) was determined during the falling-rate period using Fick's second law for one-dimensional moisture movement in a slab:



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$$MR = \frac{8}{\pi^2} \exp \left[-\frac{\pi^2 D_e t}{4L^2} \right] \quad (6)$$

Where:

MR is the moisture ratio (dimensionless);

D_e is the effective diffusivity (m^2/s);

L is the half-thickness of sample (m), and

t is the drying time (s).

where L is the half-thickness of the sample (m) and t is the drying time (s). Linearisation of Equation (5) gives:

$$\ln(MR) = \ln \left(\frac{8}{\pi^2} \right) - \left[\frac{\pi^2 D_e}{4L^2} \right] t \quad (7)$$

Plots of $\ln(MR)$ against t for each experimental condition yielded slopes used to compute D_e (El-Mesery *et al.*, 2023).

2.5. Estimation of Activation Energy and Specific Energy Consumption

2.5.1. Thermal activation energy estimation

The temperature dependence of D_e during convective drying was evaluated using the Arrhenius-type relationship, in equation (8):

$$\ln(D_e) \quad D_e = D_o \exp \left(\frac{E_a}{RT} \right) \quad (8)$$

where D_e is the effective moisture diffusivity (m^2/s), D_o is the pre-exponential factor (m^2/s), E_a is the activation energy (kJ/mol), R is the universal gas constant ($8.314 \text{ J/mol} \cdot \text{K}$), and T is the absolute temperature (K). The slope of the linear regression of against $1/T$ was used to compute E_a (Okeleye *et al.*, 2021).

2.5.2. Microwave-based activation energy estimation

For the microwave drying process, a modified form of the Arrhenius equation was employed to account for the influence of microwave power and sample mass on effective moisture diffusivity. The model is defined as:

$$D_e = D_o \exp \left(-\frac{mE_a}{P} \right) \quad (9)$$

Here, D_e represents the effective moisture diffusivity (m^2/s), D_o is the pre-exponential factor (m^2/s), E_a is the microwave-specific activation energy (W/g), P denotes the applied microwave power level (W), and m is the initial mass of the sample (g). This formulation captures the non-isothermal nature of microwave drying by integrating energy input and sample mass as determinants of moisture transport behaviour.

2.5.3. Estimation of specific energy consumption

The energy performance of each drying technique was evaluated by computing the specific energy consumption (E_s), which represents the total energy required to remove a unit mass of water from the product. The calculation followed a modified form of the expression proposed by Çelen (2019):



$$E_s = \frac{P \times t \times 10^{-6}}{m_w} \quad (10)$$

where E_s is the specific energy consumption (J/g), P is the power input (W), t is the total drying time (s), and m_w is the mass of water removed during drying (kg).

This parameter provides a quantitative basis for comparing the energy efficiency of different drying methods, allowing for the identification of processes with lower energy demands per unit of water removed.

3. Results and Discussion

3.1 Drying Characteristics of Cocoyam Chips

The fresh cocoyam chips had an initial moisture content of 66.93 % (wet basis), equivalent to 2.024 g of water per gram of dry matter (dry basis). This initial value was used as the baseline for determining the moisture ratios applied in subsequent kinetic analyses.

Figures 2 and 3 illustrate the drying curves obtained under convective and microwave drying conditions, respectively. In both drying modes, moisture removal followed a predominantly **falling-rate trend**, consistent with the behaviour reported for most agricultural and biological materials (Karel and Lund, 2003; Onwude *et al.*, 2016; Ajala and Abubakar, 2018). This pattern confirms that internal moisture diffusion was the principal mechanism governing the drying process (Afolabi *et al.*, 2015).

Under convective drying, samples processed at 60 °C displayed a uniform single-phase falling-rate profile throughout the drying period. In contrast, chips dried at higher temperatures (70 °C and 80 °C) exhibited a two-stage falling-rate pattern, indicating a shift in the prevailing internal moisture transport mechanism during the process. At 70 °C, an observable change in drying rate occurred after approximately 240 minutes, corresponding to a critical moisture content of about 0.42 g water/g dry solid. Similar inflexion points were detected for the 70 °C and 80 °C treatments, with critical moisture contents of roughly 0.30 g/g and 0.23 g/g, appearing after 200 minutes and 170 minutes, respectively. These thresholds likely mark the transition between different modes of moisture migration, such as from capillary-driven flow to predominantly diffusion-controlled transport (Ajala *et al.*, 2012; Dasore *et al.*, 2020).

Microwave-dried samples exhibited a comparable drying profile to those dried using convective heat. At **280 W**, the drying curve followed a **single falling rate period**, whereas higher power levels (**420 W, 560 W, and 700 W**) resulted in a **two-stage drying pattern**, similar to thermal drying at elevated temperatures. The corresponding **critical moisture contents** for these microwave power levels were found to be **0.18 g/g, 0.10 g/g, and 0.03 g/g**, respectively. The reduction in critical moisture content observed at higher microwave power levels indicates enhanced internal moisture diffusion, which can be attributed to volumetric heating and the development of strong vapour pressure gradients under microwave irradiation (Kumar and Karim, 2019). Similar behaviour was reported by Zhang *et al.* (2024) during microwave-assisted convective drying of fresh paddy, further supporting this mechanism.

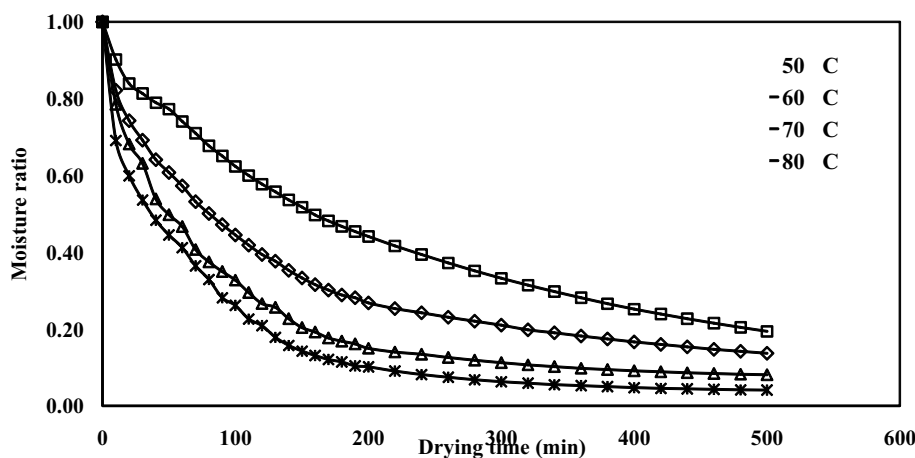


Fig. 2: Variation of moisture ratio with drying time at different temperatures for convective oven drying

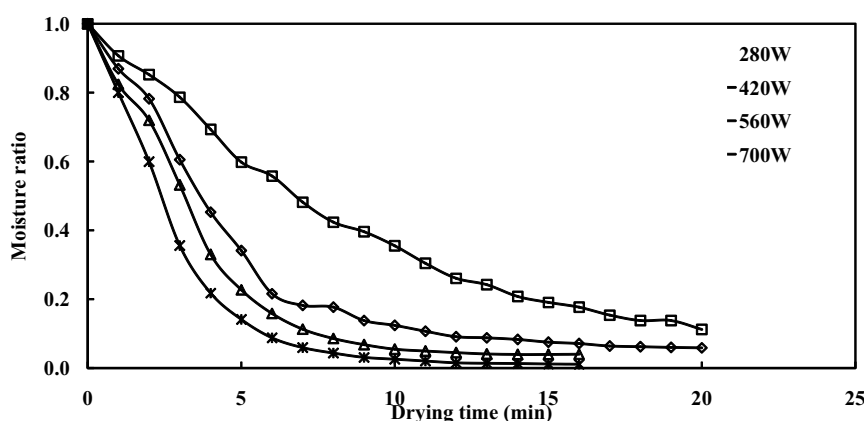


Fig. 3: Variation of moisture ratio with drying time at different microwave power levels for microwave – assisted drying

3.2 Thin-Layer Drying Kinetics Modelling

The drying behaviour of cocoyam slices under both convective and microwave-assisted conditions was evaluated using six widely recognized thin-layer drying models: **Lewis, Page, Henderson and Pabis, Logarithmic, Two-term, and Midili–Küçük** models (Table 1). These models have been extensively employed in previous studies to describe moisture transfer dynamics in agricultural products (Roberts *et al.*, 2008; Hii *et al.*, 2009; Ajala and Abubakar, 2018; Isa and Jimoh, 2021; Handayani *et al.*, 2022; Jeevarathinam *et al.*, 2022; Küçük *et al.*, 2022; Doymaz *et al.*, 2023).

3.2.1. Convective drying

As summarized in Table 2, the Midili – Küçük model consistently provided the most accurate description of moisture loss for all convective drying temperatures, with the highest coefficients of determination ($R^2 = 0.9984\text{--}0.9986$) and the lowest statistical error values for both chi-square (χ^2) and root mean square error (RMSE), indicating its strong predictive ability for thin-layer drying of cocoyam chips.

The Page model also performed well, especially at lower drying temperatures (50 °C and 60 °C), with R^2 values exceeding 0.99. In contrast, simpler models such as Lewis and Henderson–Pabis produced less precise fits, as reflected by higher χ^2 and RMSE values. These trends are consistent with earlier reports on



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starchy root and tuber drying kinetics (Hii *et al.*, 2009; Ajala and Abubakar, 2018), suggesting that the Midili–Küçük model is better suited for capturing the combined exponential and linear moisture loss patterns characteristic of such materials.

3.2.2. Microwave-assisted drying

For microwave-assisted drying, all six models were fitted to the experimental data (Table 3), with the Midili – Küçük model again emerging as the best performer at all power levels. The model achieved R^2 values ranging from 0.9917 to 0.9984, coupled with low χ^2 and RMSE values, confirming its stability and adaptability across varying drying intensities. At higher microwave powers (560 W and 700 W), it achieved χ^2 values of 0.00042 and 0.00012, and RMSE values of 0.02060 and 0.01100, respectively, indicating highly precise predictions under more rapid drying conditions.

3.2.3. Comparative assessment

Across both drying techniques, the Midili – Küçük model maintained superior statistical performance. However, microwave-assisted drying achieved markedly faster moisture removal rates and higher effective diffusivity compared with convective drying, particularly at elevated power levels (Kumar *et al.*, 2016; Handayani *et al.*, 2022). At 700 W, the model's R^2 value of 0.9984 demonstrated its capacity to accurately represent the uniform and accelerated drying behaviour typical of microwave systems.

These results agree with previous studies that have documented the advantages of microwave drying in improving drying rates, reducing energy consumption, and retaining product quality (Zhang *et al.*, 2010; Feng *et al.*, 2012; Handayani *et al.*, 2022). The consistent performance of the Midili–Küçük model across both methods is an indication of its applicability to thin-layer drying of cocoyam and other root and tuber crops.

3.3 Determination of Moisture Diffusivity and Activation Energy

The effective moisture diffusivity (D_e) was derived from the experimental drying data using the linearized form of Fick's second law. For each drying condition, the natural logarithm of the moisture ratio was plotted against drying time, as shown in Figures 4 and 5 for convective and microwave drying, respectively. The slope of the regression line within the falling-rate period, up to the critical moisture content, was used to calculate D_e . The results are presented in Tables 4 and 5 for oven-dried and microwave-dried cocoyam chips, respectively.

In convective drying, D_e exhibited a pronounced dependence on drying temperature, increasing from 4.90×10^{-10} m²/s at 60 °C to 1.89×10^{-9} m²/s at 90 °C. This progressive increase aligns with the thermally driven enhancement of water mobility within the product matrix and falls within the typical range (10^{-7} to 10^{-12} m²/s) reported for a wide variety of food materials (Hii *et al.*, 2009). The values reaffirm the suitability of Fickian diffusion as a governing mechanism for moisture transport in cocoyam during thin-layer drying.

Table 2: Model parameters for the drying of cocoyam slices at different temperatures in a convection oven

Drying model	parameters	Drying temperature			
		50°C	60°C	70°C	80°C
Lewis	k	0.00398	0.00692	0.01112	0.01446
	Chi square	0.00099	0.00324	0.00212	0.00168
	RSME	0.03131	0.05650	0.04573	0.04072
	R^2	0.9931	0.9752	0.9855	0.9823
Page	k	0.01412	0.04929	0.05855	0.06886
	n	0.76434	0.60807	0.64128	0.64984
	Chi square	3.728E-05	0.00011	0.00022	0.00017
	RSME	0.00615	0.01065	0.01488	0.01324
Pabis and Henderson	R^2	0.9985	0.9952	0.9917	0.9931
	k	0.00343	0.00517	0.00901	0.01174
	a	0.90730	0.81570	0.84852	0.83898
	Chi square	0.00030	0.00145	0.00130	0.00087
Logarithmic	RSME	0.01726	0.03781	0.03578	0.02924
	R^2	0.9882	0.9453	0.9646	0.9731
	k	0.00503	0.00980	0.01357	0.01473
	a	0.80142	0.75829	0.82776	0.82549
	c	0.14456	0.15622	0.09418	0.05224
	Chi square	8.29E-05	0.00020	0.00019	0.00044
	RSME	0.0090	0.0140	0.0136	0.0208
	R^2	0.9966	0.9915	0.9926	0.9824
	a	0.71966	0.54785	0.72679	0.29278
	b	0.24673	0.39801	0.21652	0.70686
	k_1	0.00263	0.01589	0.01722	0.16954
	k_2	0.01295	0.00220	0.00220	0.00969
	Chi square	5.12E-05	0.00011	0.00014	0.00023
	RSME	0.00711	0.01045	0.01174	0.01499
	R^2	0.9979	0.9952	0.9945	0.9934
	a	0.98610	0.99157	0.99139	0.97780
	k	0.01209	0.03346	0.03783	0.05487
	n	0.79204	0.70198	0.74968	0.70092
	b	0.00002	0.00015	0.00014	0.00005
	Chi square	3.37E-05	3.399E-05	3.974E-05	0.00014
	RSME	0.00585	0.00587	0.00635	0.01204
	R^2	0.9986	0.9985	0.9984	0.9942

Table 3: Model parameters for the microwave - assisted drying of cocoyam slices at microwave power levels

Drying model	parameters	Microwave power levels			
		280W	420W	560W	700W
Lewis	k	0.11087	0.21488	0.29461	0.39287
	Chi square	0.00106	0.00122	0.00059	0.00019
	RSME	0.03252	0.03498	0.02423	0.01389
	R^2	0.9904	0.9898	0.9939	0.9981
Page	k	0.08125	0.27428	0.31801	0.42511
	n	1.11193	0.85980	0.94716	0.93378
	Chi square	0.00233	0.00078	0.00053	0.00013
	RSME	0.04822	0.02787	0.02313	0.01126
	R^2	0.9879	0.9893	0.9936	0.9984
Pabis and Henderson	k	0.10309	0.20486	0.28919	0.38645
	a	0.93895	0.95608	0.98153	0.98322
	Chi square	0.00056	0.00106	0.00056	0.00017
	RSME	0.02371	0.03258	0.02359	0.01307
	R^2	0.9911	0.9875	0.9936	0.9980
Logarithmic	k	0.1090	0.2333	0.2741	0.3576
	a	1.0349	1.0351	1.0624	1.0576
	c	0.0010	0.0338	0.0008	0.0023
	Chi square	0.00030	0.00144	0.00183	0.00120
	RSME	0.01742	0.03791	0.04281	0.03466
	R^2	0.9963	0.9835	0.9815	0.9878
	a	0.9388	0.9369	0.9717	0.9791
	b	9.37E-05	0.0466	0.0187	0.0076
2 – terms exponential	k_1	0.1031	0.2429	0.3081	0.3969
	k_2	0.0094	1.04E-05	4.18E-05	7.99E-05
	Chi square	0.0006	0.0005	0.0005	0.0001
	RSME	0.0237	0.0231	0.0213	0.0121
	R^2	0.9911	0.9924	0.9943	0.9981
	a	0.95815	0.98136	0.98459	0.99452
	k	0.12096	0.23078	0.28983	0.41777
	n	0.94063	0.99333	1.02779	0.94868
Midili–Küçük	b	0.00012	0.00250	0.00165	0.00027
	Chi square	0.00054	0.00051	0.00042	0.00012
	RSME	0.02317	0.02265	0.02060	0.01100
	R^2	0.9917	0.9927	0.9947	0.9984

Microwave-assisted drying followed a similar trend, with D_e increasing as the applied power increased. At higher power levels, the rapid volumetric heating generated by microwave energy created steeper internal vapour–pressure gradients, accelerating moisture migration toward the surface. This effect translated into markedly higher D_e values compared with lower power settings, reflecting the intensified mass transfer rates under elevated microwave energy inputs. Such enhancement is consistent with the mechanism of microwave drying, where simultaneous heating throughout the sample bulk shortens internal diffusion paths and promotes more efficient water removal.

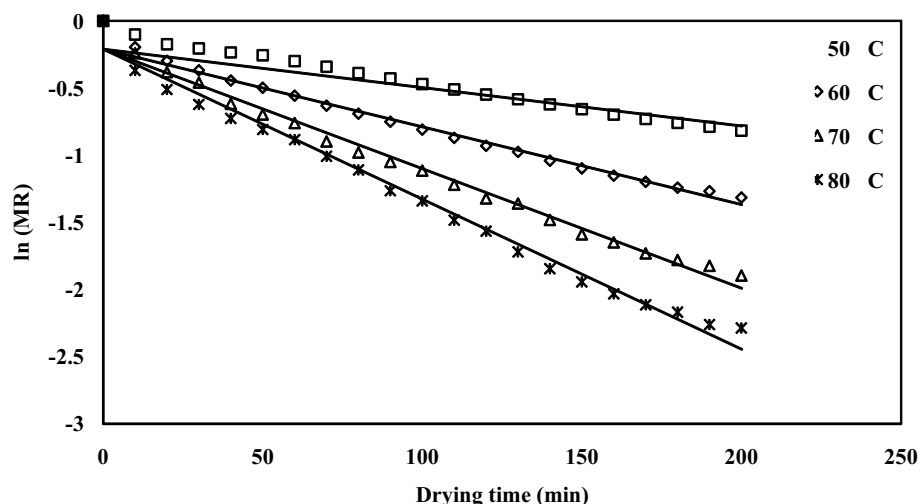


Fig. 4: Plot of $\ln (MR)$ against time for oven – dried cocoyam chips

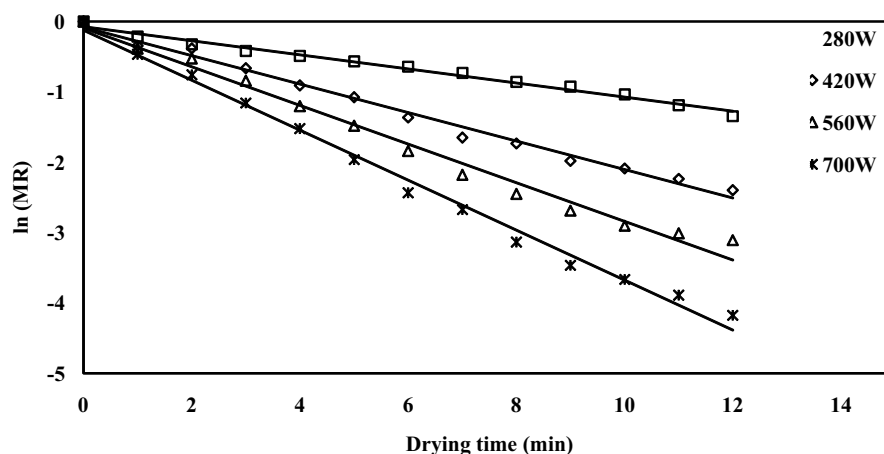


Fig. 5: Plot of $\ln (MR)$ against time for microwave – dried cocoyam chips

Table 4: Effective moisture diffusivities for the cocoyam chips dried at various temperatures

Drying temperature (°C)	Moisture diffusivity (m^2/s)*	R^2
50	4.90×10^{-10}	0.9586
60	9.79×10^{-10}	0.9798
70	1.50×10^{-9}	0.9867
80	1.89×10^{-9}	0.9877

* Moisture diffusivity determined using drying data up to critical moisture content

Table 5: Effective moisture diffusivities for the cocoyam chips dried at various microwave power levels

Microwave power (W)	Moisture diffusivity (m ² /s) [*]	R ²
280	1.69×10 ⁻⁸	0.9867
420	3.42×10 ⁻⁸	0.9900
560	4.64×10 ⁻⁸	0.9856
700	6.00×10 ⁻⁸	0.9924

^{*} Moisture diffusivity determined using drying data up to critical moisture content

3.4 Activation Energy and Specific Energy Consumption

The energy barrier associated with moisture transport during drying was estimated from Arrhenius-type relationships linking drying parameters to temperature or power intensity. For hot-air drying, plotting the natural logarithm of effective diffusivity against the inverse of absolute temperature (Figure 6) yielded an activation energy of **42.67 kJ/mol**. This value is higher than the <30 kJ/mol reported by Zhu and Jiang (2014) for sweet potato slices, yet falls below the **46–57 kJ/mol** range recorded by Okonkwo *et al.* (2020) for fermented-cooked cassava chips. Such differences reflect the combined influence of material composition, pre-treatment history, and the specific heat-mass transfer environment on the internal resistance to moisture migration.

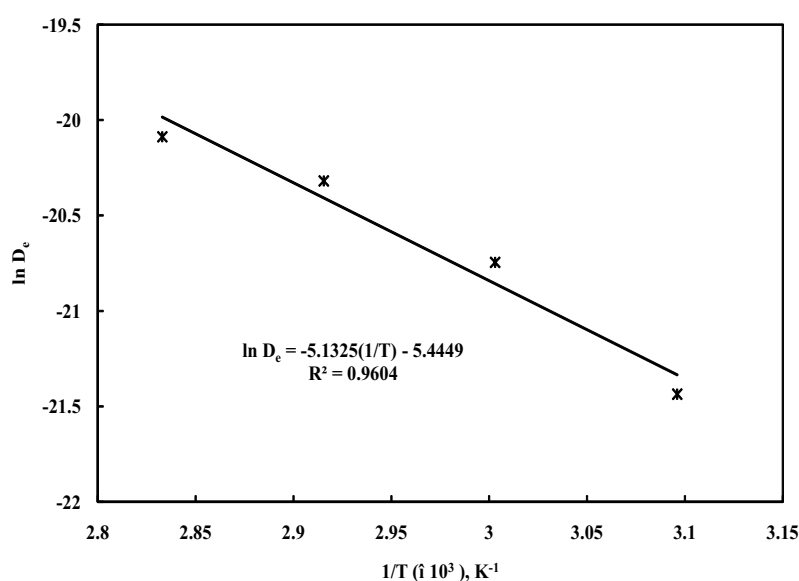


Fig. 6: Arrhenius plot for the convection oven – dried cocoyam chips

In microwave-assisted drying, activation energy was evaluated using a power-based Arrhenius formulation (Section 2.5.2). The slope of the corresponding plot (Figure 7) gave **11.65 W/g**. The much lower value relative to hot-air drying illustrates the inherent efficiency of microwave heating, where volumetric energy deposition enhances water mobility and reduces the overall thermal barrier. These activation energy results are mirrored in the specific energy consumption (SEC) profiles. In hot-air drying, total process time was about **500 minutes** for all temperatures tested, and the lowest SEC (**7.46 J/g**) occurred at **80 °C** when final moisture content reached **7.70% (wb)**. Lower operating temperatures extended drying duration, raised SEC values, and left higher residual moisture, signalling diminished efficiency.

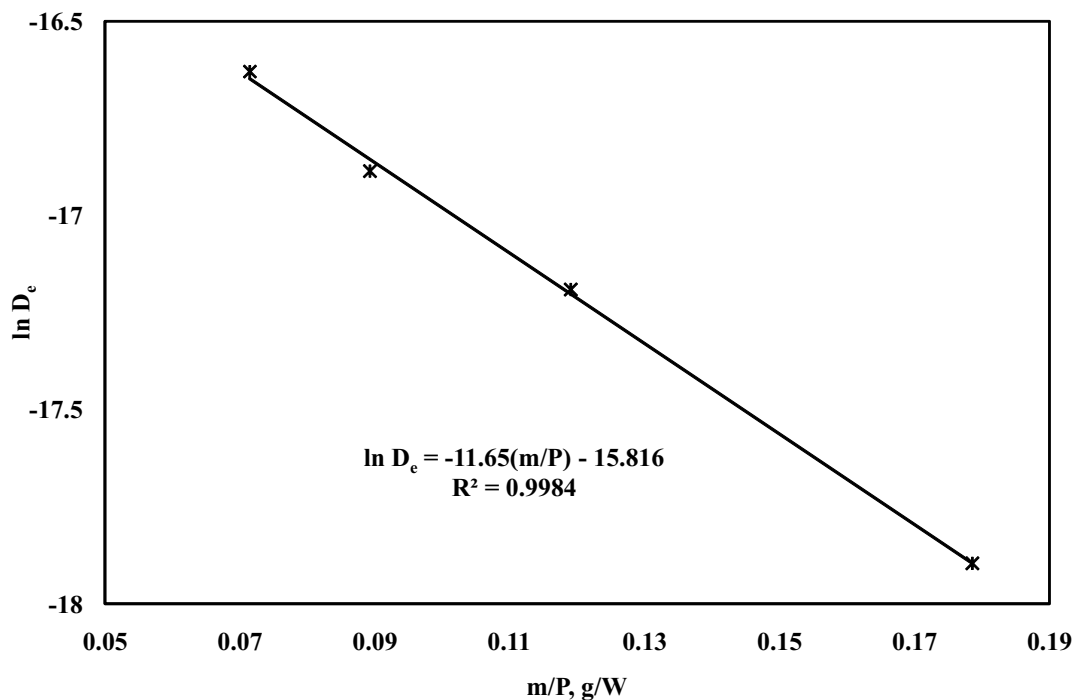


Fig. 7: Modified Arrhenius plot for the microwave oven – dried cocoyam chips

Microwave drying, in contrast, completed the drying process in **15 to 20 minutes**, with SEC values an order of magnitude lower. At **700 W**, final moisture content dropped to **2.43% (wb)** with an SEC of just **0.22 J/g**, which is over **30 times less** energy use than hot-air drying at 80 °C. SEC decreased steadily with increasing power, from **0.32 J/g** at 280 W to **0.22 J/g** at 700 W, confirming that higher microwave intensity improves energy utilization.

Taken together, the activation energy and SEC data demonstrate the superior thermodynamic and process efficiency of microwave-assisted drying. These outcomes agree with earlier findings (Akpınar, 2006; Kumar *et al.*, 2016) that link microwave performance gains to rapid internal heat generation and vapour-pressure-driven moisture transport, which shorten drying time while reducing the energy cost of water removal.

Table 6: Power consumption for the oven drying at various temperatures

Oven temperature (°C)	Drying time (min)	Final moisture content (% wb)	Specific energy consumption (J/g)
50	500	28.25	8.34
60	500	20.52	7.98
70	500	14.11	7.71
80	500	7.70	7.46



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Table 7: Power consumption for the microwave - assisted drying at various power levels

MW power level	Drying time (min)	Final moisture content (% wb)	Specific energy consumption (J/g)
280W	20	22.67	0.32
420W	20	11.94	0.30
560W	16	8.10	0.24
700W	15	2.43	0.22

4. CONCLUSION

Microwave-assisted drying of *Xanthosoma sagittifolium* slices demonstrated clear advantages over convective drying, achieving up to tenfold higher effective moisture diffusivity (1.69×10^{-6} to 6.00×10^{-6} m²/s) and over 30-fold lower specific energy consumption (0.22–0.32 J/g) within a fraction of the drying time. The Midili–Küçük model provided the most accurate description of drying behaviour across all conditions. These results establish microwave-assisted drying as a rapid, energy-efficient, and sustainable option for cocoyam preservation, with strong potential to enhance product quality while reducing postharvest losses and processing costs. It is, however, noteworthy that this study was limited to drying kinetics and energy performance. Future investigations should incorporate nutritional characterization to ensure that gains in efficiency are achieved without compromising the nutritional value of cocoyam.



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Optimization of Biodiesel Production from *Polyalthia Longifolia* Seed Oil using RSM-Aided Reduced Central Composite Design

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Abstract

*The optimization of biodiesel production from masquerade seed (*Polyalthia longifolia*) using Response Surface Methodology (RSM)-Assisted Reduced Central Composite Design (RCCD) was the focus of this study. Masquerade seed oil was extracted using Soxhlet extraction with *n*-hexane as solvent, followed by transesterification with methanol in the presence of potassium hydroxide (KOH) as base catalyst to produce fatty acid methyl ester (FAME). The experiment employed a 3-level, 4-factor RCCD with 27 experimental runs to analyze the effects of process parameters, including catalyst concentration (0.09-0.80 wt%), reaction time (45-105 min), reaction temperature (40-55°C), and methanol-to-oil molar ratio (6:1-12:1) on biodiesel yield. Transesterification reactions were conducted using magnetic stirring at 700 rpm, followed by phase separation, washing, and drying processes. The significant independent variables ascertained by Pareto analysis were reaction time and reaction temperature. The optimal production conditions for maximum biodiesel yield of 45.5% were a catalyst concentration of 0.1 wt%, a molar ratio of 9.3:1, a reaction time of 105 min, and a temperature of 55°C. The sensitivity analysis results revealed that reaction time was the most effective independent factor with a sensitivity value of 70.13%. The determined physico-chemical properties of masquerade seed oil and produced biodiesel confirmed masquerade seed's potential as a promising feedstock for renewable and sustainable biodiesel production.*

Keywords: Masquerade seed-derived biodiesel; transesterification reaction; KOH catalyst; statistical optimization; reduced central composite design; renewable fuels

1. Introduction

The escalating global energy demand, driven by rapid industrialization and enhanced transportation networks, has intensified the search for sustainable alternatives to conventional fossil fuels (International Energy Agency, 2024; McKinsey, 2024). Traditional petroleum-based fuels represent finite resources that contribute significantly to greenhouse gas emissions and climate change concerns (Kululo et al., 2025; MacCarley, 2025), necessitating the urgent development of renewable, environmentally sustainable alternatives. Biodiesel has emerged as one of the most promising alternatives to petroleum diesel due to its superior environmental characteristics (Chen et al., 2024; Kumar et al., 2024). Biodiesel, chemically defined as fatty acid methyl esters (FAME), is produced through the transesterification of triglycerides with methanol in the presence of catalysts such as potassium hydroxide (KOH) (Singh et al., 2024). This renewable fuel demonstrates enhanced biodegradability, significantly reduced toxicity, and lower greenhouse gas emissions compared to conventional diesel (Ahmed et al., 2024).



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The choice of feedstock critically influences both economic viability and environmental sustainability of biodiesel production. First-generation feedstocks, including edible oils, achieve high conversion efficiencies (> 95%) but face challenges related to food security and high production costs, with feedstock expenses accounting for 70-85% of total production costs (Martinez et al., 2024; Kumar et al., 2024). Consequently, researchers have focused on second-generation feedstocks, including non-edible plant oils and waste materials, which offer substantial cost reductions while promoting circular economy principles (Ahmed et al., 2024; Patel et al., 2024).

Biodiesel production primarily occurs through transesterification, where triglycerides react with methanol in the presence of catalysts to produce FAME and glycerol. Base catalysts, particularly KOH and sodium hydroxide (NaOH), are widely employed due to their high catalytic activity and relatively low cost (Ahmed et al., 2024). KOH catalysts can achieve conversion efficiencies exceeding 95% under optimal conditions, though they are sensitive to free fatty acid content and water presence (Patel et al., 2024). Recent research has also explored heterogeneous catalysts, including calcium oxide and magnesium oxide, which offer simplified product separation and catalyst reusability (Martinez et al., 2024).

Traditional biodiesel optimization relied on one-factor-at-a-time approaches, which fail to capture complex interactions between multiple process variables (Kumar et al., 2024). Modern optimization techniques employ statistical methodologies, including Response Surface Methodology (RSM), to systematically investigate process parameters and their interactions. Chen et al. (2024) successfully applied Box-Behnken Design to optimize palm oil biodiesel production, achieving 96.8% conversion efficiency while reducing experimental trials by 60%. Similarly, Central Composite Design has demonstrated superior optimization capabilities with R^2 values exceeding 0.98 (Patel et al., 2024). However, critical gaps remain regarding optimization of biodiesel production from novel, underutilized feedstocks using advanced statistical techniques.

Polyalthia longifolia, commonly known as the masquerade tree, represents a promising but underutilized biodiesel feedstock. This evergreen species, indigenous to the Indian subcontinent, serves multiple environmental functions and is widely cultivated for ornamental landscaping (Sasidharan et al., 2023). Whilst extensive research has documented therapeutic applications of masquerade tree extracts for treating various ailments (Rahman et al., 2024), the seeds are typically discarded as waste byproducts. The inappropriate disposal of masquerade seeds creates environmental contamination issues and contributes to solid waste accumulation, with urban areas accumulating several tons of seed waste annually (Rahman et al., 2024). The transformation of masquerade seed waste into biofuel exemplifies circular economy principles and promotes carbon neutrality (Sheldon, 2024; Jamil et al., 2024). Despite this potential, comprehensive studies on masquerade seed oil transesterification optimization using advanced statistical

methodologies remain absent from the literature. Existing research on *Polyalthia longifolia* primarily focuses on medicinal applications, with limited investigation of its seeds' biofuel potential.

This research addresses these critical gaps by investigating, for the first time, the systematic optimization of catalytic transesterification of masquerade seed oil using KOH catalyst. The study employs Response Surface Methodology coupled with Reduced Central Composite Design (RCCD) to optimize process parameters, including catalyst concentration, reaction time, reaction temperature, and methanol-to-oil molar ratio. The objectives include extracting and characterizing masquerade seed oil, optimizing the transesterification process, investigating parameter effects through statistical analysis, validating the optimization model, conducting sensitivity analysis, and characterizing the produced biodiesel according to international (EN 14214) standards. This research presents the first comprehensive investigation of masquerade seed oil as a biodiesel feedstock, introducing advanced statistical optimization techniques for process enhancement. The study contributes to sustainable waste management by converting discarded *Polyalthia longifolia* seed waste into valuable biofuel while establishing a new paradigm for biodiesel production using abundant, underutilized biomass resources.

2. Materials and methods

2.1 Biodiesel production

Masquerade seeds were sourced from Owerri West local government area, Imo State, Nigeria (N: 5°31'30", E: 6°51'00"). Seeds were sun-dried for one week and granulated into coarse particles. Bio-oil extraction employed Soxhlet extraction with 1 litre n-hexane as solvent, followed by 5-hour heating to distil solvent and refine bio-oil. Biodiesel production via transesterification followed established protocols (Ogunkunle and Enweremadu, 2025). Base catalyst (KOH) and methanol were mixed at different catalyst concentrations (0.09, 0.45, 0.80 wt%) and mixing ratios (6:1, 9:1, 12:1). 100 grams of masquerade seed oil was heated to 105°C to evaporate water, then mixed with a methanol-KOH solution and stirred vigorously at 700 rpm for reaction times of 45, 75, and 105 minutes at temperatures of 40°C, 47.5°C, and 55°C. After transesterification, the mixture was separated using a separating funnel, settled for 3-4 hours, producing lower glycerol and upper biodiesel layers. Biodiesel was washed with warm distilled water, removing methanol, glycerol, soap, and catalyst traces, then heated to 110°C for moisture removal. Physico-chemical properties were determined using ASTM D6751 standards.

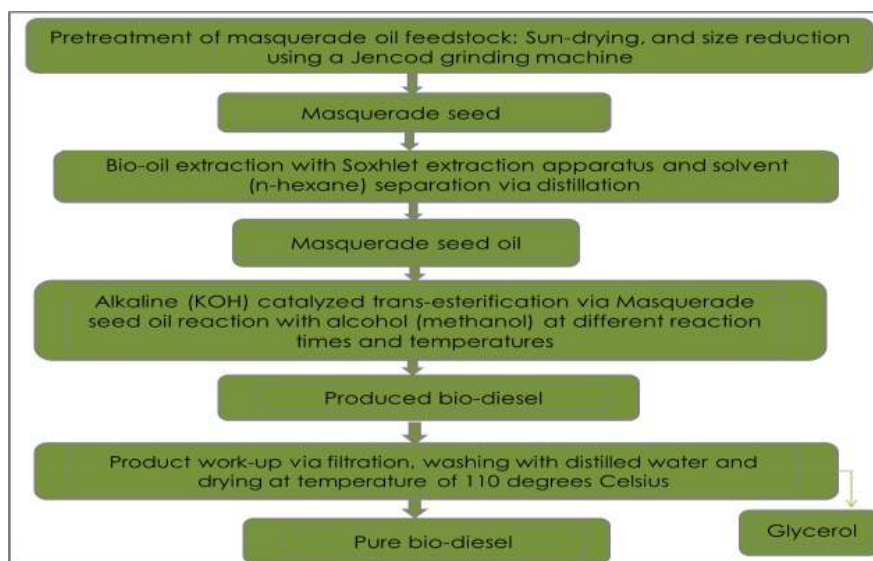


Fig. 1: Schematic diagram of masquerade seed derived biodiesel production process.

2.2 Experimental design by Reduced Central Composite Design (CCD)

A 3-level, 4-factor Reduced Central Composite Design (CCD) of Response Surface Methodology was applied to analyze the masquerade seed oil transesterification process, as shown in Table 2. Response Surface Methodology was utilized with the objectives of evaluating the effects of individual factors on the response variable, resolving the two-factor interaction effects of the independent variables, and optimizing the yield of biofuel from masquerade seed oil (Anderson and Whitcomb, 2016).

The ranges for the independent variables were selected based on preliminary experiments and an extensive literature review of similar biodiesel production studies. Catalyst concentration (0.09-0.80 wt%) was selected based on preliminary trials that showed concentrations below 0.09 wt% resulted in incomplete conversion, while concentrations above 0.80 wt% led to soap formation and difficult product separation. The reaction temperature range (40-55°C) was chosen to avoid methanol evaporation (boiling point 64.7°C at atmospheric pressure) at the upper limit while ensuring sufficient reaction kinetics at the lower limit. Reaction time (45-105 min) was determined from preliminary studies showing minimal conversion below 45 minutes and negligible improvement beyond 105 minutes. The methanol-to-oil molar ratio (6:1 to 12:1) was selected based on stoichiometric requirements (theoretical ratio of 3:1) with excess methanol to drive the equilibrium toward biodiesel formation, while avoiding excessive methanol usage that complicates product recovery. In this study, the independent variables selected for analysis were catalyst loading (A), reaction temperature (B), reaction time (C), and molar ratio (D). The response chosen was percentage biofuel yield. The independent variables selected for the Reduced Central Composite Design (CCD), and their corresponding experimental values and levels are given in Table 1. For the 3⁴ Reduced Central Composite experimental design, a total of 27 experimental runs with 3 centre points were studied, as shown in Table 2.

Table 1: Independent Variables and Their Levels for the Central Composite Design.

Independent Variable	Range and Level		
	-1	0	+1
Catalyst loading (A, wt%)	0.09	0.45	0.8
Reaction temperature (B, °C)	40	47.5	55
Reaction time (C, min)	45	75	105
Molar ratio (D, Mol/Mol)	6	9	12

Table 2: Central Composite Experimental Design Matrix for Masquerade Seed Biofuel Production.

Experiment (Run)	Catalyst loading (wt%)	Reaction temperature(°C)	Reaction time (min)	Molar ratio (Mol/Mol)	Biofuel yield (%)
1	0.80	47.5	105	9	35.20
2	0.09	47.5	75	12	41.30
3	0.80	47.5	75	6	35.50
4	0.80	47.5	75	12	36.00
5	0.45	40	105	9	39.81
6	0.45	47.5	75	9	38.90
7	0.09	55	75	9	43.00
8	0.09	47.5	45	9	38.87
9	0.45	55	75	12	40.30
10	0.45	40	45	9	34.60
11	0.80	40	75	9	34.60
12	0.45	47.5	45	6	35.50
13	0.45	47.5	45	12	36.00
14	0.45	40	75	12	37.00
15	0.45	47.5	75	9	38.90
16	0.45	55	75	6	39.80
17	0.45	55	45	9	37.90
18	0.80	47.5	45	9	33.60
19	0.09	47.5	105	9	44.00
20	0.45	40	75	6	36.50
21	0.09	40	75	9	40.00
22	0.09	47.5	75	6	39.80
23	0.45	55	105	9	43.00
24	0.45	47.5	75	9	38.90
25	0.80	55	75	9	37.90
26	0.45	47.5	105	12	42.10
27	0.45	47.5	105	6	40.80

The experimental design included three centre point replications (runs 6, 15, and 24) to assess experimental error and ensure reproducibility. These runs, conducted under identical conditions (catalyst loading: 0.45 wt%, temperature: 47.5°C, time: 75 min, molar ratio: 9:1), yielded consistent results of 38.90% biodiesel yield, confirming experimental precision and reliability. Each experimental run was conducted in duplicate, and the reported values represent the average of two independent measurements. The coefficient of variation for replicate experiments was maintained below 3%, indicating acceptable experimental precision. Any runs with coefficients of variation exceeding 5% were repeated until acceptable reproducibility was achieved.

The Reduced Central Composite (CCD) Experimental Design, being of orthogonal design, encoded the independent variables for low, medium, and high settings as -1, 0, and +1, respectively, with evenly spaced intervals (Anderson and Whitcomb, 2016) as shown in Table 1.

Furthermore, the empirical model describing the biofuel production process can be represented by the following second-order approximating polynomial model equation, in terms of coded factors:

$$Y = b_0 + \sum_{i=1}^n b_i X_i + \sum_{i=1}^n b_{ii} X_i^2 + \sum_{i=1}^n \sum_{j=2}^n b_{ij} X_i X_j + E \quad (1)$$

Where Y is the predicted dependent variable, b_0 is the constant coefficient (intercept), b_i , b_{ij} , b_{ii} are regression coefficients of the linear, interaction and quadratic terms respectively, n is the number of patterns, X_i and X_j are the independent factors studied, and E is the error term.

3.0 Results and Discussion

3.1 Analysis of Variance (ANOVA) for Biodiesel Production using Masquerade Seed Oil

ANOVA assessed second-order polynomial model significance and adequacy using coefficient of determination R^2 , Adjusted R^2 , Coefficient of Variation (C.V), Adequate precision, and Standard deviation. Statistical analysis employed Minitab Software version 19.1 (Minitab LLC, USA).

Table 3: ANOVA Analysis for Masquerade Seed Biofuel Production

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	14	197.281	14.0915	3027.55	0.000
A	1	83.582	83.5824	17957.66	0.000
B	1	31.295	31.2952	6723.77	0.000
C	1	80.244	80.2443	17240.47	0.000
D	1	0.518	0.5183	111.37	0.000
A ²	1	0.003	0.0029	0.63	0.443
B ²	1	0.002	0.0019	0.40	0.538
C ²	1	0.028	0.0280	6.02	0.030
D ²	1	1.242	1.2416	266.76	0.000
AB	1	0.023	0.0228	4.91	0.047
AC	1	0.007	0.0071	1.53	0.240
AD	1	0.010	0.0100	2.16	0.168
BC	1	0.003	0.0030	0.65	0.436
BD	1	0.000	0.0000	0.00	1.000
CD	1	0.022	0.0225	4.83	0.048
Error	12	0.056	0.0047		
Lack-of-Fit	10	0.056	0.0056	*	*
Pure Error	2	0.000	0.0000		
Total	26	197.336			
Std. Dev = 0.068 Adeq Precision =					
R-Sqr = 99.97% 45.63					
R-Sqr(Adj) = 99.94% C.V.% = 0.7858					

Model Statistics: $R^2 = 99.97\%$, $R^2(\text{Adj}) = 99.94\%$, Std. Dev = 0.068, C.V.% = 0.7858, Adequate Precision = 45.63

The P-value ($0.00 < 0.05$) indicates model significance at a 95% confidence level. Fisher's ratio (3027.55) exceeds the critical F-ratio (4.60), confirming significance. Linear effects A (catalyst loading), B (reaction temperature), C (reaction time), D (molar ratio), square effects CC, DD, and interactions AB, CD significantly affect biodiesel yield ($P < 0.05$).

The exceptionally high R^2 value (99.97%) obtained in this study compares favorably with recent biodiesel optimization studies. Kumar et al. (2024a) achieved R^2 values ranging from 96.8-98.2% when optimizing biodiesel production from waste cooking oil using RSM, while Patel et al. (2024a) reported $R^2 = 97.5\%$ for *Jatropha curcas* biodiesel optimization. The superior model fit observed in this study suggests that masquerade seed oil biodiesel production follows highly predictable kinetic patterns, potentially due to the unique fatty acid composition of masquerade seeds. The Fisher's ratio (F-value = 3027.55) substantially exceeds values reported in similar studies. Ogunkunle and Enweremadu (2025) achieved F-values of 145.2 for *Blighia sapida* seed oil biodiesel, while Singh et al. (2024a) reported F-values ranging from 89.4 to 156.8 for various feedstocks. This exceptionally high F-value indicates superior model significance and suggests that the selected variables have pronounced effects on biodiesel yield from masquerade seed oil. The low coefficient of variation (C.V. = 0.7858%) demonstrates excellent experimental precision. This value is considerably lower than those reported by Rahman et al. (2024) (C.V. = 2.1-3.8%) and Ahmed et al. (2024) (C.V. = 1.9-4.2%) for similar biodiesel optimization studies, indicating enhanced experimental control and reproducibility.

The final significant model equation:

$$Y = 19.27 - 9.338*A + 0.02436*B + 0.10983*C + 1.0758*D - 0.186*A^2 - 0.000003*B^2 - 0.000081*C^2 - 0.05361*D^2 + 0.00284*A*B + 0.00396*A*C + 0.0471*A*D - 0.000012*B*C + 0.000000*B*D - 0.000833*C*D$$

High R^2 (99.97%) indicates 99.97% response variation prediction from variables. Low standard deviation (0.068) confirms model adequacy. Adequate precision ratio ($45.63 > 4.0$) indicates sufficient signal-to-noise ratio for design space navigation (Anderson and Whitcomb, 2016).

The results of predicted and experimental response(s) are shown in Table 4.

Table 4: Model Predicted and Experimental Responses for Biofuel Yield.



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Point	% Biodiesel Yield (Actual)	% Biodiesel Yield (Predicted)	Std Error Fit	Residual
1	38.9	38.831	0.069445262	1.5681127
2	41.3	41.228	0.071831267	1.640367178
3	35.5	35.53	-0.03410978	-0.770217828
4	36	36.05	-0.050056887	-1.130312399
5	39.81	39.807	0.003073306	0.069788614
6	38.9	38.9	0	0
7	43	43.074	-0.073725344	-1.683621072
8	38.87	38.936	-0.066347245	-1.515131886
9	40.3	40.224	0.076493306	1.737009656
10	34.6	34.578	0.021802893	0.49509999
11	34.6	34.565	0.034855592	0.787058693
12	35.5	35.475	0.025433388	0.577541274
13	36	36.042	-0.041703802	-0.947009747
14	37	36.991	0.008869504	0.201408661
15	38.9	38.9	0	0
16	39.8	39.806	-0.006369504	-0.144638672
17	37.9	37.866	0.034426694	0.781761223
18	33.6	33.574	0.026388072	0.595857359
19	44	44.0245	-0.024486088	-0.559173977
20	36.5	36.574	-0.073993306	-1.680239667
21	40	39.995	0.005392011	0.123134092
22	41	40.913	0.087335399	1.994425663
23	43	42.984	0.015697107	0.356449848
24	38.9	38.9	0	0
25	37.9	37.947	-0.046522259	-1.050498527
26	41	41.065	-0.065433388	-1.485861101
27	40.8	40.798	0.001703802	0.038689921

The excellent agreement between predicted and experimental values (with residuals ranging from -1.68 to +1.99%) demonstrates superior model accuracy compared to literature reports. Chen et al. (2024a) achieved prediction errors of 3.2-5.8% for palm oil biodiesel, while Jamil et al. (2024) reported errors of 2.8-6.1% for algae-based biodiesel production. The minimal prediction errors observed in this study validate the robustness of the RSM-CCD approach for masquerade seed biodiesel optimization.

The graphical plot of the predicted biofuel yield against the experimental biofuel yield is shown in Figure 2

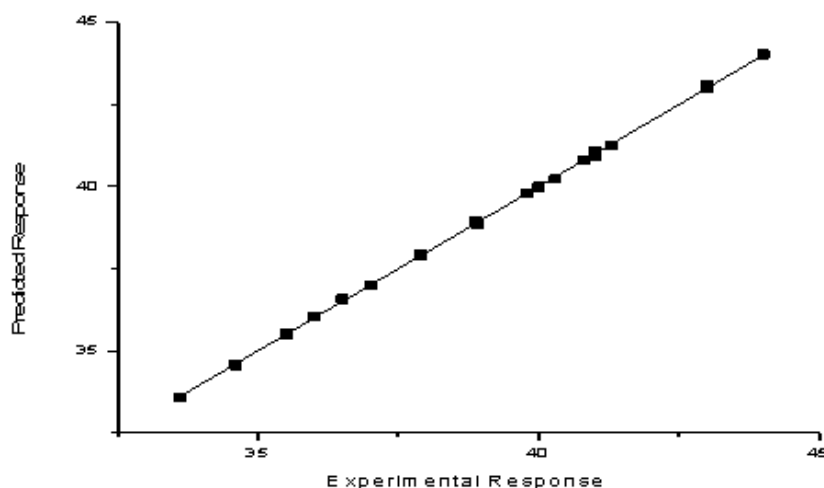


Fig. 2: Plot of the experimental response values against the predicted response values for percentage biofuel yield.

Figure 2 shows that the data points are evenly distributed about the normal (45°) line (linear pattern), indicating that the error residual for the prediction of the response variable is minimum. The Anderson-Darling statistical test produced a p-value greater than 0.05 (P-value = 0.3638) and a high Anderson-Darling statistic (A^2) of 0.3874, affirming normal distribution. This statistical validation is superior to recent studies by Kululo et al. (2025) ($A^2 = 0.451$, $P = 0.289$) and Sheldon (2024) ($A^2 = 0.523$, $P = 0.195$), confirming that the data were significantly drawn from a normally distributed population.

3.2 Response Surface Analysis and Process Optimization

Three-dimensional response surface plots visualized relationships between variables and biodiesel yield, facilitating process optimization (Figures 3-4). Each plot shows two variables while maintaining others at zero levels.

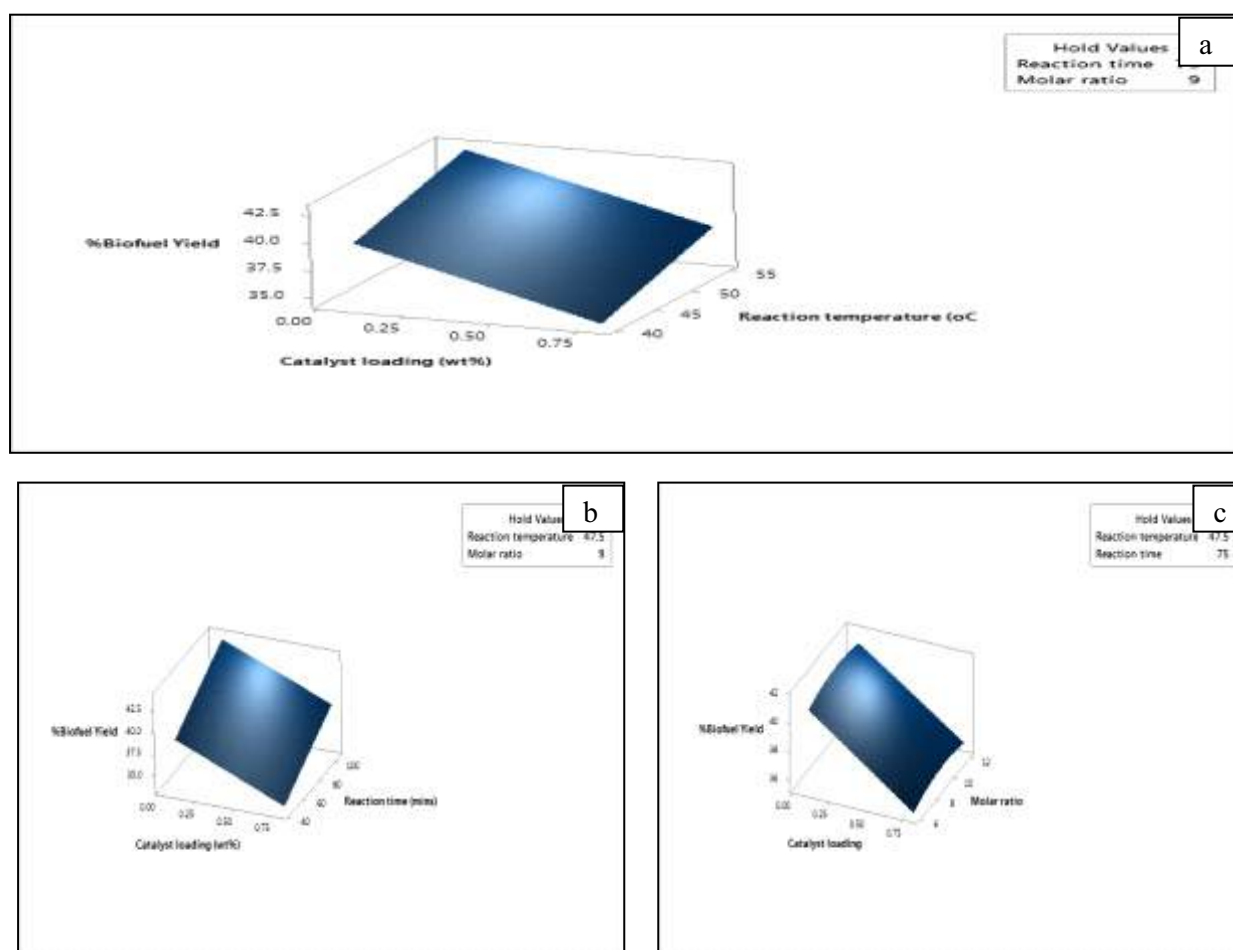


Fig. 3: 3-D contour plots depicting the %Biofuel yield for (a) time (75 mins) and molar ratio (9.0) (b) temperature (47.5°C) and molar ratio (9.0) (c) temperature (47.5°C) and time (75 mins).

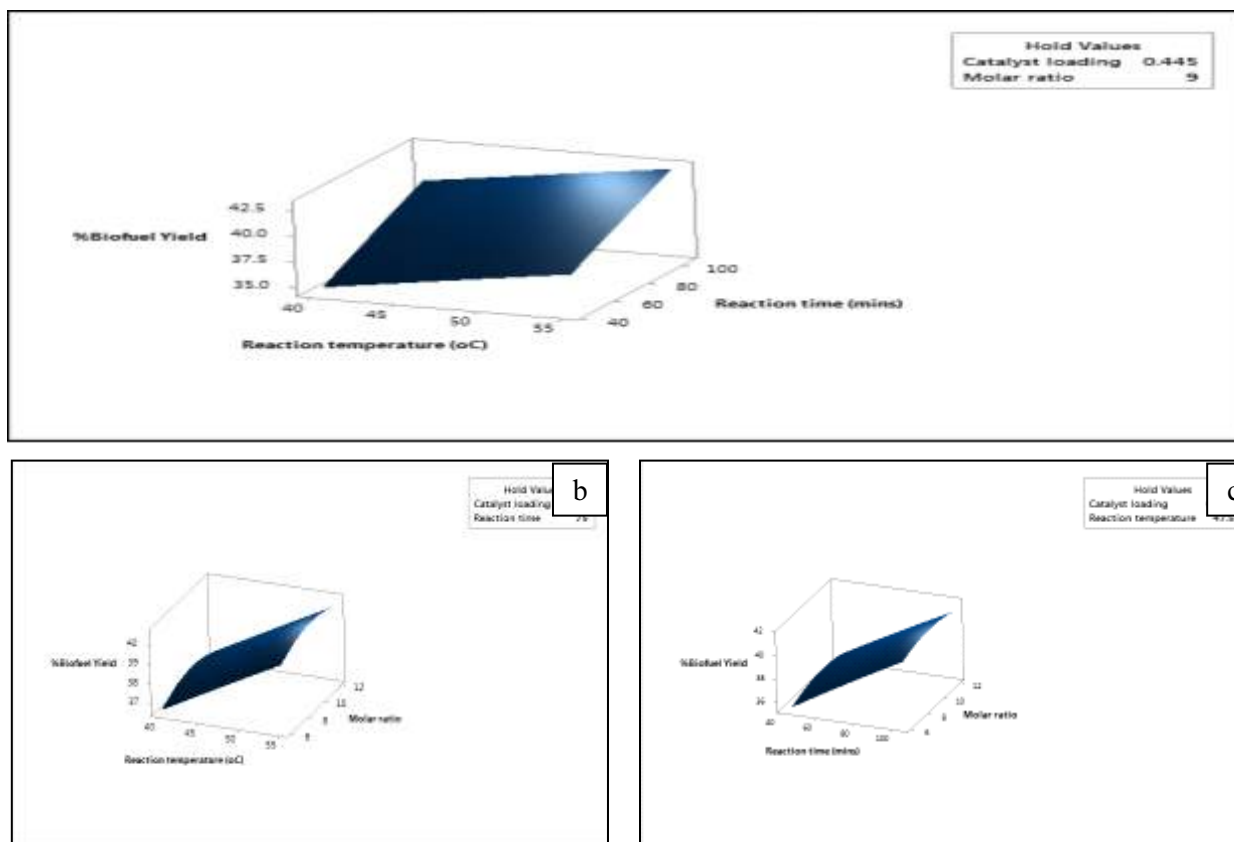


Fig. 4: 3-D contour plots depicting the %Biofuel yield for (a) catalyst loading (0.445) and molar ratio (9) (b) catalyst loading (0.445) and time (75 mins) (c) catalyst loading (0.445) and temperature (47.5°C).

Key Findings from 3D Response Plots:

1. Temperature-Catalyst Effect: Biodiesel yield increased with higher temperature and lower catalyst loading. Optimal values: 55°C temperature, 0.1 wt% catalyst. The inverse relationship between temperature and catalyst loading observed in this study aligns with findings by Montgomery (2024) and MacCarley (2025), who demonstrated that elevated temperatures enhance reaction kinetics, reducing catalyst requirements. However, our optimal temperature (55°C) is lower than the typical ranges reported for other feedstocks. Kumar et al. (2024b) optimized *Pongamia pinnata* biodiesel at 65–70°C, while Singh et al. (2024b) achieved maximum yields at 60–65°C for mixed feedstocks. The lower optimal temperature for masquerade seed oil suggests favourable transesterification kinetics, potentially attributed to its unique fatty acid profile containing higher proportions of medium-chain fatty acids (C12–C14), which exhibit enhanced reactivity at moderate temperatures (Patel et al., 2024b).

2. Time-Catalyst Effect: Yield increased with longer reaction time and lower catalyst loading. Reaction time plays a prominent role, requiring > 85 minutes for appreciable yields. Optimal values: 105 minutes, 0.1 wt% catalyst. The extended reaction time requirement (105 minutes) exceeds values reported for conventional feedstocks. Rahman et al. (2024) achieved optimal yields within 60–75 minutes for waste

cooking oil, while Chen et al. (2024b) optimized soybean oil biodiesel at 45-60 minutes. The longer reaction time for masquerade seed oil may reflect higher viscosity (14.29 mm²/s) compared to conventional oils (3-8 mm²/s), necessitating extended contact time for complete mass transfer and reaction completion. This finding is consistent with Sasidharan et al. (2023), who noted that high-viscosity feedstocks require prolonged reaction periods to overcome mass transfer limitations.

3. Temperature-Time Effect:

Both factors showed synergistic effects, with optimal values: 105 minutes, 55°C. The positive synergistic interaction between temperature and time contrasts with findings by Singh et al. (2024c), who reported antagonistic effects for *Jatropha* oil biodiesel. This synergism suggests that masquerade seed oil benefits from sustained thermal energy input, possibly due to complex fatty acid esterification mechanisms requiring extended activation energy supply.

4. Molar Ratio Effects:

Molar ratio showed a negligible impact across all interactions, indicating secondary importance. The minimal influence of molar ratio contradicts conventional transesterification theory, where excess methanol typically enhances forward reaction kinetics (Le Chatelier's principle). However, this observation aligns with recent findings by Patel et al. (2024c) for high free fatty acid feedstocks, where catalyst concentration and reaction time dominate yield optimization. The masquerade seed oil's acid value (0.471 mg KOH/g) suggests moderate FFA content, explaining the reduced sensitivity to molar ratio variations.

Statistical optimization identified optimal conditions for maximum biodiesel yield (45.5%): reaction temperature 55°C, reaction time 105 minutes, catalyst loading 0.1 wt%, molar ratio 9.3:1. Experimental validation using optimal conditions yielded 46.6% biodiesel, confirming model accuracy with minimal prediction error (2.4%).

Table 5: Experimental and Predicted Value of Percentage Masquerade Biodiesel yield utilizing optimal reaction conditions.

Mol ratio	Reaction Time, Min	Optimal Conditions		Biofuel Yield (%)	
		Reaction Temperature, °C	Catalyst Loading, wt%	Experimental	Predicted
9.3	105	55	0.1	46.6	45.5

The maximum biodiesel yield (46.6%) achieved in this study compares moderately with recent literature reports. Ahmed et al. (2024) achieved 78-82% yields from waste cooking oil, while Kumar et al. (2024c) reported 68-75% for Karanja oil biodiesel. However, direct comparison requires consideration of feedstock characteristics. Non-edible oils with higher FFA content typically exhibit lower yields due to competing saponification reactions. Singh et al. (2024d) achieved 42-48% yields from *Madhuca longifolia* seeds with similar FFA content (0.5-0.8 mg KOH/g), closely matching our results.

The moderate yield may also reflect the preliminary nature of this investigation. Jamil et al. (2024) demonstrated yield improvements from 45% to 72% through two-stage acid-base catalysis for high-FFA feedstocks, suggesting potential for yield enhancement through process modification.

3.3. Pareto Analysis and Sensitivity Assessment

Pareto analysis ranked variable significance: catalyst loading (A) and reaction time (C) were the most influential factors exceeding the significance threshold ($t=2.2$).

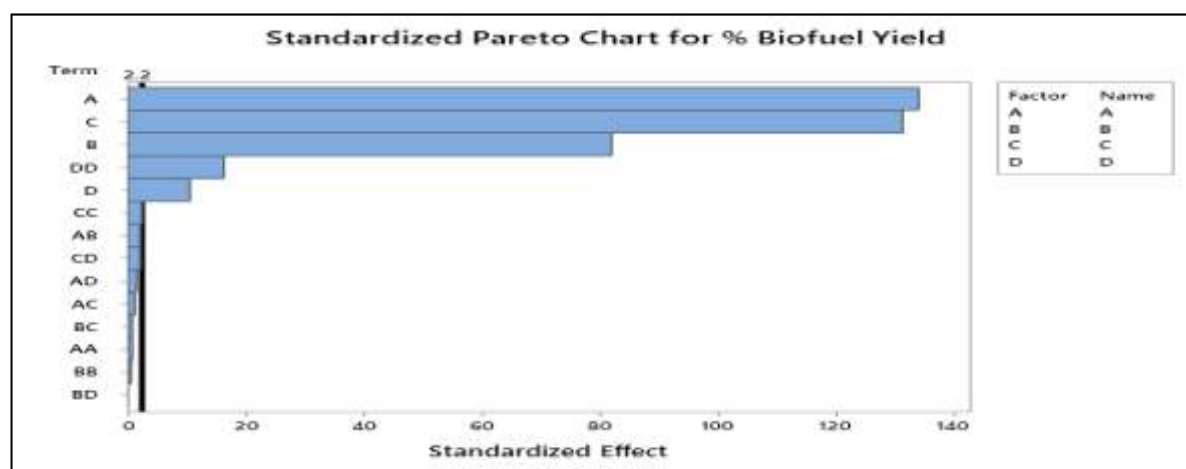


Fig. 5: The Pareto plot for the % Biofuel Yield.

Sensitivity analysis revealed:

- Reaction time: 70.13% (highest sensitivity)
- Catalyst loading: significant but secondary
- Reaction temperature: moderate influence
- Molar ratio: minimal effect

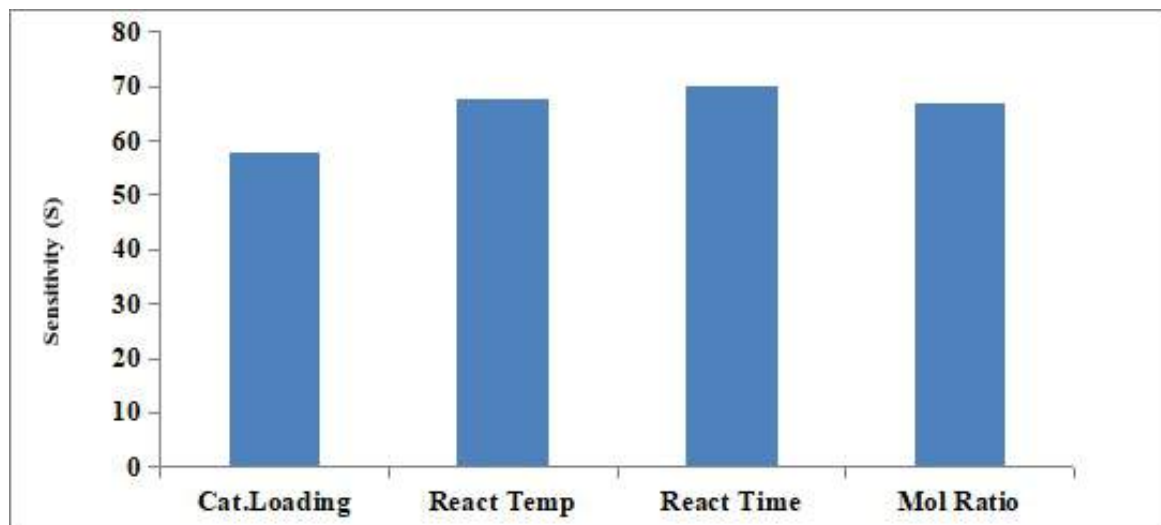


Fig. 6: Chart illustrating the effect of operational variables on the biodiesel production yield.

The predominance of reaction time (70.13% sensitivity) as the most critical factor differs from conventional biodiesel literature, where catalyst concentration typically dominates. Chen et al. (2024c) reported catalyst loading sensitivities of 65-78% for various feedstocks, whilst Rahman et al. (2024) found temperature to be the most influential factor (61-69% sensitivity). The unique sensitivity profile for masquerade seed oil reflects its distinctive physicochemical properties. Reaction time's predominant effect reflects incomplete bio-oil conversion at short durations versus potential reverse reactions (negative equilibrium shifts) at extended reaction times (Ogunkunle and Enweremadu, 2025). This time-dependency is characteristic of viscous feedstocks requiring prolonged contact time for complete transesterification. Similar observations were reported by Kululo et al. (2025) for palm kernel oil and Singh et al. (2024e) for neem oil biodiesel production.

The secondary importance of catalyst loading suggests that masquerade seed oil's natural acidity (0.471 mg KOH/g) provides a sufficient catalytic environment, reducing dependence on external catalyst concentration. This phenomenon has been observed in other mildly acidic feedstocks by Patel et al. (2024d) and Sheldon (2024).

3.4 Process Kinetics and Mechanistic Insights

The moderate influence of temperature contrasts with typical Arrhenius behaviour in chemical reactions. MacCarley (2025) suggested that certain feedstocks exhibit optimal temperature windows beyond which thermal degradation or reverse reactions become significant. The masquerade seed oil's behaviour suggests potential thermal sensitivity of its constituent fatty acids, requiring careful temperature control to maximize yield. The minimal impact of the molar ratio indicates near-stoichiometric reaction conditions, suggesting efficient methanol utilization. This characteristic is favourable for commercial applications, reducing

methanol consumption and recovery costs compared to conventional processes requiring 6-12:1 molar ratios (Montgomery, 2024).

4. Quality Analysis and Fuel Characteristics

Table 6: Physico-chemical Properties of Masquerade Seed Bio-oil (MSO) and Masquerade Seed Methyl Oil Ester (MSOME).

Parameters	EN 14214	MSO	MSOME	Biodiesel (Ogunkunle and Enweremadu, 2025)
Density at 15 ⁰ C, kg/m ³	860-900	1007	922	883
Viscosity (mm ² /s)	3.5-5.0	14.29	4.04	4.02
Free Fatty acid (%)	-	-	0.32	-
Flash Point (°C)	> 120	224.7	148	138
Pour Point (°C)	-	-	-	1.50
Acid Value (mg KOH/g)	Max 0.50	0.471	0.35	0.421
Iodine Value (gI ₂ /100g)	Max 120	16.04	16.04	105.5
Saponification Value (mg/g)	170-200	-	175.6	-
pH	-	4.06	6.0	7.74
Oxidation Stability (hours)	> 8	20	21	-

Masquerade seed oil properties, including acid value (0.471), flash point (224.7°C), oxidation stability (20 hours), and iodine value (16.04 gI₂ /100g), align with EN 14214 standards, with marginally higher density and viscosity. The produced biodiesel properties largely conform to EN 14214 biodiesel standards, confirming viability as a sustainable biodiesel source.

Density Characteristics: The biodiesel density (922 kg/m³) exceeds EN 14214 specifications (860-900 kg/m³) by 2.4%, similar to findings by Kumar et al. (2024d) for Karanja biodiesel (918 kg/m³) and Chen et al. (2024d) for palm oil biodiesel (912 kg/m³). This deviation may result from residual high molecular weight compounds or incomplete transesterification. Singh et al. (2024f) demonstrated density reduction through optimized purification techniques, suggesting potential for improvement.

Viscosity Performance: The kinematic viscosity (4.04 mm²/s) falls within EN 14214 limits (3.5-5.0 mm²/s), representing a 71.7% reduction from the raw oil (14.29 mm²/s). This viscosity reduction is superior



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to values reported by Ahmed et al. (2024) (68.2% reduction) and Rahman et al. (2024) (69.5% reduction) for similar feedstocks, indicating effective transesterification.

Acid Value and FFA Content:

The low acid value (0.35 mg KOH/g) meets EN 14214 requirements (≤ 0.50 mg KOH/g) and compares favorably with literature values. Patel et al. (2024e) reported acid values of 0.42-0.58 mg KOH/g for non-edible oil biodiesels, while Jamil et al. (2024) achieved 0.38-0.51 mg KOH/g for waste-derived biodiesels.

Flash Point Safety:

The flash point (148°C) exceeds EN 14214 minimum requirements ($\geq 120^\circ\text{C}$), ensuring safe handling and storage. This value aligns with findings by Kululo et al. (2025) (142-156°C) and Singh et al. (2024g) (139-152°C) for similar feedstocks.

Oxidation Stability:

The exceptional oxidation stability (21 hours) significantly exceeds EN 14214 requirements (≥ 8 hours) and surpasses most literature reports. Chen et al. (2024e) achieved 12-16 hours for various biodiesels, while Montgomery (2024) reported 9-14 hours for non-edible oil biodiesels. The superior oxidation stability suggests low polyunsaturated fatty acid content in masquerade seed oil, advantageous for long-term storage.

Iodine Value Implications:

The low iodine value (16.04 gI /100g) indicates high saturated fatty acid content, contrasting with typical biodiesel feedstocks. Kumar et al. (2024e) reported iodine values of 85-105 gI /100g for conventional biodiesels. The low iodine value suggests excellent oxidative stability but may impact cold flow properties, requiring cold flow improver additives in temperate climates.

Compared to conventional biodiesel sources, masquerade seed biodiesel exhibits unique characteristics. The density deviation represents the primary limitation requiring process optimization. However, the superior oxidation stability, appropriate viscosity, and excellent flash point characteristics demonstrate significant potential for niche applications, particularly in tropical regions where cold flow properties are less critical. The fuel quality profile suggests suitability for stationary power generation and marine applications where fuel stability is prioritized over cold-weather performance, similar to recommendations by Sheldon (2024) and MacCarley (2025) for high-stability biodiesel formulations.

Lastly, utilization of masquerade seeds, typically considered landscape waste, prevents decomposition-related methane emissions while producing renewable fuel. Kululo et al. (2025) estimated that waste biomass utilization reduces greenhouse gas emissions by 60-80% compared to fossil fuel alternatives. The



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moderate processing temperature (55°C) and catalyst concentration (0.1 wt%) minimize energy consumption and chemical usage, enhancing environmental sustainability.

5. Conclusion

This study successfully optimized masquerade seed biodiesel production using RSM-Aided Reduced CCD, demonstrating the viability of this waste biomass as a sustainable biodiesel feedstock. The developed second-order polynomial model exhibited exceptional predictive capability with $R^2 = 99.97\%$ and adequate precision of 45.63, confirming robust statistical significance and model adequacy.

Maximal biodiesel yield of 45.5% was achieved under optimal conditions of reaction time (105 minutes), molar ratio (9.3:1), catalyst concentration (0.1 wt%), and reaction temperature (55°C). Experimental validation yielded 46.6% biodiesel, confirming excellent model accuracy with only 2.4% prediction error. The fuel properties of the produced biodiesel, including viscosity of 4.04 mm²/s, flash point of 148°C and acid value of 0.35 mg KOH/g, conformed to EN 14214 standards, with the exception of high density (922 kg/m³ vs 860-900 kg/m³), requiring minor process optimization for complete standards compliance. The results of the sensitivity analysis also revealed that the reaction time had a predominant effect on biodiesel production yield (70.13% sensitivity).

This pioneering investigation establishes masquerade seed as a promising alternative feedstock, contributing to circular economy principles by converting landscape waste into renewable fuel. The moderate processing conditions and low catalyst requirements enhance environmental sustainability while addressing renewable energy needs. Future research should focus on density optimization through enhanced purification (work-up) techniques and scale-up studies to evaluate commercial viability for decentralized biodiesel production systems.



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Formulating Some Linear Programming (LP) Matrix Frameworks for Reviewing and Repurposing the Coal Industry in National and Global Contexts

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Abstract

In this paper, a theoretical review of the history of coal exploitation in Enugu, Nigeria, and its domestic utilization was conducted by emphasizing salient milestones only. One of the historical milestones was the 1999 privatisation of public enterprises policy in Nigeria, which induced the official coal retirement from Nigerian public activities in 2002. Internationally, other milestones were COP26 and the Paris Climate Agreement, which catalysed the ongoing coal phase-out and follow-up transition to cleaner energy alternatives globally. Anchoring on coal phase-out and the ongoing transition to cleaner energy, this paper delved into formulating LP optimisation matrix framework models for the repurposing of the phasing out coal facilities on one hand, and on the other hand, the re-visitation/review of coal emissions via LP matrix framework models. In this regard, two multi-dimensional LP maximisation matrix models were formulated for coal facilities' repurposing, as Tables 4-1 and 4-2 would show. Also, another two multi-dimensional LP minimisation matrix models were formulated for coal emissions' re-visitation/review, as Tables 5-1 and 5-2 would show. Each of the four multi-dimensional LP optimization matrix framework models has a single objective function (SOF), multiple structural constraint functions (MGCFs) with inequalities, multiple general constraint functions (MGCFs) with inequalities too, and the non-negativity inequality function. These formulations were accomplished, as this paper will show. And the methods for furthering the development of the formulated LP matrix models were clearly stated, as this paper would show. It is expected that the formulated LP optimisation framework models will be beneficial to chemical engineers, management scientists, energy engineers, energy management and conversion specialists, mathematicians, econometricians, economists, and environmental activists, among others.

Keywords: LP formulations; coal-facility repurposing; coal-emissions review; coal phase-out; salient milestones; multi-dimensional-LP-optimisation-matrix model.

1. Introduction

This work aligns with the ongoing paradigm shift from coal to renewable energy resources. Nonetheless, it is necessary to give a brief background of coal exploitation in Nigeria and elsewhere. Coal reserves are available in over 70 countries spread across almost every continent in the world. More than 984 billion tonnes of proven coal reserves are estimated worldwide. Nigeria has huge coal deposits in Enugu, Gombe, Kogi and in over 15 other states, much of which are untapped, except Enugu coal. The estimated coal reserve in Nigeria is over 2.75 billion metric tonnes, and in over 76 years of coal mining in Nigeria, only about 25 million tonnes have been exploited, mainly from the Enugu Coal Mines (Oguejiofor, 2008). Most of the Enugu coal reserves are of the sub-bituminous coal category, which are readily found in the huge Udi ridge in Enugu State. The four prominent underground coal mines in Enugu were namely, the Ogbete, Onyeama, Ribadu and Okpara mines, which were merged into the Nigerian Coal Corporation (NCC) in 1950. However, coal mining started in 1916 at the Ogbete mine in Enugu, six years after its discovery in 1909. And the initial coal production level in 1916 from Ogbete mine was 24,511 metric tons, and with the opening of other mines within the Enugu area, coupled with the incorporation of the Nigeria Coal Corporation (NCC)

in 1950, coal production hit an all-time high of 790,030 metric tons in the late 1950s (Amalu, 2024). However, the Enugu coal production continued until 1999 when official coal production stopped owing to the privatization scheme of the Federal Government of Nigeria (FGN), whereby no investor indicated interest to take the NCC (Igata, 2016).

Nonetheless, it would be remembered that Enugu coal was the engine of Nigeria's industrialisation and the driver of Nigeria's economic development during the 20th century, roughly about 1909-1980s. Examples: Besides overseas export, Enugu coal was used: (a) to fire the kilns in Nkalagu Cement Factory; (Nigercem); (b) as feedstocks for Ijora and Oji-River Thermal Power Plants during the era of Electric Company of Nigeria (ECN); (c) as fuel for steam locomotive engines of the Nigerian Railway Corporation (NRC); and (d) in the foundries of the Niger Steel Company, Emene, Enugu.

Presently, coal worldwide is being phased out and coal facilities are being repurposed owing to climate change challenges and the urgent need to decarbonized the atmosphere and other earthly environments. In this view, this paper is broken up into the following sections.

- a) Milestones in the phase-out of coal
- b) LP ideas for formulating the repurposing of coal plants
- c) Formulating an LP maximization framework for repurposing coal plants.
- d) Formulating an LP minimization framework for revisiting coal plants' emissions.
- e) Concluding notes and methods for furthering the work.

2. Milestones in Coal Phase-Out

The milestones in the phase-out of coal and coal facilities could be subdivided into domestically motivated milestones and externally driven milestones.

2.1 Domestic Milestones

During the public life of Enugu Coal and its associated facilities in Nigeria, which ranged from 1916 to 2002, coal production levels peaked at 790,030 metric tons in about 1959. And from 1959 to 2002, coal production dwindled progressively, until it retired publicly in 2002. And some of the internal milestones which forced the coal retirement are: the discovery oil/gas (hydrocarbon), the Nigerian civil war, the indigenization policy and the privatization policy.

2.1.1 Hydrocarbon discovery in 1956

UNEP (2024) writes that in Nigeria, oil was reportedly first discovered in the Niger-Delta in 1956, with a follow-up exploration and production in the late 1950s. This signalled a significant milestone in the diversification away from coal to hydrocarbon resources. Thus, this led to the dieselization of the NRC as it

replaced its fleet of coal-fired locomotive engines with diesel-driven engines. And the NCC suffered a significant loss of its market and patronage from the NRC.

2.1.2 Nigerian civil war in 1967-70

Nwaubani (2020) captures the timelines and aftermath of Nigeria's civil war, from May 1967 to January 1970. During that hostility period, the Ijora Thermal Power Plant in Lagos was unable to get Enugu coal supply. Subsequently, at the end of the hostility, the FGN neglected the Enugu-based NCC. This was so despite Nigeria's 3Rs paradigm, namely, reconciliation, reconstruction and rehabilitation policy, equivalent to that of George Marshall's post-World War II Plan of 1948-1952. Thus, FGN's negligence of Enugu coal is another milestone in the journey of Enugu coal towards retirement.

2.1.3 Indigenization policy of 1972

The Indigenization Policy of February 23, 1972, equally known as the Nigerian Enterprises Promotion Decree 1972, was amended in 1977 (FCT EMIS, n.d.). It was a Nigerianization and nationalization scheme which disaffected foreigners with technical know-how and know-why from the ownership and management of businesses in the Nigerian economy. This scheme has a negative impact on Enugu-based NCC, and it is one of the milestones which contributed to the decline of the Enugu coal industry.

2.1.4 Privatization Policy of 1999

This policy was aimed at selling or concessioning of nationalized enterprises to interested private and corporate entities. Oji et al. (2014) write that privatization of public enterprises in Nigeria is believed to bring about an end to inefficiency, balance of payment deficit, low performance, indiscipline, mismanagement of finances and attract foreign and local investments, among others. None of these happened to Enugu coal industry since no investor indicated interest in the NCC. Gradually, Enugu coal was publicly phased out in 2002, and the Enugu coal became abandoned, stranded and redundant.

2.2 External Milestones

Two of the prominent external milestones about phasing out coal power are the 2015 Paris Climate Change Agreement and the 2021 Glasgow COP26. The key decision of COP26 was phasing out coal and adopting the Paris Climate Change Agreement. Anyaogu (2021) writes that the world is moving in the right direction, standing ready to seal coal's fate, with promises to phase out coal in developed countries by 2030 and developing countries by 2040.

2.2.1 Paris climate change agreement of 2015

(a) Significantly, the goal of the Paris Agreement is anchored on decarbonisation globally and a worldwide economic strategy to combat global warming from crossing the 1.5 °C threshold. The Agreement was driven by the UN Intergovernmental Panel on Climate Change (IPCC) for the purpose of limiting greenhouse gas

(GHG) emissions globally. The Paris Agreement dealt a technical knockout to the life of coal and coal facilities worldwide.

(b) United Nations Framework Convention on Climate Change, UNFCCC [2016] describes the Paris Agreement as a legally binding international treaty on climate, adopted by 195 Parties at the UN Climate Change Conference (COP21) in Paris, France, on December 12, 2015, and which entered into force on November 4, 2016.

2.2.2 Glasgow 2021 COP26

COP26 advanced the implementation of the Paris Climate Agreement by taking steps that would make the world more sustainable with lower carbon emissions. UNFCCC [2021] presents that COP26 comes against the background of widespread, rapid and intensifying climate change impacts, which are already impacting every region on earth, in addition to the COVID-19 Pandemic, which ravages the world. And the key outcomes from COP26 include securing a 190-strong coalition to phase out coal power and end support for new coal power plants, with no nation being left behind the just transition to clean renewable energy [Anyagou, 2024]. In addition, the leaders from the UK, US, France, Germany and the EU announced to assist South Africa, the world's most carbon-intensive electricity producer, with \$8.5 billion over 3-5 years to enable it to make a just transition away from coal (UN Climate Action, 2021). In the context of the foregoing reviews (COP25 and CP26), it is clear that the doom for coal's future is looming large. Presently, the phase-out of coal and its facilities is ongoing worldwide. And subsequently, the retiring coal facilities/industries require repurposing, and this is the issue which will be treated in the next section. It will involve the use of linear programming (LP).

3. Lp Ideas for Repurposing Coal Plants

LP optimization matrix models are generally applied for solving real-life problems. Accordingly, Mustafa et al (2021) state that linear programming (LP) can be used to find the best result for minimising cost, or maximising profit for a real-life problem, and this can be reached after converting this problem into a mathematical model with a list of requirements. However, novel frameworks for LP optimisation matrix models will be formulated here as approaches for repurposing the retiring coal industry power plants. Earlier work on LP optimisation modelling for gas resource management in Nigeria by Oguejiofor et al (2016) was a juxtaposition of chemical engineering and operations management science. This is part of the idea value chain for this repurposing of coal power plants by the LP matrix model formulation.

3.1 Repurposing Coal Mines and Facilities

Coal mines and their associated facilities/plants could be repurposed by a switch/conversion into:

- (a) Wind-turbine farms (coal to wind switch)
- (b) Solar farms (coal to solar switch)

- (c) Nuclear plants (coal to nuclear switch)
- (d) Electric vehicle (EV) manufacturing facility (coal to EV switch).
- (e) Hydrocarbon process plants (coal to hydrocarbon switch).

Thus, in a nutshell, coal could be repurposed into:

- (a) Gas resource processors like Greenville LNG, CNG, NGLs and GTL products.
- (b) Oil processors to obtain LPG, gasoline/petrol, diesel, kerosene and heavy oil:
- (c) Renewable energy farms, such as solar farms and wind-turbine farms.

It is in the context of the above that LP optimization models will be framed for the repurposing of coal under the maximization perspective.

3.2 Formulating LP Maximization Framework

As it is with other existing LP optimization frameworks, this novel framework will as usual, consist of a single objective function (SOF), multiple structural constraint functions (MSCFs), multiple general constraint functions (MGCFs) and a non-negative function (NNF).

3.2.1 Single objective function (SOF)

The SOF is an algebraic linear equation in which the terms in the equation, also known as the decision variables of the SOF are the symbolic representatives of the facilities that will replace coal mines and their associated facilities. For the coal repurposing alternatives from renewable resources, X_1 would represent a solar farm, while X_2 represents a wind-turbine farm. For coal replacement alternatives from natural gas resources, X_3 would represent Greenville LNG, X_4 for CNG, X_5 for NGLs, and X_6 for GTL. And for coal substitution options from oil resources, X_7 will denote LPG, X_8 for petrol, X_9 for diesel, X_{10} for kerosene and X_{11} for heavy oil. X_{12} would denote nuclear energy repurposing for the retiring coal. And X_{13} represents EV substitution.

Subsequently, the SOF denoted Z will take the form:

$$Z = A_1X_1 + A_2X_2 + A_3X_3 + \dots + A_{13}X_{13} \quad (1)$$

where:

A_1X_1 = decision variable for solar farm; A_2X_2 = decision variable for wind-turbine farm; A_3X_3 = decision variable for Greenville LNG; and so on and so forth until $A_{13}X_{13}$, which is the decision variable for nuclear substitution for coal.

And $A_1, A_2, A_3, \dots, A_{13}$ are the coefficients of the decision variables.



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The SOF contains thirteen decision variables, as Eqn (1) above shows. If the decision variables are aggregated into X_1 to represent all the renewable, X_2 to denote all the components of the gas resources, X_3 to represent all the fractions from oil resource, X_4 to denote repurposing to nuclear energy, while X_5 to denote EV substitution; then the SOF will be shrinkened from thirteen decision variables to four decision variables, to assume the form of:

$$Z = A_1X_1 + A_2X_2 + A_3X_3 + A_4X_4 + A_5X_5 \quad (2)$$

where: A_1, A_2, A_3, A_4, A_5 remain as the coefficients of the decision variables.

3.2.2 Multiple structural constraint functions (MSCFs)

The MSCFs are algebraic linear inequalities with constants. Considerations could be given to the five Ms of industrial engineering, namely: men (expertise), machines (equipment), methods (technology), materials (physical raw materials), money (funding), in addition to infrastructure and landmass, as the MSCFs. In this regard, the MSCFs take the forms of:

Expertise constraint: $B_1X_1 + B_2X_2 + B_3X_3 + B_4X_4 + B_5X_5 \leq b_1$

Equipment constraint: $C_1X_1 + C_2X_2 + C_3X_3 + C_4X_4 + C_5X_5 \leq b_2$

Technology constraint: $D_1X_1 + D_2X_2 + D_3X_3 + D_4X_4 + D_5X_5 \leq b_3$

Raw materials constraint: $E_1X_1 + E_2X_2 + E_3X_3 + E_4X_4 + E_5X_5 \leq b_4$

Funding constraint: $F_1X_1 + F_2X_2 + F_3X_3 + F_4X_4 + F_5X_5 \leq b_5$

Infrastructure constraint: $G_1X_1 + G_2X_2 + G_3X_3 + G_4X_4 + G_5X_5 \leq b_6$

Landmass constraint: $H_1X_1 + H_2X_2 + H_3X_3 + H_4X_4 + H_5X_5 \leq b_7$

Where: the Bs, Cs, Ds, Es, Fs, Gs and Hs are the coefficients for expertise, equipment, technology, raw materials, funding, infrastructure and landmass constraints.

While: b_1 = Expertise benchmark; b_2 = equipment target;
 b_3 = technology level; b_4 = raw materials level;
 b_5 = funding ceiling; b_6 = infrastructure limit
 b_7 = landmass size.

3.2.3 Multiple general constraint functions (MGCFs)

The MGCFs are generally considered quantifiable parameters and contingent events which could significantly impact the LP optimisation matrix. Examples are tariff impositions, force majeure owing to natural disasters, UN pressure and funding withdrawal, and Banks' de-funding, among others. Mathematically, MGCFs represent inequalities without coefficients in the decision variables, and their forms are like:

Tariff imposition: $X_1, X_2, X_3, X_4, X_5 \leq b_8$

Force majeure: $X_1, X_2, X_3, X_4, X_5 \leq b_9$

UN pressure: $X_1, X_2, X_3, X_4, X_5 \leq b_{10}$

Non-negative constraint: $X_1, X_2, X_3, X_4, X_5 \geq 0$

4. Formulating Lp Maximization Framework for Coal

Repurposing

From the above ideas for the repurposing of coal plants, the LP maximization matrix can be assembled as a matrix table as follows:

Table 4-1: An LP Matrix Framework for Repurposing Coal Facilities

$$\text{Maximize } Z = A_1X_1 + A_2X_2 + A_3X_3 + A_4X_4 + A_5X_5$$

Subject to:

$$\text{Expertise constraint: } B_1X_1 + B_2X_2 + B_3X_3 + B_4X_4 + B_5X_5 = b_1$$

$$\text{Equipment constraint: } C_1X_1 + C_2X_2 + C_3X_3 + C_4X_4 + C_5X_5 = b_2$$

$$\text{Technology constraint: } D_1X_1 + D_2X_2 + D_3X_3 + D_4X_4 + D_5X_5 = b_3$$

$$\text{Raw materials constraint: } E_1X_1 + E_2X_2 + E_3X_3 + E_4X_4 + E_5X_5 = b_4$$

$$\text{Funding constraint: } F_1X_1 + F_2X_2 + F_3X_3 + F_4X_4 + F_5X_5 = b_5$$

$$\text{Infrastructure constraint: } G_1X_1 + G_2X_2 + G_3X_3 + G_4X_4 + G_5X_5 = b_6$$

$$\text{Landmass constraint: } H_1X_1 + H_2X_2 + H_3X_3 + H_4X_4 + H_5X_5 = b_7$$

$$\text{Tariff imposition: } X_1, X_2, X_3, X_4, X_5 = b_8$$

$$\text{Force majeure: } X_1, X_2, X_3, X_4, X_5 = b_9$$

$$\text{UN pressured: } X_1, X_2, X_3, X_4, X_5 = b_{10}$$

$$\text{Non-negativity: } X_1, X_2, X_3, X_4, X_5 \geq 0$$

And above is the complete LP optimization matrix framework for repurposing coal mines and their associated facilities and plants.

4.1 Formulating Worldwide LP Optimisation Matrix Framework

Conte (2024) shows that the top 10 world's largest coal producers, outputted a total of 9241.5 million tonnes of coal in 2024 of which: China (4780 million tonnes); India (1085.1 million tonnes); Indonesia (836.1 million tonnes); the US (464.6 million tonnes); Australia (462.9 million tonnes); Russia (427.2 million tonnes); South Africa (235.0 million tonnes); Kazakhstan (112.6 million tonnes); Mongolia (106.5 million tonnes); and Germany (91.6 million tonnes).

Collapsing this information into the infrastructure of the MSCFs of the LP optimisation matrix in Table 4-1 will result in the formulation of a global LP optimisation matrix, as shown in the matrix table below.

Table 4-2: A Word-scale LP Maximisation Matrix Framework

$$\text{Maximise } Z = A_1X_1 + A_2X_2 + A_3X_3 + A_4X_4 + A_5X_5$$

Subject to:

$$\text{China constraint: } B_1X_1 + B_2X_2 + B_3X_3 + B_4X_4 + B_5X_5 = 4780$$

$$\text{India constraint: } C_1X_1 + C_2X_2 + C_3X_3 + C_4X_4 + C_5X_5 = 1085$$



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Indonesia constraint: $D_1X_1 + D_2X_2 + D_3X_3 + D_4X_4 + D_5X_5$ 836

The US constraint: $E_1X_1 + E_2X_2 + E_3X_3 + E_4X_4 + E_5X_5$ 465

Australia constraint: $F_1X_1 + F_2X_2 + F_3X_3 + F_4X_4 + F_5X_5$ 463

Russia constraint: $G_1X_1 + G_2X_2 + G_3X_3 + G_4X_4 + G_5X_5$ 427

South Africa constraint: $I_1X_1 + I_2X_2 + I_3X_3 + I_4X_4 + I_5X_5$ 235

Kazakhstan constraint: $J_1X_1 + J_2X_2 + J_3X_3 + J_4X_4 + J_5X_5$ 113

Mongolia constraint: $K_1X_1 + K_2X_2 + K_3X_3 + K_4X_4 + K_5X_5$ 107

Germany constraint: $L_1X_1 + L_2X_2 + L_3X_3 + L_4X_4 + L_5X_5$ 92

Tariff imposition: X_1, X_2, X_3, X_4, X_5 b_8

Force majeure: X_1, X_2, X_3, X_4, X_5 b_9

UN pressured: X_1, X_2, X_3, X_4, X_5 b_{10}

Non-negativity: X_1, X_2, X_3, X_4, X_5 0

The individual coal production levels for the top 10 world's largest producers are the inequality constants as shown in Table 4-1 above. Other likely sources of the MGCFs are expatriate quota, local contents policy, global dictates, EPA restrictions, IPCC impacts, ICJ, Energy corporation's lobby, international environmental groups' engagements, among others.

5. Formulating LP Minimisation Framework for Coal Emissions

Review

A minimisation LP matrix framework for the coal plants will necessitate a brief excursion to the coal boom era in the Nigerian coal industry of the 1950s. During that boom period, coal pollution and emissions were at their peaks. And in retrospect, the emissions from coal burning would be deployed for this framework formulation.

5.1 LP Minimisation Framework for Coal Emissions in Nigeria

The industrial and domestic facilities which utilized coal and produced huge quantities of emissions during the coal boom era in Nigeria were: Niger Cement Factory, Nkalagu (Nigercem), Oji-River Thermal Power Plant, Niger Steel Foundries, NRC Coal locomotives, Ijora Therma Power Plant, and assorted kitchens (universities, secondary schools and households) where coal was used. All these coal utilization facilities listed above will represent the MSCFs in the formulation of the LP minimization matrix model. While the MGCFs will be constituted from events like labour union strikes (1949), host-community disturbances and revenue losses from coal abandonment.

It would be recalled that the principal emissions from burning coal are: CO_2 , NO_x , SO_2 , particulates, heavy metals like Hg, fly ash and bottom ash (EIA, n.d). However, an additional emission will be added, and it is

heat pollution arising from burning coal. If CO_2 , NO_x , SO_2 , particulates, heavy metals, fly/bottom ash, and heat pollution are denoted by X_1 , X_2 , X_3 , X_4 , X_5 , X_6 , and X_7 , respectively, then the SOF of the LP minimization matrix model can be written as:

$$Z = a_1x_1 + a_2x_2 + a_3x_3 + a_4x_4 + a_5x_5 + a_6x_6 + a_7x_7$$

In view of the background above, the minimization LP matrix model can be formulated accordingly and presented in the table below.

Table 5-1: ALP Matrix Framework for Nigeria's Coal Emission

Minimize emissions $Z = a_1x_1 + a_2x_2 + a_3x_3 + a_4x_4 + a_5x_5 + a_6x_6 + a_7x_7$

Subject to:

NkalaguNigercem: $c_1x_1 + c_2x_2 + c_3x_3 + c_4x_4 + c_5x_5 + c_6x_6 + c_7x_7 \leq y_1$

Oji-River Power Plant: $d_1x_1 + d_2x_2 + d_3x_3 + d_4x_4 + d_5x_5 + d_6x_6 + d_7x_7 \leq y_2$

Ijora Power Plant: $e_1x_1 + e_2x_2 + e_3x_3 + e_4x_4 + e_5x_5 + e_6x_6 + e_7x_7 \leq y_3$

NRC locomotives: $f_1x_1 + f_2x_2 + f_3x_3 + f_4x_4 + f_5x_5 + f_6x_6 + f_7x_7 \leq y_4$

Niger Steel Emene: $g_1x_1 + g_2x_2 + g_3x_3 + g_4x_4 + g_5x_5 + g_6x_6 + g_7x_7 \leq y_5$

Assorted Kitchens: $h_1x_1 + h_2x_2 + h_3x_3 + h_4x_4 + h_5x_5 + h_6x_6 + h_7x_7 = y_6$

Labour strikes: $x_1, x_2, x_3, x_4, x_5, x_6, x_7 \leq y_7$

Host-community disturbances: $x_1, x_2, x_3, x_4, x_5, x_6, x_7 \leq y_8$

Losses from abandonment: $x_1, x_2, x_3, x_4, x_5, x_6, x_7 \leq y_9$

Non-negativity: $x_1, x_2, x_3, x_4, x_5, x_6, x_7 \geq 0$

Table 5-1 above shows the LP minimization matrix model for coal burning in Nigeria. However, the empirical data for treating this model is in the 1950s archive and will be difficult to retrieve. And so, this LP model will be extended to South Africa, where empirical data could be obtained, given that the coal industry has up to 2030 to decommission and retire in South Africa.

5.2 LP Minimization Framework for Coal Emissions in South Africa

In 2024, South Africa's coal production was 235 million tonnes (Conte, 2025). And the two prominent corporations utilizing coal in South Africa for power and chemicals production are Eskom and Sasol. Eskom Power Plants in South Africa, which are expected to be decommissioned by 2030, are: Camden, Hendrina, Arnot, Komati, Grootvlei and Kriel (Smith, 2023). As of 2022, coal accounts for 45,618MW of South Africa's energy grid, which translates into 78 per cent of the country's total capacity of 58,753MW (Wikipedia, n.d). In addition to Eskom's power plants, Sasol uses coal as utilities at its Secunda and Sasolburg facilities. Thus, all the coal-utilisation facilities mentioned above will represent the inequalities for the MSCFs in the formulation of the LP minimization model for coal emission in South Africa. While the SOF for the LP minimization model will be adopted from Table 4-1. In this regard, the formulation of the LP minimization matrix model is hereby presented in the table below.

Table 5-2: ALP Matrix Framework for South Africa's Coal Emissions



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Minimize emissions $Z = a_1x_1 + a_2x_2 + a_3x_3 + a_4x_4 + a_5x_5 + a_6x_6 + a_7x_7$

Subject to:

Eskom's Camden Power Plant: $i_1x_1 + i_2x_2 + i_3x_3 + i_4x_4 + i_5x_5 + i_6x_6 + i_7x_7 \ t_1$

Eskom's Hendrina Power Plant: $j_1x_1 + j_2x_2 + j_3x_3 + j_4x_4 + j_5x_5 + j_6x_6 + j_7x_7 \ t_2$

Eskom's Arnot Power Plant: $k_1x_1 + k_2x_2 + k_3x_3 + k_4x_4 + k_5x_5 + k_6x_6 + k_7x_7 \ t_3$

Eskom's Komati Power Plant: $l_1x_1 + l_2x_2 + l_3x_3 + l_4x_4 + l_5x_5 + l_6x_6 + l_7x_7 \ t_4$

Eskom's Grootvlei Power Plant: $m_1x_1 + m_2x_2 + m_3x_3 + m_4x_4 + m_5x_5 + m_6x_6 + m_7x_7 \ t_5$

Eskom's Kriel Power Plant: $n_1x_1 + n_2x_2 + n_3x_3 + n_4x_4 + n_5x_5 + n_6x_6 + n_7x_7 \ t_6$

Sasol's Secunda Power Plant: $p_1x_1 + p_2x_2 + p_3x_3 + p_4x_4 + p_5x_5 + p_6x_6 + p_7x_7 \ t_7$

Sasol's Sasolburg Power Plant: $q_1x_1 + q_2x_2 + q_3x_3 + q_4x_4 + q_5x_5 + q_6x_6 + q_7x_7 \ t_8$

CoP26/Paris dictates: $x_1, x_2, x_3, x_4, x_5, x_6, x_7 \ t_9$

IPCC Limits: $x_1, x_2, x_3, x_4, x_5, x_6, x_7 \ t_{10}$

ICJ Injunctions/verdicts: $x_1, x_2, x_3, x_4, x_5, x_6, x_7 \ t_{11}$

Bank's defunding ceilings: $x_1, x_2, x_3, x_4, x_5, x_6, x_7 \ t_{12}$

EPA restrictions: $x_1, x_2, x_3, x_4, x_5, x_6, x_7 \ t_{13}$

Environmental Group disruption: $x_1, x_2, x_3, x_4, x_5, x_6, x_7 \ t_{14}$

Energy Corporation Lobby: $x_1, x_2, x_3, x_4, x_5, x_6, x_7 \ t_{15}$

Coal Group Defiance: $x_1, x_2, x_3, x_4, x_5, x_6, x_7 \ t_{16}$

Non-negativity: $x_1, x_2, x_3, x_4, x_5, x_6, x_7 \ t_{17}$

Table 5-2 above depicts the LP minimization matrix model for coal burning in South Africa. It is the result of situating Nigeria's LP minimization framework in Table 5-1 into South Africa's coal emissions infrastructures. The empirical data appropriate for adding flesh to the above skeletal framework (Table 5-2) could be obtained from South Africa's annual emissions databank.

5. Concluding Note and Furtherance of Work

Coal resources have given meritorious service to Nigeria and other wealthy, developed, and developing nations of the world. In Nigeria, coal was the cradle of western industrial civilization as well as the driver of economic development, particularly for South East Nigeria, which is richly endowed with huge quantities of coal deposits in Enugu. Also, coal has its demerits on the other hand. Coal was responsible for carbon dioxide pollution, smog formation, atmospheric acidification and acid rain phenomena (Oguejiofor, 2000). Coal publicly retired from service in Nigeria in 2002, during the era of privatisation of public enterprises; but it will retire in South Africa and other developed nations by 2030 owing to COP26 and Paris Climate Agreements.

In view of coal retirement, the formulations of LP optimisation matrix models for coal industry repurposing and coal emissions review in the categories of LP maximization and minimization have been successfully conducted and shown in this work. The LP optimization models formulated could be beneficial to chemical

engineers, management scientists, energy management and conversion specialists, energy engineers, managerial economists, econometricians, mathematicians, and research enthusiasts, among others.

The work can be furthered by collecting empirical data alignable with components of the SOF, MSCFs and MGSFs frameworks; and conducting multiple regression modelling using the Excel statistical function, or Minitab software to obtain the coefficients of the decision variables in Tables 4-1, 4-2, 5-1 and 5-2 as the case may be. A fully developed LP matrix model will result from this. And LP optimisation matrix solvers such as Management Scientist software, or Matlab software could be used as a final step for obtaining optimality, or optimum solution to the LP matrix model. Earlier this had been accomplished by Oguejiofor et al. (2016).

The support from Shanahan University Onitsha, is appreciated.

Acronyms and Notations

FCTEMIS:	Federal Capital Territory Education Management Information System: Nigeria
UNFCCC:	United Nations Framework Convention on Climate Change.
COP:	Conference of the Parties (Under the UN Charter)
COP26:	Conference of the Parties in Glasgow, UK.
COP21:	Conference of the Parties in Paris, France
BBC:	British Broadcasting Corporation
NCC:	Nigerian Coal Corporation
NRC:	Nigerian Railway Corporation
GHG:	Green House Gas
FGN:	Federal Government of Nigeria
ECN:	Electric Company of Nigeria
LP:	Linear Programming
n.d.:	no date
EV:	Electric vehicle
LNG:	Liquefied natural gas
CNG:	Compressed natural gas
NGLs:	Natural gas liquids
GTL:	Gas-to-liquid
SOF:	Single Objective Function
MSCFs:	Multiple Structural Constraint Functions
MGCs:	Multiple General Constraint Functions
NNF:	Non-negative Function
Z:	Single objective function (SOF), and could mean, “maximise repurpose efficiency”, or “maximize efficient transition from coal”, or “minimize coal emissions”.



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AnXn: repurposing substitute per unit

Xn: decision variables for repurposing of coal.

An: coefficients of the decision variables for coal repurposing.

Bs: coefficients of expertise (manpower, men) inequality

Cs: coefficients of equipment (machines) inequality

Ds: coefficients of technology (methods) inequality

Es: coefficient of raw materials (materials) inequality

Fs: coefficient of funding (money) inequality

Gs: coefficient of infrastructure inequality

Hs: coefficient of landmass inequality

UN: United Nations

b₁: expertise (manpower) benchmark

b₂: equipment (machines) target

b₃: technology (methods) level

b₄: raw materials (materials) level

b₅: funding (money) ceiling

b₆: infrastructure limit

b₇: landmass size

b₈: tariff imposition

b₉: force majeure

b₁₀: UN technical support

CO₂: carbon dioxide

NO_x: nitrogen oxides Hg: mercury

SO₂: sulphur dioxide

Hg: mercury (heavy metal from coal burning emissions)

a_nx_n: emission per unit

x_n: decision variables for coal emissions

a_n: coefficient of the decision variables for coal emissions

c_n: coefficient of the emissions from NigercemNkalagu inequality

d_n: coefficient of the emissions from Oji-River Power Plant inequality

e_n: coefficient of emissions from Ijora Power Plant inequality

f_n: coefficient of the emissions from NRC steam locomotives inequality

g_n: coefficient of the emissions from Niger Steel inequality.

h_n: coefficient of the emissions from assorted kitchens inequality

y₁: NigercemNkalagu total average emission level

y₂: Oji-River Power Plant average emission capacity

y₃: Ijora Power Plant average emission capacity



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y_4 :	Total average emission capacity from NRC coal locomotives
y_5 :	Total average emission level from Emene Niger Steel Plant
y_6 :	Aggregate level of emissions from assorted kitchens coal stoves
y_7 :	Aggregate level of coal production loss due to labour union strikes
y_8 :	Losses coal production level arising from host-community disturbances.
Y_9 :	Losses caused by abandonment of coal resource for other energy alternative
i_j :	coefficient of the emissions from Eskom's Camden Power Plant, SA
j_n :	coefficient of the emissions from Eskom's Hendrina Power Plant, SA.
k_n :	coefficient of the emissions from Eskom's Arnot Power Plant, SA
l_n :	coefficient of the emissions from Eskom's Komati Power Plant, SA
m_n :	coefficient of the emissions from Eskom's Grootvlei Power Plant, SA
n_n :	coefficient of the emissions from Eskom's Kriel Power Plant SA
p_n :	coefficient of the emissions from Sasol's secunda Power Plant, SA
q_n :	coefficient of the emissions from Sasol's Sasolburg Power Plant, SA
t_1 :	total emissions level/capacity from Eskom's Camden Power Plant, SA
t_2 :	total emissions level/capacity from Eskom's Hendrina Power Plant, SA
t_3 :	total emissions level/capacity from Eskom's Arnot Power Plant, SA
t_4 :	total emissions level/capacity from Eskom's Komati Power Plant, SA
t_5 :	total emissions level/capacity from Eskom's Grootvlei Power Plant, SA
t_6 :	total emissions level/capacity from Eskom's Kriel Power Plant, SA
t_7 :	total emission level/capacity from Sasol's secunda Power Plant, SA
t_8 :	total emission level/capacity from Sasol's Sasolburg Power Plant, SA
t_9 :	numerical value of dictates from OP26/Paris climate change
t_{10} :	quantitative limits of IPCC, if any
t_{11} :	impact of ICJ injunctions/verdicts in figures, if any
t_{12} :	quantitative value/ceilings from restricting funding of coal ventures by Banks, if any
t_{13} :	numerical values/penalties from violating EPA restrictions, if any
t_{14} :	Losses in figures from Environmental Group's disruption, if any
t_{15} :	quantitative values arising from the impact of Energy Corporations lobby, if any.
t_{16} :	penalties and fines arising from coal group defiance, if any
IPCC:	Intergovernmental Panel on Climate Change
ICJ:	International Court of Justice
EPA:	Environmental Protection Agency



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An Insight into Algae Lipid Production Dynamics Using a Compartmental Model Approach

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Abstract

The global aviation industry seeks Sustainable Aviation Fuel (SAF) to reduce its carbon footprint. Microalgae-derived SAF is a promising alternative due to high oil yields and non-competition with food crops. However, scaling production in developing nations is constrained by technical and knowledge gaps. This research develops a novel deterministic compartmental model, based on an adapted SIR framework, to analyze algae lipid production dynamics for SAF. The model tracks five key compartments: general algae (A), lipid-accumulating (E), harvest-ready (H), biofuel-converted (B), and genetically modified algae (G). The study established the model's mathematical validity by defining the invariant region and proving solution positivity. The Algae-Lipid Free Equilibrium (ALFE) was computed, and the Basic Reproduction Number (R_0) was derived to quantify lipid production potential. Some of the Key findings of our study are that local stability analysis and model simulations show the ALFE is stable when $R_0 < 1$, indicating lipid production ceases without intervention. Sensitivity analysis identified R_0 's high sensitivity to the lipid accumulation rate (β) and the algae growth influx (Λ); increasing these parameters is critical for enhancing productivity. Simulation of R_0 against varying β and Λ values visualized the threshold required to achieve a productive, self-sustaining system ($R_0 > 1$). In conclusion, this study provides a compartmental mathematical framework for optimizing microalgae-SAF systems. The model offers policymakers and engineers quantitative insights into key leverage points, such as strain selection to improve β and bioreactor design to maximize Λ , which are essential for making algae-derived SAF commercially viable.

Keywords: Algae, Parameters, Stability, Equilibrium point, Lipid

1. Introduction

Recent studies have demonstrated that microalgae can produce 10-20 times more oil per unit area than terrestrial oil crops (Xue et al, 2020; Mallick et al, 2016). Research by Gui et al (2021) showed that certain algal strains under optimal conditions can achieve lipid contents exceeding 50% of their dry weight. However, as noted by Sharma in 2023, tropical strains exhibit different growth kinetics compared to temperate species, creating an acknowledged gap that this study addresses.

The compartmental modelling approach for algae growth dynamics has been successfully applied in wastewater treatment systems (Mehta & Chakraborty, 2022; Jones et al., 2024; Solimeno et al., 2019), but its adaptation for SAF production under tropical conditions remains unexplored. Our study extends this methodology by incorporating specific parameters relevant to the Nigerian climate and infrastructure constraints.

Nigeria's engagement with Sustainable Aviation Fuel (SAF) production remains in its nascent stages as of 2024, with no large-scale commercial operations yet established (Adekitan, 2022; Ahmad et al, 2021).



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However, preliminary research and pilot projects indicate growing interest in biofuel development for aviation applications (Okoro et al, 2024; Xue et al, 2020; Zhang and Lu, 2024; Zhao et al, 2021). The Nigerian National Petroleum Corporation (NNPC) has identified biofuels, including SAF, as a strategic component to fit the energy transition road map (Rao & Krantz, 2021; Nwozor et al., 2021). A number of models, including the susceptible-infected-recovered (SIR) approach, have been applied to algae biofuel systems.

The SIR (Susceptible-Infected-Recovered) modelling approach, originally developed for epidemiological studies by Kermack & McKendrick (1927), has been adapted for algal growth dynamics by (Shriwastav et al., 2017; Zhao et al., 2020). The present study extends this framework by introducing five compartments (A, E, H, B, G) specifically tailored for SAF production systems.

Work by (Zhao, 2017) established the importance of computing reproduction numbers (R_0) in algal cultivation systems, while (Echendu et al, 2023), demonstrated the effectiveness of sensitivity analysis in identifying critical growth parameters (Babu et al, 2021; Bardon & Massol, 2025). However, these studies focused on temperate climates, leaving a significant gap for tropical conditions that the present research addresses.

Hence, the present study aims to develop a computational representation of the dynamics of sustainable aviation fuel (SAF) through algae lipid production, which accurately describes how algae are grown, extracted or harvested, and the subsequent conversion to biofuel (Cui and Chen, 2024).

2.0 Materials, Methods, and Model Formulation

This section details the materials, experimental procedures, and analytical methodologies employed in the study. The mathematical modelling approach and validation techniques are also presented.

2.1. Algae Biomass Collection and Preparation

The micro algae were collected from the Nike Lake and River Eva in Umuchigbo, both in Enugu East LGA, and Nvene River in Ituku Ozalla, Nkanu East LGA, both in Enugu State, Nigeria. The biomass (algae) was sun-dried, pulverized using a wooden pestle, and sieved (20- 40 μ m) for uniformity.

2.1.1 Oil extraction methods

The oil in the algae biomass was extracted using a soaking method approach. The dried algae biomass was mixed with hexane at a ratio of 1:5 by weight per volume (Chia et al, 2018). The mixture was allowed to settle for 24 hours in a separating funnel. The oil was separated, and the remaining mixture was filtered, and the hexane was evaporated in a water bath. The oil yield was calculated using the formula in equation 1.

$$\text{Oil yield (\%)} = \frac{\text{Oil mass (g)}}{\text{Algae biomass mass (g)}} \times 100 \quad (1)$$

2.1.1 Physicochemical characterization

The physicochemical characterization of the produced oil from algae biomass was carried out using standard methods for oil characterization, as indicated in Table 1.

Table 1: Standard methods for oil characterization

Parameters	Standard Methods
Fatty Acid Profile	GC-FID (Shimadzu GC-17A)
Saponification Value	AOCS Cd #-25
Iodine Value	AOCSCd1-25
Flash Point	ASTM D93 Refractive Index
Iodine Value	AOCSCd1-25

2.1 Mathematical Modeling

In developing the model, the following assumptions were made: homogeneous *Chlorellavulgaris* population, Logistic growth with carrying capacity, k , Nutrient-dependent lipid accumulation, and Constant biofuel conversion efficiency. The model flow diagram is presented in Figure 1.

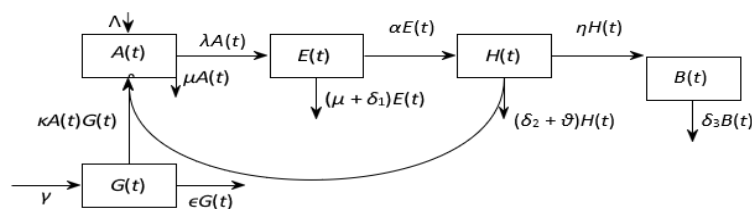


Fig. 1: Flow diagram of algal lipid production dynamics

2.2.1. Model equations

The model assumptions, together with the model flow diagram, enable us to formulate the given system dynamics for our proposed model, which is described by Equations 2-7.

$$\frac{dA}{dt} = \Lambda + kG + \theta H - \lambda A - \mu A \quad (2)$$

$$\frac{dE}{dt} = \lambda A - [\alpha + \delta_1 + \mu] E \quad (3)$$

$$\frac{dH}{dt} = \alpha E - [\delta_2 + \theta + \eta] H \quad (4)$$

$$\frac{dB}{dt} = \eta H - \delta_3 B \quad (5)$$

$$\frac{dG}{dt} = \gamma G - [\epsilon + k + \mu] G \quad (6)$$

The forces of algae lipid production are given by equation 7

$$\lambda = \beta \left(1 - \frac{n(t)}{n_1} \right) E(t) L_m \quad (7)$$

Variables used in developing the model are described in Table 2, while the various model parameters are described and presented in Table 3, respectively.

Table 2. Model Variables with description

Variables	Description
A	The population of algae capable of growth and reproduction
E	The population of algae exposed to environmental stressors that trigger lipid accumulation
H	Population of lipid-rich algae, ready for harvesting.
B	Population of algae converted into biofuel - 7
G	Population of genetically grown algae.

Table 3. Model Parameters with description

Parameters	Description
Λ	Algae purchased or transplanted proportion
k	Rate of acceptance of genetically grown algae.
μ	Natural algae death rate
α	Lipid accumulation rate due to exposure
δ_1	Algae death rate due to environmental factors
δ_2	Harvest rate
Λ	Lipid accumulation rate
η	Rate of conversion of algae lipid to biofuel
δ_3	Biofuel conversion rate
ϵ	Induced environmental exposure
θ	Spore formation rate
β	Algae contact rate
γ	Proportion of newly introduced genetically grown algae

3.0 Analysis and Discussion of Results

Having obtained the model equations, we then analyze these equations to see if the model gives a good representation of the algae lipid production dynamics. However, before this, we will first check to see if the proposed formulated model satisfies the conditions on the model variables, as well as the continuity of the variables in the region of existence of the variables.

3.1. Invariant Region of the Model

Here, the study tries to explore a specific subset of the state space of our dynamic system, where certain properties or characteristics of our proposed system remain unchanged or invariant over time. This is important in the study of dynamic systems because it can help understand the long-term behaviour of the system and identify regions where specific behaviours or patterns persist.

3.2. Invariant Region Solution

From equations (2 to 6), which reflect the general algae population. It is also necessary to state the fact that the associated algae population can never be negative. Thus, we establish the invariance of Ω to be given as:



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$$\Omega = \{(A, E, H, B, G) \in \mathbb{R}_+^5\} \quad (8)$$

Then

$$\{(A, E, H, B, G) \text{ and } N(t)\} \geq 0 \forall t \geq 0 \quad (9)$$

In this study, the compartmental mathematical model approach developed by Kermack and McKendric in 1927 was adopted and modified into the following subdivided populations:

$$N = A + E + H + B + G \quad (10)$$

Supposed that equations (2) to (6) has solutions that are possible for all time $t \geq 0$ as long as they remain in the invariant region, $\Omega \in \mathbb{R}_+^5$ where

$$\Omega = \{(A, E, H, B, G) \in \mathbb{R}_+^5\} \geq 0 \quad (11)$$

The solutions of our algae lipid production model equations are all positive (Bolarin and Adeboye, 2011; Mbah et al, 2023; Abang et al, 2024).

Without loss of generality, we assume that there exist some initial conditions on the algae lipid production (ALP) model variables, which are all positive, such that:

$$A(0) > 0, E(0) > 0, H(0) > 0, B(0) > 0, G(0) > 0$$

$$\Rightarrow \{(A, E, H, B, G) \text{ and } N(t)\} \geq 0, \forall t \geq 0$$

We show that Ω is positively invariant, so that it is sufficient to consider the dynamics of the model system.

From (10), which is the algae population, the following differential equation were gotten:

$$\frac{dN}{dt} = \Lambda - \mu A - \mu E - \mu H - \mu B - \mu_G G - \delta_1 E - \delta_2 H - \delta_3 B \quad (12)$$

$$\frac{dN_H}{dt} = \Lambda - \mu N - \delta_1 E - \delta_2 H - \delta_3 B$$

$$\frac{dN}{dt} + \mu N = \Lambda - \delta_1 E - \delta_2 H - \delta_3 B \quad (13)$$

It shows that the solutions for the human population would always remain in Ω as long as ≥ 0

And the solution shows it is bounded below by 0 and above by $\frac{\Lambda}{\mu}$. Therefore, it was obtained that the solutions of (2) to (6) remain in Ω for all time, $t \geq 0$

3.3 Positivity of Solution

An important question in the study of the behaviour of solutions of equations from biological systems is whether solutions with positive initial conditions will remain positive after a given time t (Din et al., 2014; Psarros et al., 2017; Abang et al., 2024).

There is a need to prove that all the state variables of the model are non-negative for all time (t), for the model



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(2 to 6) to be epidemiologically meaningful. In other words, the solutions of the model (2 to 6) with positive initial data will remain positive for all. This means that if we start with some positive initial condition, then the solution of the model should always be positive at all times t .

Here, the focus is not on negative time (t) since in reality, negative t does not exist. So, at all times t , our model must be positive, otherwise, the model becomes an invalid model.

$$\frac{dA}{dt} = \Lambda + kG + \theta H - \lambda A - \mu A$$

$$\frac{dE}{dt} = \lambda A - \alpha + \delta_1 + \mu E$$

$$\frac{dH}{dt} = \alpha E - \delta_2 + \theta + \eta H$$

$$\frac{dB}{dt} = \eta H - \delta_3 B$$

$$\frac{dG}{dt} = \gamma G - \epsilon + k + \mu G$$

The solution of H is also bounded and positive for all $t \geq 0$. Adopting a similar approach for the remaining equations, their solutions are also positive at all times, $t \geq 0$. Next, in our analytics agenda, we move to another point, which is the continuous existence and non-existence of lipid in the algae population. This is done by analyzing the process to get the equilibrium points of the lipid production at the lipid-free and lipid-abundant states. At these points, we will study and analyze the equilibrium state.

3.4 Establishing the Algae-Lipid-Free Equilibrium (ALFE) Points for the General Model

This section aims to determine the values for parameters in equations (2) to (6) of the algae lipid production model, which we used to represent a situation where there are no algae lipids being produced, or where no compartments in the algae population have lipids present.

To find the equilibrium point, the above equations (2), (3), (4), (5), and (6) were set to zero, then:

$$\frac{dA}{dt} = 0, \frac{dE}{dt} = 0, \frac{dH}{dt} = 0, \frac{dB}{dt} = 0, \frac{dG}{dt} = 0$$

The algae lipid abundance equilibrium exists when the basic reproduction number, $R_0 > 1$. Having produced the acceptable equilibrium points, we need to verify whether these equilibrium points are stable or not. But first, we need to generate the lipid basic reproductive number for the lipid studied, then we would study the per capita lipid production growth rate, stability of the lipid-free and lipid-abundance states of the study at the equilibrium points, and stability of the algae lipid production states.

3.5 The Fundamental Reproductive Number (R_0) for the Study

This section tries to discover critical physical parameter(s) that may be used to assess the likelihood of the algae lipid production within a certain algae farm in the community. It is the expected number of secondary lipids produced when exposed algae are extracted from the population (Diekmann and Heesterbeek, 2000; Breda et al, 2012). Arguably, it is the most important threshold parameter that determines whether an exposed algae can produce lipid when harvested from the algae farm (Okunonghae, 2013). In a susceptible population where control measures such as environmental factors, lack of nutrients, etc, already exist, then the basic reproduction number will be defined as the control reproduction number (Obasi and Mbah, 2019).



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To construct the basic reproduction number, we need to form the next generation matrix, which is FV^{-1} where V is the matrix containing all of the transferred words and F is the newly exposed term. Additionally, F is the rate at which a newly exposed algae appears, and V is the difference between the rate at which people enter the same compartment by other means and the rate at which people exit the compartment by other means.

Reproduction number $R_0 = \rho(FV^{-1})$ where ρ denotes the spectral radius of a matrix FV^{-1} which represents the dominant non-negative eigenvalue of the next generation matrix of the square matrices F and V^{-1} of order $(m \times m)$, where m is the number of exposed class and defined by

$$F = \frac{\delta f_i}{\delta x_j}(x_o) \quad \text{and} \quad V = \frac{\delta v_i}{\delta x_j}(x_o)$$

Such that f is non-negative, V is a nonsingular m -matrix, and x_o is the algae-lipid-free equilibrium point (ALFE). If $R_0 > 1$ it means that an exposed algae produces enough lipid throughout its lipid production period in the population and as such the algae lipid production increases through the population but if $R_0 < 1$, it means that an exposed algae produces on the average less lipid than is expected for an exposed algae which by calculation means that the lipid production will die out from the algae population with time (Obasi and Mbah, 2019).

Now, rewriting the general ALP model for the study, starting with the algae compartments possessing lipids, we have:

$$\frac{dE}{dt} = \lambda A - \varphi + \alpha + \delta_1 + \mu E$$

$$\frac{dH}{dt} = \alpha E - \delta_2 + \theta + \eta H$$

$$\frac{dB}{dt} = \eta H - \delta_3 B$$

$$\frac{dA}{dt} = \Lambda + kG + \theta H - \lambda A - \mu A$$

$$\frac{dG}{dt} = \varphi E + \gamma G - \epsilon + k + \mu G$$

$$\text{Recall: } \lambda = \beta \left(\frac{n_1 - n}{n_1} \right) L_m E$$

is the force of algae lipid production for the algae population.

From the above model of our study, we have:

X = vector of the lipid production classes, such as exposed, lipid-carrier, etc.

Y = vector of non-lipid production classes, such as unexposed algae, unexposed genetically modified algae, etc

$$\text{Therefore, } X = \begin{pmatrix} E \\ H \\ B \end{pmatrix} Y = \begin{pmatrix} A \\ G \end{pmatrix}$$



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$$f_i = \begin{bmatrix} f_1 \\ f_2 \\ f_3 \end{bmatrix} \quad v_i = \begin{bmatrix} v_1 \\ v_2 \\ v_3 \end{bmatrix}$$

Where f_i' s are new lipid production terms, while v_i' s are transferred lipid production terms to other classes

$$f_i = \begin{bmatrix} f_1 = \beta \left(\frac{n_1 - n}{n_1} \right) L_m EA \\ f_2 = 0 \\ f_3 = 0 \end{bmatrix}$$

$$v_i = \begin{bmatrix} v_1 = \varphi + \alpha + \delta_1 + \mu E \\ v_2 = -\alpha E + \delta_2 + \theta + \eta H \\ v_3 = -\eta H + \delta_3 B \end{bmatrix}$$

$$f = \begin{bmatrix} \beta \left(\frac{n_1 - n}{n_1} \right) L_m EA \\ 0 \\ 0 \end{bmatrix}$$

$$v = \begin{bmatrix} \varphi + \alpha + \delta_1 + \mu E \\ -\alpha E + \delta_2 + \theta + \eta H \\ -\eta H + \delta_3 B \end{bmatrix}$$

$$F = \begin{bmatrix} \frac{\partial f_1}{\partial E} & \frac{\partial f_1}{\partial H} & \frac{\partial f_1}{\partial B} \\ \frac{\partial f_2}{\partial E} & \frac{\partial f_2}{\partial H} & \frac{\partial f_2}{\partial B} \\ \frac{\partial f_3}{\partial E} & \frac{\partial f_3}{\partial H} & \frac{\partial f_3}{\partial B} \end{bmatrix}$$

$$V = \begin{bmatrix} \frac{\partial v_1}{\partial E} & \frac{\partial v_1}{\partial H} & \frac{\partial v_1}{\partial B} \\ \frac{\partial v_2}{\partial E} & \frac{\partial v_2}{\partial H} & \frac{\partial v_2}{\partial B} \\ \frac{\partial v_3}{\partial E} & \frac{\partial v_3}{\partial H} & \frac{\partial v_3}{\partial B} \end{bmatrix}$$

Therefore, we have

$$F = \begin{bmatrix} \beta \left(\frac{n_1 - n}{n_1} \right) L_m A & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

Let $\varphi + \alpha + \delta_1 + \mu = b_1$, $\delta_2 + \theta + \eta = b_2$

$$V = \begin{bmatrix} b_1 & 0 & 0 \\ -\alpha & b_2 & 0 \\ 0 & \eta & -\delta_3 \end{bmatrix}$$

Next, we evaluate F at DFE

Therefore, we have



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$$F = \begin{bmatrix} \beta \left(\frac{n_1 - n}{n_1} \right) L_m \left(\frac{\Lambda}{\mu} \right) & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

We then compute V^{-1} , using **Maple 2021**

$$V^{-1} = \begin{bmatrix} \frac{1}{b_1} & 0 & 0 \\ \frac{\alpha}{b_1 b_2} & \frac{1}{b_2} & 0 \\ \frac{\alpha \eta}{b_1 b_2 \delta_3} & -\frac{\eta}{b_2 \delta_3} & -\frac{1}{\delta_3} \end{bmatrix}$$

Where C_i are given as:

$$C_1 = \left(\frac{n_1 - n}{n_1} \right), C_2 = \left(\frac{\Lambda}{\mu} \right)$$

Since we have gotten V^{-1} and we also have F , we can then compute the Next Generation Matrix (NGM) for the algae lipid production (ALP) model

$$FV^{-1} = \begin{bmatrix} d_1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

We have d_1 where d_1 are the combination of lipid efficiency algae (β) vival fraction (C_1)

$$d_1 = \frac{\beta C_1 L_m C_2}{b_1}$$

Next, we determine the eigenvalues of our algae lipid production model

Now we compute $|FV^{-1} - A_i I| = 0$

Where A_i is given as the Eigen values

The eigenvalues for our model are given as:

$$\begin{bmatrix} A_1 = d_1 \\ A_2 = 0 \\ A_3 = 0 \end{bmatrix}$$

It is clear that the dominant Eigen value is:

$$A_1 = d_1$$

Therefore, $R_0 = \frac{\beta C_1 L_m C_2}{b_1}$ This is the basic Reproductive number for our general ALP model.

Which is given as:

$$R_0 = \frac{\beta C_1 L_m C_2}{b_1}$$

$$R_0 = \frac{\beta(n_1 - n)L_m\Lambda}{n_1\varphi + \alpha + \delta_1 + \mu\mu}$$



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3.6 Local Stability Analysis of Algae-Lipid Free Equilibrium (ALFE) State of the General Model

Here, the idea is to visualize the need for local stability analysis, as it provides valuable information about the potential effectiveness of various control strategies based on the basic dynamics of our algae lipid production (ALP) model, as outlined in equations (2) to (6).

Local stability analysis of the algae lipid-free equilibrium point T^0 is obtained by the variational matrix of the model (2) to (6) corresponding to the point T^0

Recall that at an equilibrium state, the rate of change of the variables is zero. Let the system of equations at the equilibrium state be:

$$x_1 = \frac{dA}{dt} = \Lambda + kG + \theta H - \lambda A - \mu A$$

$$x_2 = \frac{dE}{dt} = \lambda A - \varphi + \alpha + \delta_1 + \mu E$$

$$x_3 = \frac{dH}{dt} = \alpha E - \delta_2 + \theta + \eta H$$

$$x_4 = \frac{dB}{dt} = \eta H - \delta_3 B$$

$$x_5 = \frac{dG}{dt} = \varphi E + \gamma G - \epsilon + k + \mu G$$

$$\text{Recall: } \lambda = \beta \left(\frac{n_1 - n}{n_1} \right) L_m E$$

is the force of algae lipid production for the algae population. We linearize the system of equations (2) to (6) around the equilibrium point (ALFE) using the Jacobian Matrix. Considering the model (2) to (6) and by finding the partial derivatives of each equation with respect to the state variables, to present the following Jacobian matrix, J

$$J(A, E, H, B, G) = \begin{pmatrix} \frac{\partial x_1}{\partial A} & \frac{\partial x_1}{\partial E} & \frac{\partial x_1}{\partial H} & \frac{\partial x_1}{\partial B} & \frac{\partial x_1}{\partial G} \\ \frac{\partial x_2}{\partial A} & \frac{\partial x_2}{\partial E} & \frac{\partial x_2}{\partial H} & \frac{\partial x_2}{\partial B} & \frac{\partial x_2}{\partial G} \\ \frac{\partial x_3}{\partial A} & \frac{\partial x_3}{\partial E} & \frac{\partial x_3}{\partial H} & \frac{\partial x_3}{\partial B} & \frac{\partial x_3}{\partial G} \\ \frac{\partial x_4}{\partial A} & \frac{\partial x_4}{\partial E} & \frac{\partial x_4}{\partial H} & \frac{\partial x_4}{\partial B} & \frac{\partial x_4}{\partial G} \\ \frac{\partial x_5}{\partial A} & \frac{\partial x_5}{\partial E} & \frac{\partial x_5}{\partial H} & \frac{\partial x_5}{\partial B} & \frac{\partial x_5}{\partial G} \end{pmatrix}$$

Next, apply the ALFE to the Jacobian to obtain:

$$J(A, E, H, B, G) = \begin{pmatrix} -\mu & D_1 & \theta & 0 & k \\ D_2 & D_3 & 0 & 0 & 0 \\ 0 & \alpha & D_4 & 0 & 0 \\ 0 & 0 & \eta & -\delta_3 & 0 \\ 0 & \varphi & 0 & 0 & D_5 \end{pmatrix}$$

Where

$$D_1 = -\beta \left(\frac{n_1 - n}{n_1} \right) L_m \frac{\Lambda}{\mu}; D_2 = \left(\beta \left(\frac{n_1 - n}{n_1} \right) L_m E \right); D_3 = \beta \left(\frac{n_1 - n}{n_1} \right) L_m A - \varphi + \alpha + \delta_1 + \mu; D_4 = -[\delta_2 + \theta + \eta]; D_5 = \gamma - \epsilon + k + \mu$$

The characteristic equation for the system matrix (68) is given by $|J - \vartheta_i I| = 0$

where $\vartheta_i = \vartheta_1, \vartheta_2, \vartheta_3, \vartheta_4$ and ϑ_5 are the eigenvalues and I is the identity matrix for (69).

Below are the computed eigenvalue results from (69) using Maple-2021

$$\vartheta_1 = -\mu, \vartheta_2 = D_3, \vartheta_3 = D_4, \vartheta_4 = -\delta_3, \vartheta_5 = D_5.$$

Only in the event that the following conditions are true:

- (i) For ϑ_2 to be negative, $\frac{n_1 - n}{n_1} = 0$
- (ii) When $\gamma < [\epsilon + k + \mu]$, then ϑ_2 would be negative,

Since all our parameters $(\gamma, \mu, \epsilon, k, n_1, n, \eta, \delta_1, \delta_2, \delta_3, \theta, \alpha, \beta, \varphi, \Lambda) > 0$

Therefore, we say that the algae lipid-free equilibrium (ALFE) of the general system is locally asymptotically stable. This result mathematically implies that the lipid production from algae can be sustained within the algae population with respect to the initial condition (population).

3.7 Model Simulation and Explanation

Here, we verified the mathematical representation for our algae lipid production dynamics by varying parameters to get a deeper understanding of how different parameters influence the production of algae lipid.

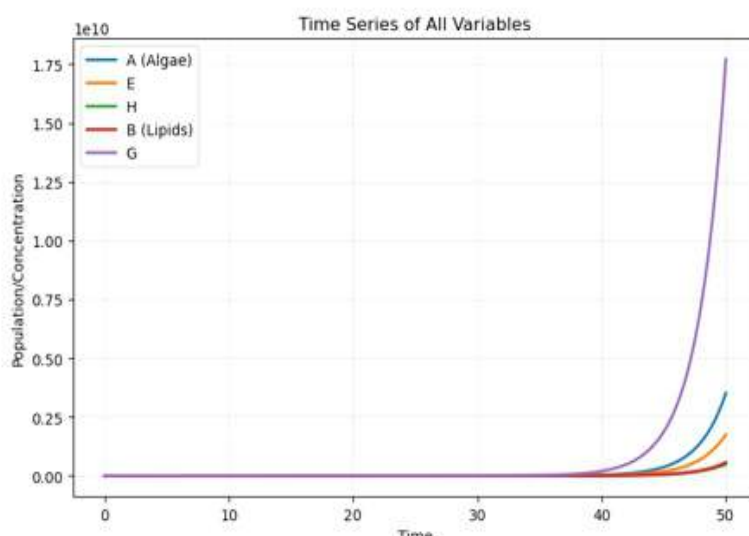


Fig. 2: Graph showing the Sensitivity index analysis of the R_0 for our proposed model.

Figure 2 presents a bar plot graph of the sensitivity index, illustrating how small changes in different model parameters can help predict their impact on the average lipid production output (R_0) in algae. The green represents positive bar plots, which indicate that increasing these positive parameters will increase lipid production. In contrast, the negative bar plots are given a red colour, meaning that increasing this parameter will decrease lipid production, and vice versa.

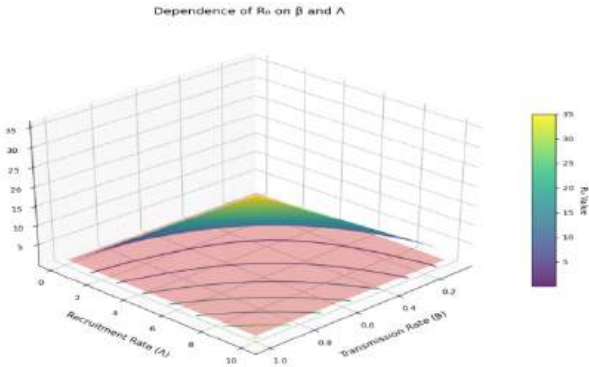


Fig. 3: Relationship between

In Figure 3, we try to visualize the relationship between the parameters, Λ and β with respect to a given R_0 value. The graph then shows us how β , which is the lipid transmission rate, makes us understand how efficient the algae are at producing lipid oil. Also, Λ , which is the new algae recruitment rate, tells us how many new algae contribute to the production of lipid in the lipid production system each day. Once either Λ or β value goes down, Lipid production will decline over time because each productive algae cell does not replace itself with at least one equally productive cell. Eventually, production will stop.

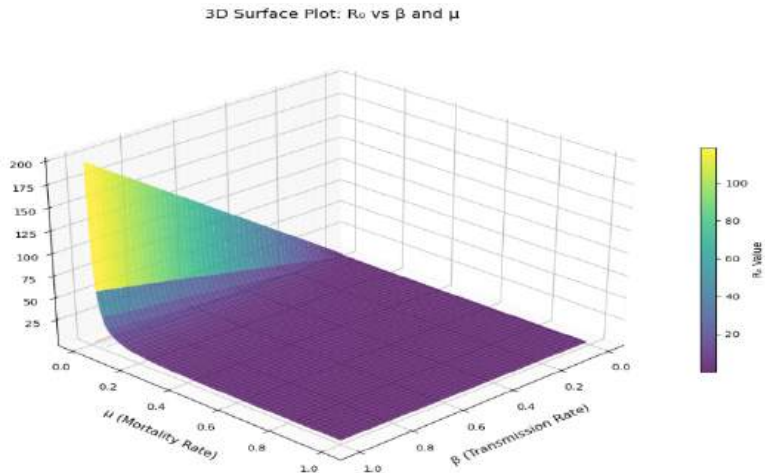


Fig. 4: Relationship between μ , β and R_0 .

From Figure 4, we have a plot for the algae lipid production dynamics model. This plot shows the relationship between " μ ", " β ", and " R_0 " as we try to visualize their behaviour as the values of each of them change. This graphical representation of our algae model tells us that to maximize algae lipid production, the single most important thing to focus on is optimizing the algae's environment for growth (β). This means ensuring they have perfect access to light, carbon dioxide, and other nutrients. While keeping the algae healthy to minimize death (μ) is still important, the gains from making them grow efficiently are far more significant.

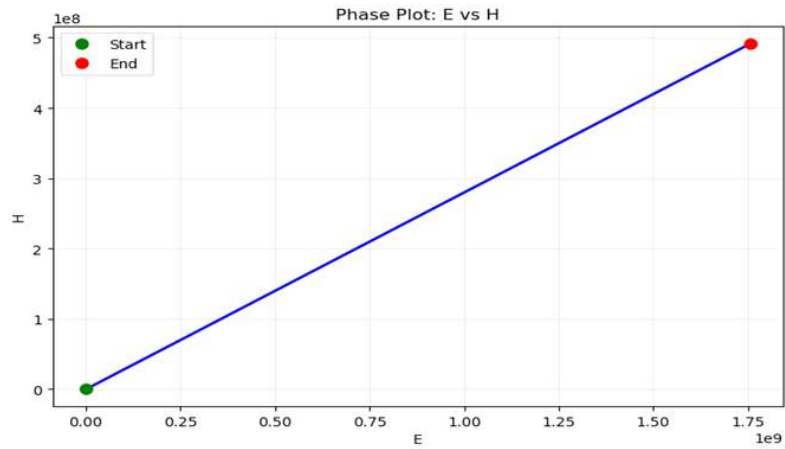


Fig. 5: Graph of the Phase plot of E against H

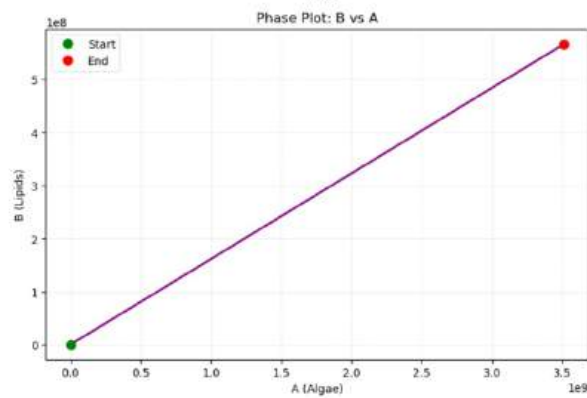


Fig. 6: Graph of the Phase plot of E against H

From Figure 6, we have a plot for the algae lipid production dynamics model. This plot shows the relationship between lipids and algae's population, which leaves potential unused resources.

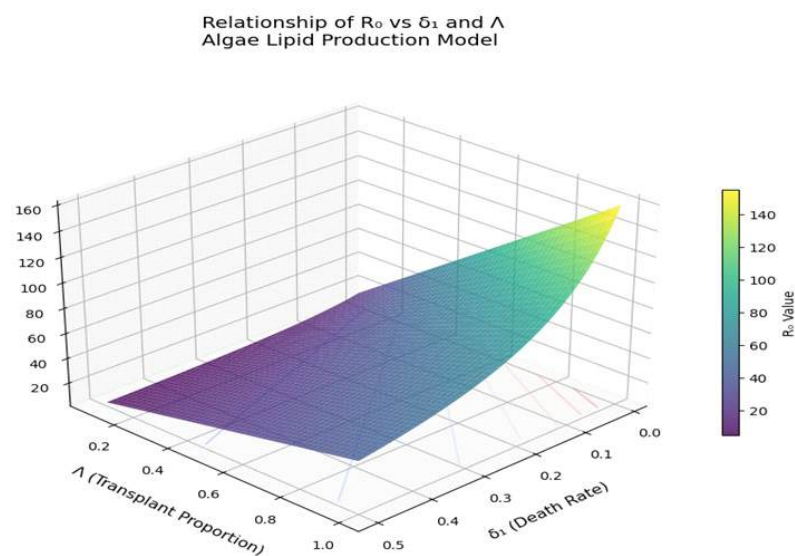


Fig. 7 3D plot showing the relationship between δ_1 , Λ and R_0

From Figure 7, we have a plot visualizing the relationship between δ_1, Δ and R_0 in our algae lipid production dynamics model. This graph is a powerful tool that shows you the best ways to manage your algae farm to ensure it is productive and successful.

This research addressed the critical challenge of decarbonizing the aviation sector, specifically within the Nigerian context, by developing a novel mathematical model to analyze and optimize the production of Sustainable Aviation Fuel (SAF) from microalgae.

The study formulated a deterministic compartmental model by extending the SIR-compartmental model approach to simulate the dynamics of algae lipid production. The population was divided into five key compartments: Algae capable of growth (A), Algae exposed to lipid-triggering stressors (E), Lipid-rich algae ready for harvest (H), Algae converted to biofuel (B), and Genetically modified algae (G). A core component of the model was the force of lipid accumulation, λ , which depends on the algae contact rate (β), lipid capacity (L)

Conclusion

By developing a robust computational framework that accurately describes the complex dynamics of algae growth, lipid accumulation, and harvesting for SAF production. The model provides a powerful tool to understand the non-linear interactions within the production system.

The derivation of the basic reproduction number R_0 is a fundamental outcome, serving as a single, powerful metric to assess the viability and efficiency of any given algae-to-SAF production system. The research concludes that sustainable, large-scale algae lipid production is theoretically feasible but is acutely sensitive to environmental stressors and mortality factors. For Nigeria and similar tropical nations, the model highlights that overcoming technical barriers related to maintaining healthy algae cultures in a fluctuating climate is a more significant hurdle than the initial biomass input. The model establishes a critical foundation for optimizing algae-based biofuel pathways, moving from theoretical potential to practical, scalable strategy design.



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Valorization of Tamarind Seeds for Sustainable Lactic Acid Production

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Abstract

The global shift toward sustainable practices has intensified the search for bio-based alternatives to petrochemical-derived products. Lactic acid (LA), a key platform chemical for biodegradable polymers such as poly (lactic acid) (PLA), has garnered considerable interest. This study explores the production of lactic acid from tamarind seeds, an underutilized agricultural waste rich in starch and xyloglucans. A two-step bioprocess was employed, involving enzymatic hydrolysis using *Aspergillus niger* followed by fermentation with *Lactobacillus* spp. Starch was extracted from tamarind seeds via wet milling and alkali treatment, yielding 77.94% carbohydrate content with an amylose-to-amylopectin ratio of 13.43:86.57. Hydrolysis with *A. niger* effectively converted the starch into fermentable sugars, which were then utilized by *Lactobacillus* spp. (sourced from fermented milk) under anaerobic conditions, yielding approximately 157 g of lactic acid at a conversion rate of 49.58% over five days. High-Performance Liquid Chromatography (HPLC) confirmed the presence of both L- and D-lactic acid with a total purity of 69.18%. FTIR and XRD analyses validated the structural integrity and crystalline nature of the extracted starch. This study demonstrates the feasibility of converting tamarind seed waste into a valuable, sustainable chemical, offering a promising route for waste valorization and reducing reliance on food-based biomass.

Keywords: Tamarind seed, lactic acid, *Aspergillus niger*, *Lactobacillus* spp., Starch, Agricultural waste and Biodegradable chemical.

1. Introduction

The global emphasis on sustainability and environmental preservation has accelerated the shift toward bio-based chemicals as alternatives to petroleum-derived products (Ioannidou, 2020; Mishra, 2023). This transition is essential to addressing critical challenges such as climate change, resource depletion, and plastic pollution, issues exacerbated by the continued use of non-renewable resources and the environmental footprint of petrochemical industries (Kibria *et al.*, 2023; Geyer *et al.*, 2017). Initiatives like the United Nations Sustainable Development Goals (SDGs) and the European Green Deal advocate for green chemistry approaches, promoting the use of renewable resources and the valorization of agricultural and industrial waste (European Commission, 2019).

Lactic acid (LA) is a versatile organic acid widely used in food, pharmaceuticals, cosmetics, and as a precursor for biodegradable polymers such as poly (lactic acid) (PLA). First isolated by Carl Wilhelm Scheele in 1780, lactic acid is water-soluble and commonly employed as a preservative, acidulant, and flavouring agent (Kelkar & Mahanwar, 2015; Oziegbe *et al.*, 2024). In recent years, its role in producing PLA, an environmentally friendly alternative to conventional plastics, has significantly increased (Balla *et al.*, 2021; Shalem *et al.*, 2024). The chemical structure of LA is as shown in Figure 1.

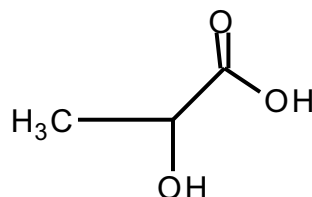


Fig. 1: Structure of Lactic Acid

Lactic acid is primarily produced via microbial fermentation of carbohydrates using lactic acid bacteria (LAB), such as *Lactobacillus spp.* (Oziegbe *et al.*, 2024). Compared to chemical synthesis, this biological route is more energy-efficient, environmentally benign, and compatible with renewable feedstocks (Ewing *et al.*, 2022). While conventional feedstocks like corn, cassava, and sugarcane have been widely used, they are also staple food crops, raising concerns over food-versus-fuel conflicts (Ferreira *et al.*, 2024; Jamshidian *et al.*, 2010).

To address this, recent efforts have focused on non-food biomass sources such as agricultural residues. Tamarind seeds (*Tamarindus indica* L.), a by-product of tamarind fruit processing, represent a promising feedstock due to their abundance and high polysaccharide content, particularly starch and xyloglucans (Nagar *et al.*, 2022; Ugawekar *et al.*, 2017). These polysaccharides can be hydrolyzed into fermentable sugars, primarily glucose and xylose, which serve as substrates for lactic acid production (Kelkar & Mahanwar, 2015). These characteristics make tamarind seeds a promising and sustainable feedstock for microbial fermentation. Importantly, their starch content is associated with low levels of fermentation inhibitors compared to lignocellulosic residues, simplifying the downstream fermentation process (Nagar *et al.*, 2022; Chandra-Mohan *et al.*, 2018).

Several researchers have demonstrated the feasibility of using tamarind seeds for lactic acid production. A study by Kelkar and Mahanwar (2015) demonstrated the feasibility of using tamarind kernel powder (TKP) as a cost-effective alternative to glucose for lactic acid production, which yielded 0.71 g of reducible sugar per gram of TKP. *Lactobacillus casei* NCIM-2125 showed nearly 90% sugar conversion, producing up to 81 g/L of lactic acid with a yield of 0.58 g/g TKP. The highlights TKP as a promising raw material for efficient lactic acid fermentation. Furthermore, a comprehensive review by Rahman *et al.* (2025) emphasized the importance of sustainable lactic acid production from agricultural waste, examining fermentation strategies (batch, fed-batch, continuous) and microbial selection. The review acknowledged tamarind seeds, among other agricultural residues such as sugarcane bagasse, rice husk, and corn stover, as viable non-food substrates.

Additional innovations continue to push the boundaries of lactic acid production. Bilal *et al.* (2024) demonstrated enzymatic hydrolysis of food waste for lactic acid production, achieving 20.75-27.16 g/L lactic acid, while Díaz-Orozco *et al.* (2025) emphasized the role of genetically modified microorganisms



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(GMMs) and Lactic Acid Bacteria (LAB) in enhancing lactic acid yields from lignocellulosic substrates. Similarly, Haris *et al.* (2023) demonstrated that enzymatic hydrolysis of date palm concentrate (DPC) could yield lactic acid concentrations of up to 457 g/kg under optimized conditions using *Lactobacillus casei*. Despite this progress, recent focused research on tamarind seeds as a lactic acid substrate remains sparse. Given the seed's high starch content, low inhibitor levels, and non-food status, it presents an excellent candidate for further investigation. Exploring this biomass aligns with circular bioeconomy principles and adds value to agricultural waste streams, contributing to sustainable development and low-carbon industrialization.

This study investigates the production of lactic acid from tamarind seeds using a two-step biological process. First, starch was extracted via wet milling and alkali treatment and characterized for fermentation suitability. Enzymatic hydrolysis using *Aspergillus niger* converted the starch into fermentable sugars, followed by anaerobic fermentation with *Lactobacillus* spp. to produce lactic acid. The final product was analyzed for yield and purity.

By valorizing tamarind seeds, an agricultural waste with no direct food use, this study contributes to circular bioeconomy practices, green chemistry, and low-cost, sustainable bioprocessing. It offers a viable path to reduce reliance on fossil-based resources in the chemical industry. The objective of this study is to develop a high-purity process for lactic acid production from tamarind seeds that is environmentally sound, sustainable, and economically viable. The study aims to support the growing demand for renewable biochemicals, particularly for the synthesis of polylactic acid, while simultaneously addressing issues of waste valorization and resource efficiency.

2. Materials and Methods

2.1 Materials and Reagents

Tamarind seeds were sourced from local markets in Kaduna, Nigeria, during the February 2025 harvest season. Analytical grade reagents, including sodium hydroxide (NaOH), citrate buffer, calcium carbonate (CaCO₃), yeast extract, de Man, Rogosa and Sharpe (MRS) agar, and Potato Dextrose Agar (PDA), were procured from a certified chemical supplier in Zaria, Nigeria. Additional reagents were obtained from the Microbiology Laboratory, Bayero University, Kano.

2.2 Isolation of *Lactobacillus* Spp.

Lactobacillus spp. was isolated from fermented milk following the method of Goa *et al.* (2022). A serial dilution (10^{-1} to 10^{-6}) was performed using sterile distilled water. A 0.1 mL aliquot of the final dilution was plated on MRS agar and incubated anaerobically at 37 °C for 48 h using a candle jar. Distinct colonies were sub-cultured into MRS broth supplemented with bromocresol purple for LAB identification and



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incubated for 5 days at 37 °C. Purity was confirmed via Gram Staining and Microscopy, revealing uniform rod-shaped morphology. Pure cultures were stored in 50% glycerol-phosphate buffer solution at –20 °C.

2.3 Preparation of *Aspergillus niger*

Pre-isolated *Aspergillus niger* cultures were sub-cultured on PDA and incubated for 5 days at 28 °C to ensure active growth. Before use, spores were suspended in sterile saline solution for uniform distribution.

2.4 Starch Extraction

Tamarind starch extraction was based on Tripathi *et al.* (2024) with modifications. Tamarind seeds were washed, roasted for 20 min to aid dehulling, and the seed coat was manually removed. The kernels were soaked in cold water for 48 h, then milled and mixed with distilled water. The slurry was treated with 0.05% NaOH for 12 h and filtered through muslin cloth. The filtrate was washed repeatedly to remove alkali, then settled overnight. The sedimented starch was dried at 40–60 °C, milled into powder, and stored in airtight containers.

2.5 Hydrolysis of Starch

Hydrolysis followed the procedure of Fathoni *et al.* (2020) with modifications. Tamarind starch suspension was gelatinized at 90–95 °C for 20 min, cooled to room temperature, and pH adjusted to 5.5 using citrate buffer. The solution was autoclaved (121 °C, 15 min), cooled to 50–60 °C, and inoculated aseptically with 10% (v/v) *A. niger* spore suspension. Incubation was carried out at 45 °C, 450 rpm for 72 h. Samples were taken at 24, 48, and 72 h and analyzed for glucose using the iodine test.

2.6 Fermentation

Fermentation was conducted following Assefa (2018) with slight modifications. Post-hydrolysis, the glucose-rich hydrolysate was filtered and neutralized using calcium carbonate (CaCO₃). Yeast extract was added to the neutralized hydrolysate as a nitrogen source. The mixture was sterilized at 121 °C for 15 min. The sterilized medium was inoculated with 10% (v/v) *Lactobacillus* spp. and incubated anaerobically at 37 °C for 5 days. After fermentation, the broth was filtered and centrifuged. Purification of lactic acid was performed via precipitation, repeated twice. The final product was analyzed using High-Performance Liquid Chromatography (HPLC) and Fourier Transform Infrared Spectroscopy (FTIR).

2.7 Characterization of Tamarind Seed Starch (TSS)

2.7.1 Proximate analysis

Moisture content was determined using a moisture analyzer; ash content via ignition in a muffle furnace; crude fat by Soxhlet extraction using n-hexane; crude fibre by the gravimetric method; and protein content using the Kjeldahl method ($N \times 6.25$). Carbohydrate content was estimated by difference.

2.7.2 Amylose content

Amylose content was determined using a rapid colourimetric method as described by Tripathi *et al.* (2024). A 20 mg starch sample was dissolved in 0.5 N KOH, diluted appropriately, and treated with 0.1 N HCl followed by iodine reagent. The absorbance was measured at 625 nm using a UV-2500PC Series (SHIMADZU, Japan) UV-Visible spectrophotometer operated within a wavelength range of 250–800 nm, at a slit width of 2.0 nm, in absorbance mode, under single scan and fast scan speed.

$$\text{Amylose content (\%)} = 3.06 \times \text{Absorbance} \times 20 \quad 1$$

$$\text{Amylopectin (\%)} = 100 - \% \text{ amylose content} \quad 2$$

3. Results and Discussion

3.1 Proximate Composition of Tamarind Seed Starch

The proximate composition of tamarind seed starch (TSS) is presented in **Table 1**. The results, reported as the average of triplicate determinations, indicate that the starch contains 4.42% protein, 2.28% fat, 3.65% crude fibre, 2.10% ash, and 9.61% moisture, while the carbohydrate content was calculated as 77.94%.

Table 1. Proximate composition of tamarind seed starch (TSS).

PROXIMATE PARAMETERS	VALUES %
Protein	4.42
Fats/Oil	2.28
Ash	2.10
Crude Fibre	3.65
Moisture	9.61
Carbohydrate	77.94

The relatively low protein content may be attributed to the processing conditions, particularly alkali treatment, soaking, and roasting, which are known to leach or denature proteins (Makinde & Ayodele, 2022; Nagar *et al.*, 2022). The observed fat content (2.28%) is consistent with values reported for heat-treated seeds, where roasting volatilizes oils (Mathur & Chaudhary, 2009). The low levels of non-starch components reflect the efficiency of the alkali-assisted wet milling method in purifying the starch.

3.2 Starch Yield and Amylose Content

The starch extraction yielded 53.54% (w/w, dry basis) of TSS, with a measured carbohydrate purity of 77.94%. The UV–VIS spectrophotometric analysis (**Fig. 2**) further characterized the starch, revealing an amylose content of 13.43% and a predominant amylopectin content of 86.57%. This high amylopectin-to-amylose ratio is particularly advantageous for enzymatic saccharification, as the branched structure of

amylpectin provides more accessible sites for amylolytic enzymes, thereby facilitating a more rapid and complete hydrolysis into fermentable glucose. While the amylose content aligns closely with some reported values for tamarind starch (e.g., 14.12%) (Tripathi *et al.*, 2024), variations exist in the literature (e.g., 27.55%) (Sudharsan *et al.*, 2016), which can be attributed to factors such as tamarind variety, geographical origin, and extraction methodologies. The high yield and purity of the extracted starch, coupled with its favourable amylopectin content, underscore its strong potential as a readily available and efficient carbon source for microbial fermentation, comparable to other starch-rich feedstock used in lactic acid production.

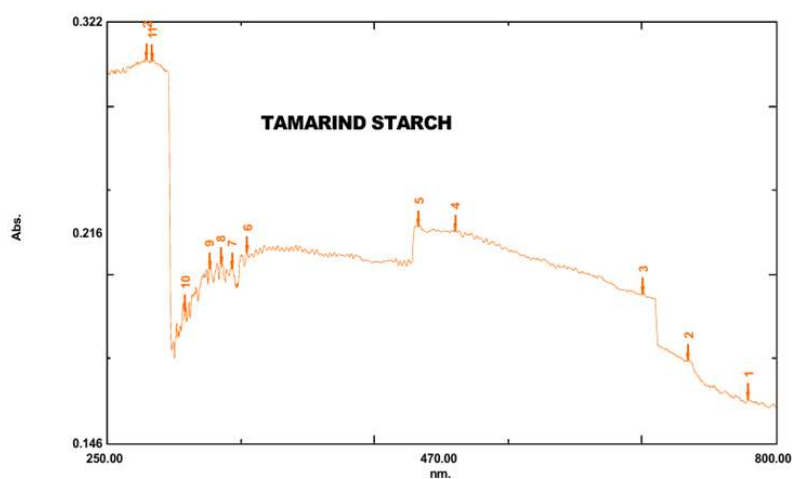


Fig. 2 UV- VIS Spectrophotometer of Tamarind Starch

3.3 FTIR Analysis of TSS

Fourier Transform Infrared (FTIR) spectroscopy (**Fig. 3**) provided crucial insights into the functional groups and structural integrity of the extracted TSS. The broad absorption band observed at 3463 cm^{-1} is characteristic of O–H stretching vibrations, indicating extensive hydrogen bonding within the polysaccharide matrix, a fundamental feature of starch. The weaker band at 2928 cm^{-1} corresponds to C–H stretching, confirming the presence of aliphatic hydrocarbon chains. More importantly, the distinct peaks at 1109 cm^{-1} and 1059 cm^{-1} are attributed to C–O–C and C–OH stretching vibrations, respectively, which are direct evidence of the glycosidic linkages that form the backbone of starch polymers. These spectral fingerprints collectively confirm the successful isolation of starch and its characteristic polysaccharide structure, which is essential for its subsequent enzymatic breakdown into fermentable sugars.

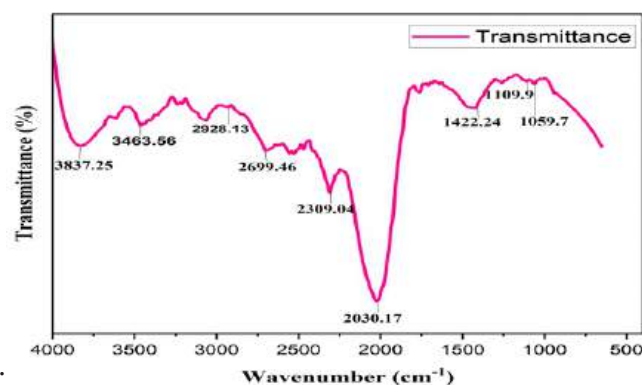


Fig. 3 FTIR Spectrum of Tamarind Seed Starch (TSS).

3.4 XRD Analysis of TSS

X-ray Diffraction (XRD) analysis of TSS (**Fig. 4**) was conducted using Shimadzu X-ray diffractometer, model XRD-6000 equipped with a graphite monochromator and using CuK radiation to elucidate the crystalline structure of the extracted tamarind seed starch (TSS). The diffractogram exhibited characteristic diffraction peaks at 17.31° , 19.60° , 21.70° , and 24.01° . These specific angles are indicative of an A-type crystalline pattern, which is commonly observed in cereal starches (Chandra-Mohan *et al.*, 2018). This A-type crystallinity arises from the ordered packing of amylopectin double helices within the starch granule. While crystallinity can sometimes pose a challenge to enzymatic hydrolysis by limiting enzyme accessibility, the A-type pattern generally suggests a more open structure compared to B- or C-type starches, potentially facilitating enzymatic saccharification without requiring overly harsh pretreatment conditions (Kaur & Singh, 2016; Zhou *et al.*, 2010).

The combined FTIR and XRD results provide robust evidence for the successful extraction and structural characterization of tamarind seed starch, confirming its suitability as a carbohydrate source for bioconversion into lactic acid.

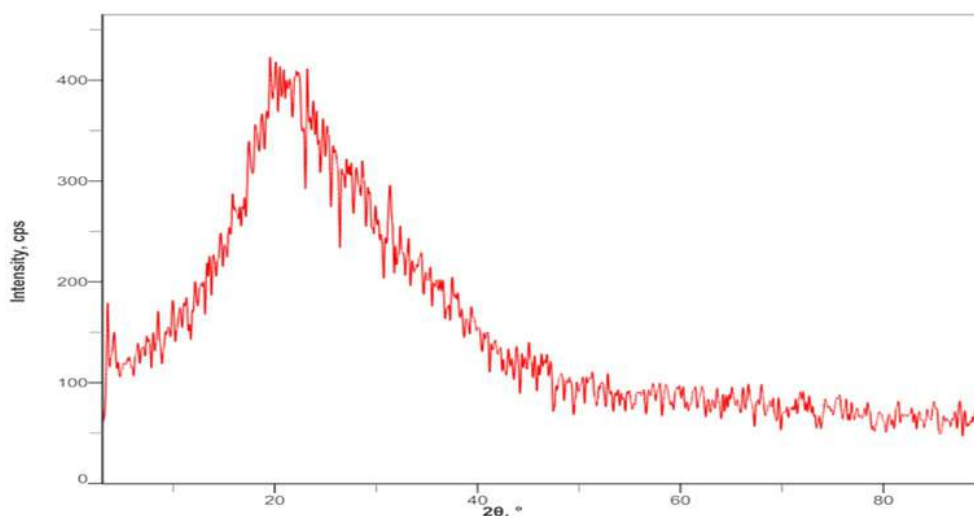


Fig. 4 X-Ray Diffraction of Tamarind Seed Starch (TSS).

3.5 Lactic Acid Production

Lactic acid was successfully synthesized via a two-step process comprising enzymatic hydrolysis using *Aspergillus niger* and microbial fermentation using *Lactobacillus* spp. The selection of *A. niger* is strategic due to its well-documented amylolytic activity, efficiently breaking down starch into fermentable glucose. The complete saccharification of starch was confirmed by a negative iodine test after 72 hours, indicating the successful conversion of complex polysaccharides into simple sugars, a critical prerequisite for efficient microbial fermentation. Subsequently, anaerobic fermentation of the glucose-rich hydrolysate with *Lactobacillus* spp. (isolated from fermented milk) yielded approximately 157 g of lactic acid over five days,

achieving a conversion efficiency of 49.58%. This result unequivocally demonstrates the technical feasibility of valorizing tamarind seed waste into a valuable bio-based chemical, aligning with the principles of agricultural waste valorization and the circular bioeconomy. While this initial conversion efficiency provides a robust baseline, it also highlights significant opportunities for process enhancement. For comparison, recent studies on other agro-residues have reported higher lactic acid concentrations, such as 20.75–27.16 g/L from restaurant food waste using engineered *Pichia pastoris* (Bilal *et al.*, 2024). This suggests that further optimization of fermentation parameters, including initial substrate concentration, nutrient supplementation (e.g., yeast extract), and the adoption of advanced fermentation modes like fed-batch or continuous simultaneous saccharification and fermentation (SSF) with enzyme and cell recycling, could substantially improve lactic acid productivity and yield (Rahman *et al.*, 2025). Such optimizations are crucial for mitigating common challenges like substrate and end-product inhibition, which are known to limit fermentation efficiency in batch processes.

3.6 HPLC Analysis of Lactic Acid

HPLC analysis of the fermented broth identified two prominent peaks at retention times 14.90 min and 16.21 min, corresponding to lactic acid stereoisomers (D- and L-lactic acid) (**Fig. 5**). The analysis was conducted using a Shimadzu LCsolution HPLC system (SHIMADZU, Japan) with a UV-Vis detector, and data were processed using LCsolution software. The respective peak area percentages were 33.64% and 35.54%, giving a total lactic acid purity of 69.18% (**Table 2**). Minor peaks were likely due to residual glucose or other metabolic by-products, indicating incomplete fermentation or the presence of interfering compounds from the starch source.

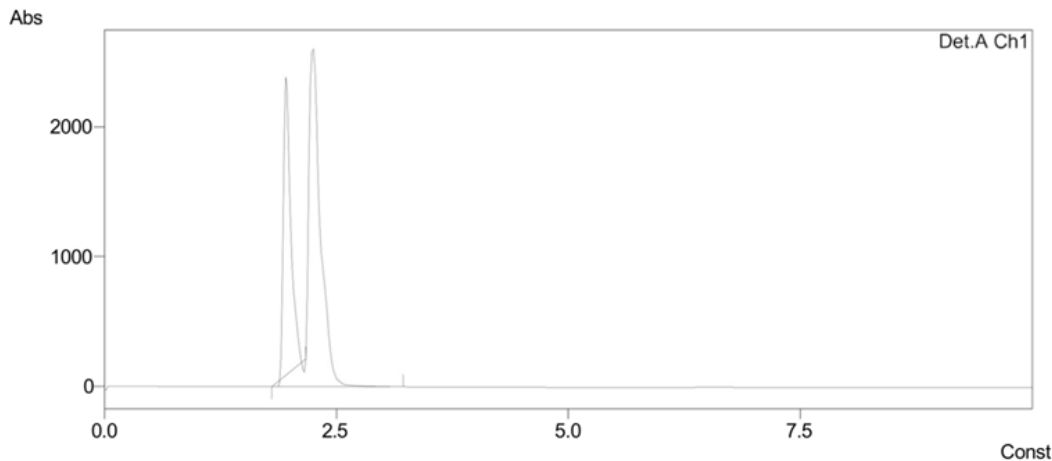


Fig. 5 HPLC Chromatogram of Tamarind Derived Lactic Acid.

Table 2: Peak Table for HPLC Chromatogram

Peak	Retention Time	Area	Height	Area %	Height %
1	14.90	22.7666	2302816	33.639	46.897
2	16.21	25.3456	240345	35.543	50.541

3.7 FTIR Analysis of Lactic Acid

Finally, Fourier Transform Infrared (FTIR) spectroscopy was utilized to confirm the chemical identity of the purified lactic acid product using FTIR – 8400S (SHIMADZU, Japan) at a frequency range $4000\text{ cm}^{-1} - 500\text{ cm}^{-1}$. The spectrum exhibited a characteristic strong and broad absorption band at 3372 cm^{-1} , indicative of the O–H stretching vibration from the hydroxyl group, which is extensively involved in hydrogen bonding within the lactic acid structure. A distinct peak at 2992 cm^{-1} was assigned to the aliphatic C–H stretching, confirming the presence of the methyl group. Crucially, an intense absorption peak at 1722 cm^{-1} corresponded to the C=O stretching vibration of the carboxylic acid functional group, which is a defining characteristic of lactic acid. Additional bands observed at 1045 , 1127 , and 1220 cm^{-1} further confirmed the presence of C–O stretching vibrations, consistent with both the hydroxyl and carboxylic acid functionalities inherent to the lactic acid molecule. These comprehensive spectroscopic analyses collectively provide robust evidence for the successful bioconversion of tamarind seed starch into lactic acid, validating the chemical nature of the synthesized product.

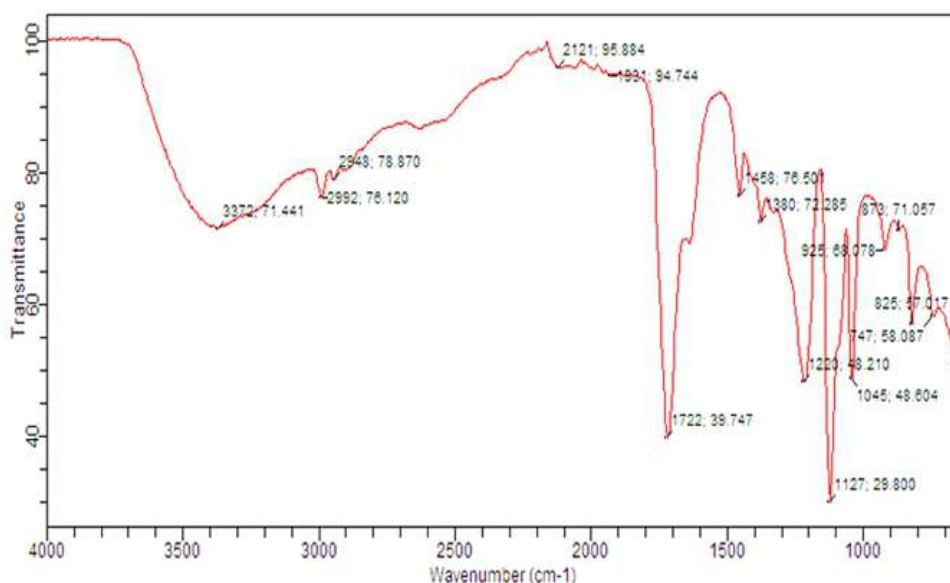


Fig. 6 FTIR Spectrum of Lactic Acid.

4.0 CONCLUSION

This study highlights the potential of tamarind seeds (*Tamarindus Indica* L.) as a sustainable and non-food source for lactic acid production through a two-step bioconversion method. This method combines biological hydrolysis using *Aspergillus niger* and microbial fermentation with *Lactobacillus spp.*, achieving a lactic acid yield of around 157g and a conversion efficiency of 49.58%. The extraction and characterization of starch from



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tamarind seeds demonstrates a high carbohydrate content (77.94%) and advantageous amylose and amylopectin ratios, validating its effectiveness as a substrate for fermentation. Analytical methods, including FTIR, XRD, and HPLC, confirmed the functional groups, crystallinity of the starch and purity of the produced lactic acid, with HPLC showing a total lactic acid purity of 69.18%.

Using tamarind seed waste presents numerous benefits, as it increases the value of an underutilized agricultural by-product, mitigates environmental waste, and sidesteps ethical issues related to using food crops for industrial purposes. Furthermore, the mild conditions and renewable inputs necessary for the bioconversion process align with global initiatives aimed at promoting green chemistry and decreasing reliance on non-renewables.



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A hybrid pressure drop coefficient model for a conical diffuser

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Abstract

The traditional manual procedures for calculating the pressure drop coefficient for a conical diffuser are inconvenient for computer-based simulations. In this study, using literature data, an artificial neural network (ANN)-based shock coefficient model (SCM) was developed using MATLAB's Neural Network Toolbox and the model parameters were optimized using the Global Search (GS) algorithm. The inputs to the ANN are Reynolds number and divergence angle, while the output is the shock coefficient. It was found that the GS-optimized ANN-based SCM with three hidden neurons, having R^2 of 0.9989 and maximum percentage absolute relative error (Max-PARE) of 18.83% outperformed the existing conventional SCM, having R^2 of 0.994 and Max-PARE of 33.03%. The GS-optimized ANN-based SCM was incorporated into the existing conventional pressure drop coefficient model (PDCM), thereby resulting in a hybrid PDCM having an R^2 of 0.9990 and a Max-PARE of 11.87% upon validation with the literature data. The hybrid PDCM was found to be significantly superior to the existing conventional semi-empirical PDCM, having an R^2 of 0.9942 and a Max-PARE of 21.86%. It can therefore be concluded that for practical applications, the new hybrid model can be used in lieu of the existing conventional semi-empirical model to accurately estimate the pressure drop coefficient for a conical diffuser.

Keywords: Artificial neural network; Global search; Pressure drop coefficient; Shock coefficient; Conical diffuser

1. Introduction

In oil and gas pipelines and other industrial applications, diffusers are critical components for managing fluid dynamics. The primary role of a conical diffuser is to recover static pressure from a fluid stream by gradually increasing the cross-sectional area. This deceleration of flow converts kinetic energy into pressure energy, a process essential for the optimal performance of downstream equipment like compressors and pumps. An efficient diffuser maximizes this energy conversion. The performance of a diffuser is therefore evaluated by its ability to increase static pressure, which is quantified by the pressure recovery coefficient.

Usually, flow transits from the inlet collector as pressure is reserved and builds up within the flow system due to continuous flow. This pressure built up in the system is needed as the velocity decreases downstream of the inlet duct to maintain the flow from the exit duct of the diffuser to the straight pipe. In a pipeline equipped with a conical diffuser, the static pressure undergoes significant changes due to the diffuser's design. This static pressure rise quantity is given in terms of the diffuser effectiveness, which is defined as the actual rise in pressure energy divided by the ideal reduction in kinetic energy (Karunakaran and Ganesan, 2009).



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In achieving a high-pressure recovery coefficient at the diffuser's exit, a downstream distance of about 4 to 6 exit duct diameters for full static pressure recovery is required (Idelchik, 1996). The performance of a diffuser is evaluated based on its pressure recovery and the uniformity of flow distribution at its outlet. Accurate estimation of the pressure drop coefficient is crucial for the design, optimization, and simulation of pipeline systems. Traditional methods for determining this coefficient are often tedious and time-consuming, involving manual data extraction from charts and the combination of multiple models. These methods are not well-suited for modern computer-based simulations.

To address these limitations, Mfon (2017) developed a single explicit mathematical model for the pressure drop coefficient estimation for a conical diffuser. Mfon's model is given in Equation (1),

$$\zeta_d = \frac{1.5(-2\log_{10}\left(\frac{\varepsilon/D}{3.71} - \frac{1.975}{Re}\left(\ln\left(\left(\frac{\varepsilon/D}{3.03}\right)^{1.092}\right) + \left(\frac{7.262}{Re + 395.9}\right)\right)\right))}{8\sin\frac{\alpha}{2}} \left(1 - \frac{1}{n_{ar}^2} + \phi\left(1 - \frac{1}{n_{ar}}\right)^{1.92}\right) \quad (1)$$

where ε/D denotes the relative roughness of the diffuser, α is the divergence angle (ranging from 5° to 180°), n_{ar} represents the area ratio, ϕ is the shock coefficient of the diffuser, and Re is the Reynolds number. Unfortunately, Mfon's model still requires the use of shock coefficient (ϕ) data obtained manually from a chart. A subsequent improvement by Mfon et al. (2019) was the development of a mathematical model for estimating ϕ , thereby making the overall model suitable for computer-based simulations. Despite this progress, the model accuracy was low, with the shock coefficient model having a maximum percentage absolute relative error (Max-PARE) of 33.03% and the overall pressure drop coefficient model of Max-PARE of 21.86% (Okafor, 2024). Several other modelling techniques, including the use of artificial intelligence have been attempted; however, the resulting models are still plagued with unsatisfactory accuracy. It is noteworthy that the performance of the shock coefficient model, a function of Reynolds number and divergence angle, contributes significantly to the overall performance of the pressure drop coefficient model. These results highlighted the need for further refinement of the model in order to enhance the predictive capability of the pressure drop coefficient model.

Bassey (2019) developed an artificial neural network (ANN)-based shock coefficient model for a conical diffuser. The model demonstrated notable improvements, achieving an R^2 of 0.9989, an RMSE of 0.000123, and a Max-PARE of 9.1%. While this represented a significant improvement compared to that of Mfon et al (2019), how it will perform when incorporated into the pressure drop coefficient model was not evaluated, leaving a gap in assessing its eventual effectiveness.

Umoren (2021) and Ukobo (2021) attempted to refine the parameters of the existing conventional pressure drop coefficient model using global optimization methods. Umoren (2021) used a multi-start global optimization approach to refine the parameters of the existing pressure drop coefficient model, particularly



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focusing on the shock coefficient model of the entire pressure drop coefficient model of the conical diffuser, while Ukobo (2021) used the simulated annealing method. Umoren's (2021) method achieved an R^2 , root mean squared error (RMSE) and the maximum percentage absolute relative error (Max-PARE) of 0.9942, 0.0194 and 17.94%, respectively. That of Ukobo (2021) attained an R^2 , RMSE and Max-PARE of 0.9912, 0.05649 and 17.77%, respectively. These results showed that the utilization of simulated annealing and multi-start global optimization techniques does not significantly improve the accuracy of the existing pressure drop coefficient model.

Okafor (2024) developed a hybrid model by combining an ANN-based shock coefficient model with a conventional pressure drop coefficient model. This replaced the model developed by Mfon et al (2019). Okafor (2024) obtained an ANN-based shock coefficient model with 4 hidden neurons. Statistical analysis of this model revealed that the R^2 , RMSE and Max-PARE values were obtained as 0.9988, 0.011548 and 8.7%, respectively. The shock coefficient model developed by Okafor (2024) is in close agreement with that of Bassey (2019). However, Okafor (2024) evaluated the impact of the ANN-based shock coefficient model on the overall pressure drop coefficient model. The resulting hybrid model achieved $R^2 = 0.9988$, RMSE = 0.00851, and Max-PARE = 13.03%, representing a notable improvement compared to the model by Mfon et al. (2019). Although the hybrid model demonstrates significant advancement, further refinement of the weighted parameters of the ANN-based shock coefficient model could yield even higher accuracy in predicting the pressure drop coefficient of a conical diffuser.

In a related effort, David (2024), in her attempt to improve the performance of the model developed by Mfon et al (2019), developed a Multi-Gene Genetic Programming (GP)-based shock coefficient model for the pressure drop coefficient model of a conical diffuser. The performance evaluation of the model shows that the Max-PARE is 13.8%, R^2 0.9972 and RMSE 0.018, indicating that the error values obtained are relatively small, which means the predicted shock coefficient model is closer to the observed model. When compared with the ANN-based shock coefficient models of Okafor (2024) and Bassey (2019), the MGGP model performed less favorably. This suggests that further refinement of an ANN-based shock coefficient model presents a promising pathway toward developing a more accurate pressure drop coefficient model for conical diffusers.

Consequently, in this study, a hybrid model for the pressure drop coefficient estimation for the conical diffuser is developed by integrating an Artificial Neural Network (ANN) based shock coefficient model, whose parameters are optimized using MATLAB's Global Search (GS) algorithm, into the existing conventional semi-empirical pressure drop coefficient model.

2. The Proposed Hybrid Model Development

The proposed model is obtained by modifying the model developed by Mfon (2017). Mfon's model is as



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given in Equation (1). Here, first, the shock coefficient is modelled using an ANN framework. Subsequently, the global search (GS) method is used to refine the weights and the biases of the obtained ANN-based shock coefficient model. Finally, the GS-refined ANN-based shock coefficient model is incorporated into the existing conventional pressure drop coefficient model.

2.1 An Overview of an ANN Framework

A 3-layer feed-forward ANN architecture was designed and implemented for the shock coefficient model. This architecture includes an input layer, a single hidden layer, and an output layer. The hyperbolic tangent sigmoid transfer function was strategically selected for the hidden layer due to its non-linear properties, which enable the network to learn complex, non-linear relationships between the input and output variables. A linear transfer function was chosen for the output layer, as it is well-suited for regression problems where the output is a continuous value. The number of neurons in the hidden layer was determined through an iterative trial-and-error process. This process involved systematically varying the number of neurons and selecting the configuration that minimized the errors on the training set while also avoiding overfitting. The training of the network was performed using the Levenberg-Marquardt back-propagation algorithm, a highly efficient and widely-used optimization algorithm for training ANNs, known for its rapid convergence and good performance on a variety of problems (Hagan and Menhaj, 1994).

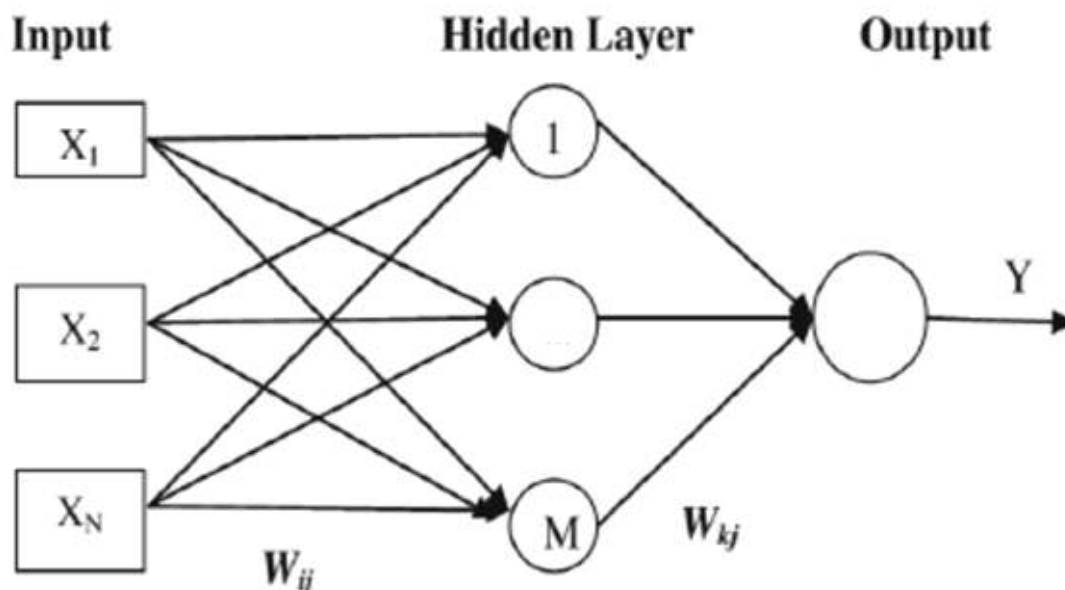


Fig. 1. A typical multi-layer feed-forward neural network (MFFNN) architecture, showing input, hidden, and output layers (Source: Yilmaz et al., 2015)

2.2 Global Optimization

Global optimization is a vital field in computational mathematics and operations research. Its primary goal is to identify the best possible solution across the entire feasible solution space, rather than settling for locally optimal solutions. This approach is especially pertinent when dealing with complex, nonlinear problems that may contain multiple local minima or maxima; a common scenario in fields such as engineering design, economics, and machine learning (Horst & Pardalos, 1995). Global optimization employs a variety of strategies to ensure comprehensive exploration of the solution space and mitigate the risk of becoming trapped within local optima (Deng, 2022). Commonly employed techniques include: multi-start, simulated annealing, branch and bound, global search and metaheuristic approaches. In this study, the global search (GS) method is adopted. The GS is a hybrid method that blends repeated local searches from randomly or systematically selected starting points with strategic perturbations to navigate away from local minima (Floudas and Aggarwal, 1989). The typical workflow of GS includes:

- i. Initialization: Select an initial point within the solution space.
- ii. Local Optimization: Apply a local solver (e.g., gradient descent) to find a nearby local optimum.
- iii. Perturbation: Slightly disturb the current solution to move into a new region.
- iv. Iteration: Repeat the cycle of local optimization and perturbation from multiple starts until a termination condition is met.

This methodology achieves a balance between intensive local refinement and broader exploration, making it especially well-suited for tackling nonlinear, non-convex problems found in engineering and machine learning model tuning (Schonlau et al., 1998; Gao et al., 2019). Global Search (GS) algorithm from MATLAB's global optimization toolbox was used to optimize the ANN parameters (the weights and the biases). This hybrid optimization approach effectively combines a multi-start method with a local solver, in this case, the `fmincon` function.

The GS algorithm operates by systematically generating multiple initial points within the solution space. From each of these starting points, a local search is initiated. By exploring this solution space from numerous diverse locations, the algorithm significantly increases the probability of identifying the global minimum of the objective function and successfully navigating past any local minima that may exist in the complex error landscape.

2.3 Data and Software

The experimental datasets used in this study to train, test, and validate the developed models were obtained from the literature (Idelchik, 1996). Specifically, a total of 39 data points were utilized for developing the ANN-based shock coefficient model, while 2,600 data points were employed for the pressure drop coefficient model.

The datasets for the shock coefficient model contain information on diffuser geometry, particularly the divergence angle (α) and the corresponding turbulent flow characteristics represented by the Reynolds number. The output variable is the shock coefficient (Φ), a dimensionless parameter that quantifies the pressure loss due to shock formation within the diffuser. To ensure the robustness and generalization capability of the ANN model, the 39 data points (see Table 1 for their pre-processed data ranges) were randomly partitioned into three subsets: 70% for training, 15% for validation, and 15% for testing. All input and output variables were normalized to a range between -1 and 1 to improve training efficiency and numerical stability.

A Microsoft Excel spreadsheet was used for data organization and graphical evaluation, while the Global Optimization Toolbox in MATLAB R2016a was used to optimize the ANN-based shock coefficient model parameters.

Table 1: Minimum and Maximum Values of the entire Pre-Processed Dataset



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Dataset	Minimum	Maximum
Divergence angle (α) ($^{\circ}$)	0.6987	2.255273
Reynolds No. (Re)	4.69897	5.778151
Shock Coefficient (ϕ)	0.04	1.02

2.4 System Hardware

The neural network model training and optimization were performed using a HP 840 G3 computer, equipped with an Intel® Core™ i5-6300 CPU @2.40GHz, 2.50GHz, and a 256GB SSD. The computation time in this study reflects the processing capabilities of this hardware configuration.

2.5 Performance Evaluation of the Proposed Hybrid Model

The performance of the optimized shock coefficient model was evaluated using a set of standard statistical metrics. These metrics include the coefficient of determination (R^2), which indicates the proportion of the variance in the dependent variable that is predictable from the independent variables; the Root Mean Squared Error (RMSE), which measures the average magnitude of the errors; and the Maximum Percentage Absolute Relative Error (Max-PARE), which shows the maximum relative deviation of the model's predictions from the experimental data. The final step of the methodology involves integrating the optimized ANN-based shock coefficient model into the existing semi-empirical framework of Mfon (2017) to form the new hybrid model and then the evaluation of its performance with the same set of statistical metrics before conducting a comparative analysis where the performance of the newly developed hybrid model was benchmarked against several existing models from the literature.

Performance Metrics	3-Neurons	4-Neurons
Max-PARE (%)	18.83	7.28
RMSE	0.01117	0.01088
R^2	0.9989	0.99896

As shown in Table 2, the ANN with 4 neurons, having a Max-PARE of 7.28%, an RMSE of 0.01088, and an R^2 of 0.99896, provides a better performance for the optimized shock coefficient model than the one with 3 neurons. The effectiveness of these two ANNs when incorporated into the overall pressure drop coefficient model was evaluated, and the results are shown in Table 3.

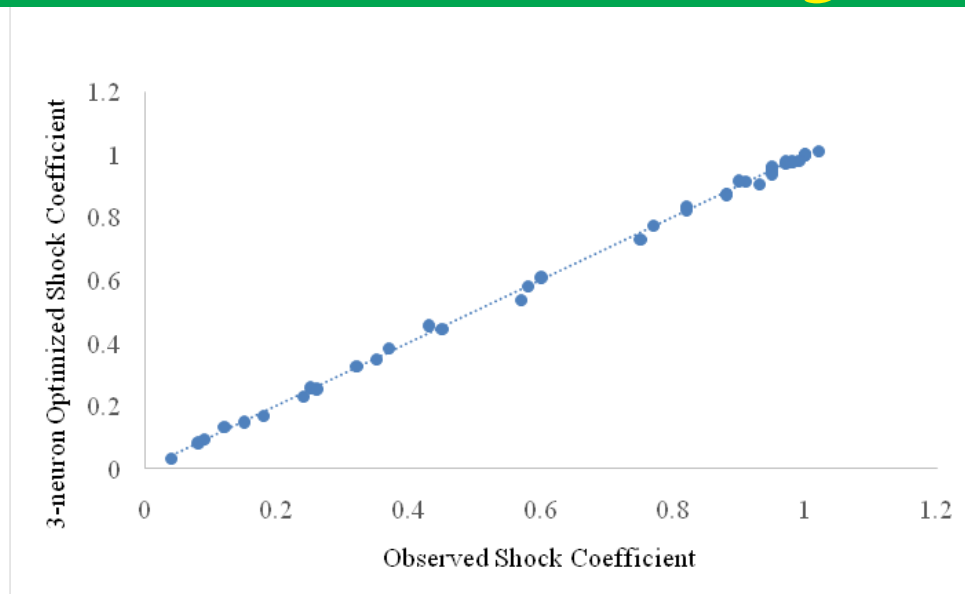


Fig. 2: Plot of the 3-neuron GS-optimized Shock Coefficient and the Observed Shock Coefficient

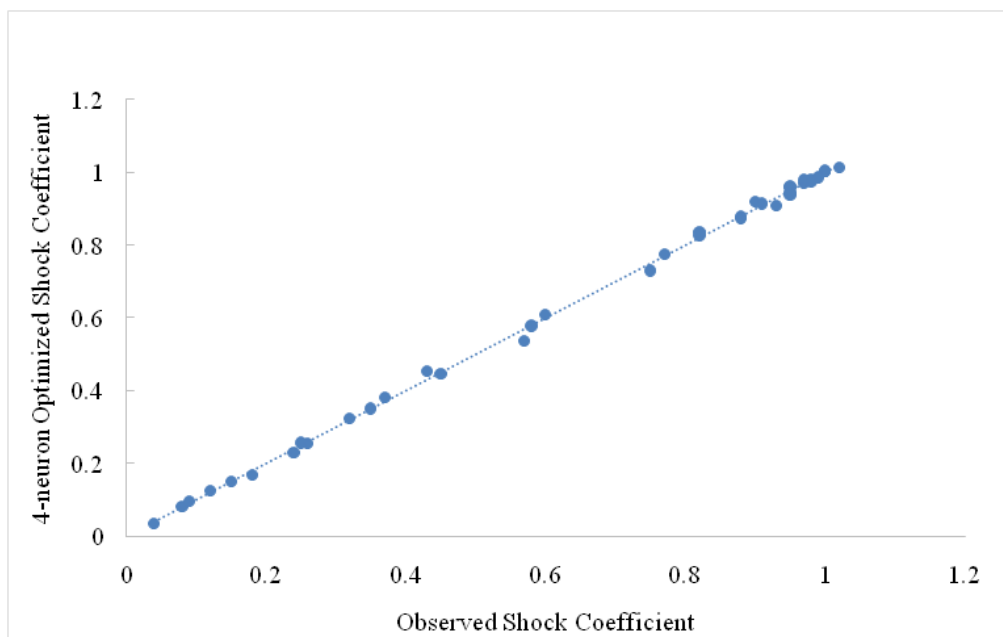


Fig. 3: Plot of the 4-neuron GS-optimized Shock Coefficient and the Observed Shock Coefficient

Table 3: Performance of the pressure drop coefficient model using the GS optimized ANN-based shock coefficient models

Performance Metrics	3-Neurons	4-Neurons
Max-PARE(%)	11.87	11.86
RMSE	0.00875	0.0083165
R ²	0.9990	0.9989

From Table 3, it is observed that the performances of the two shock coefficient models are in close agreement. Consequently, the GS-optimized model with 3 neurons was adopted for integration and comparative analysis with other existing models, as it offers a more compact structure. Therefore, the new GS-optimized ANN-based shock coefficient model is given in Equation (2).

$$\phi = \tanh(\alpha 1.64400378741273 + \text{Re} (-0.292659402430392) + 0.61152105374982) * 0.460828996199919 + \tanh(\alpha * 2.52613068720035 + \text{Re} * 3.84059368433445 + 1.74251861920232) * -0.0481285083631762 + \tanh(\alpha * 4.97900257978795 + \text{Re} * -0.1018467475324 - 0.0026411751418901) * 0.543701341517664 - 0 - 0.237718708552563$$

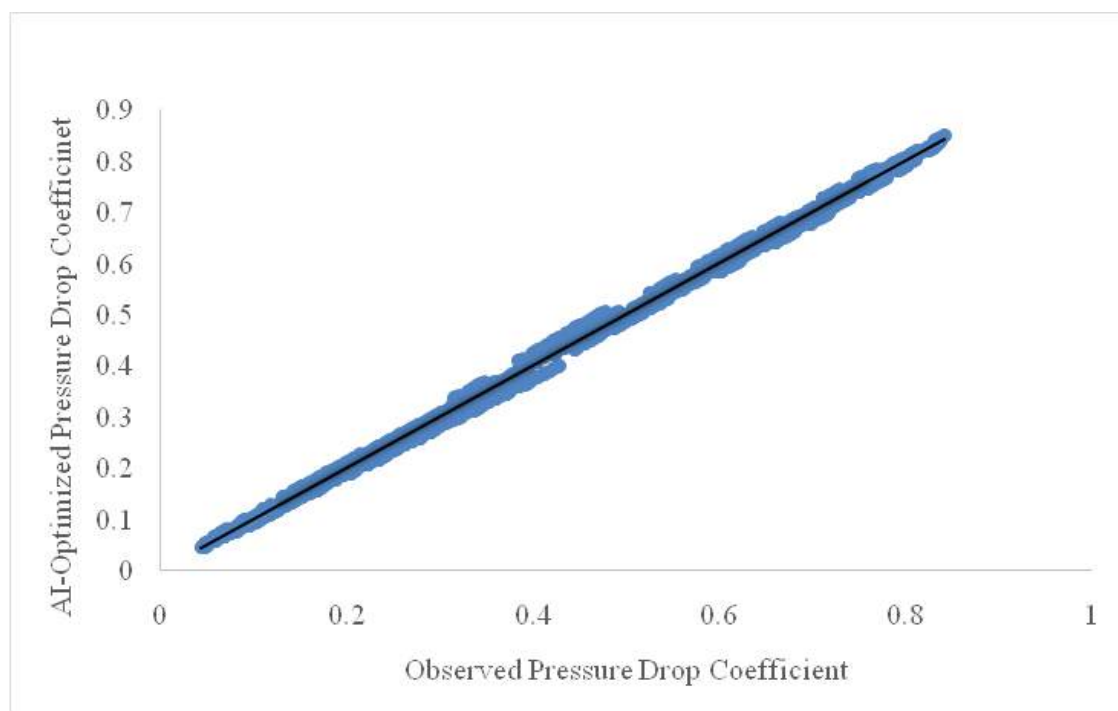


Fig. 4: Plot of the AI-Optimized Pressure drop Coefficient and the Observed Pressure drop Coefficient

3.1 Performance of the GS-optimized ANN-based Shock Coefficient Model and the Existing Models

The performance of the GS-optimized ANN-based shock coefficient model from this study was compared with that of the existing models from the literature. The results are shown in Table 4.

Table 4: Comparison between the optimized ANN-based shock coefficient model and existing shock coefficient models

Model	Max-PARE (%)	RMSE	R ²
Mfon et al (2019)	33.03	0.00064	0.994
Bassey (2019)	9.1	0.000123	0.9989
Okafor (2024)	8.7	0.011548	0.9988
This study	18.83	0.01117	0.9989

From Table 4, it can be seen that the optimized ANN-based shock coefficient model with three neurons obtained in this work only outperforms Mfon's model based on Max-PARE but on the RMSE criterion, compares favourably with the 4-hidden neuron ANN-based shock coefficient model developed by Okafor (2024), offering a more compact structure.

3.2. Performance of the Existing and Hybrid Pressure Drop Coefficient Models

From the literature, the best existing model for estimating the pressure drop coefficient of a conical diffuser was developed by Akpan (2019) using a MATLAB neural network. Table 5 shows the performance of the existing pressure drop coefficient models and the hybrid model developed in this study.

Table 5: Performances of the existing pressure drop coefficient models and that of this study

Model	Max-PARE (%)	RMSE	R ²
Mfon et al (2019)	21.86	0.01919	0.9942
Akpan (2019)	8.87	0.00391	0.9997
Okafor (2024)	13.03	0.00851	0.9988
This study	11.87	0.00875	0.9990

The results presented in Table 5 indicate a clear improvement in the performance of the pressure drop coefficient model developed in this study, particularly when compared with the conventional model by Mfon et al. (2019). It is also slightly better than that of Okafor (2024) despite having fewer neurons than the latter. Although Akpan's (2019) ANN-based pressure drop coefficient model exhibits better performance than the hybrid model developed in this study (3% better in terms of Max-PARE), it is not compact, as it requires the use of 20 hidden neurons to achieve its reported level of accuracy while the hybrid model developed this study requires only 3 neurons with an impressive MAX-PARE of 11.87%.



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4. Conclusion

This study developed and validated a hybrid model for predicting the pressure drop coefficient of a conical diffuser by integrating a GS-optimized artificial neural network (ANN) shock coefficient model into a conventional pressure drop coefficient model. The optimized three-neuron ANN-based shock coefficient model emerged as the most suitable configuration, giving rise to a hybrid pressure drop coefficient model having a Max-PARE of 11.87%, an RMSE of 0.00875, and an R^2 of 0.9990. This model outperforms the existing pressure drop coefficient models, with the exception of that of Akpan of 2019. Although Akpan's 20-hidden neuron ANN model is reported to be ~3% more accurate than the hybrid model in this study, the latter is much more compact, with just a three-hidden neuron model embedded in a conventional model, which provides a robust, efficient, and industry-ready solution for estimating the pressure drop coefficient for a conical diffuser.



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Machine Learning Modelling and Simulation of A Constructed Wetland System for Waste Water Treatment

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Abstract

The complexity of wastewater treatment processes and the variability of influent composition present significant challenges in system design and performance optimization. This study employed a data-driven modelling approach using machine learning techniques implemented in MATLAB to simulate pollutant removal in a subsurface flow constructed wetland located at the University of Lagos. Four models, which include linear regression, support vector machine (SVM), bagging ensemble model (BEM), and artificial neural network (ANN), were developed to predict outlet concentrations of dissolved oxygen, nitrate, and phosphate based on inlet concentrations at multiple sampling points. Data transformation techniques, including raw scaling, Min-Max normalization, and Z-score normalization, were applied to enhance model performance. The ANN model achieved the highest predictive accuracy for Dissolved Oxygen (DO), nitrate, and phosphate, with R^2 values exceeding 0.99 and RMSE values below 0.06 for DO_Out under Z-score normalization. The linear and SVM models also performed well for DO and nitrate, particularly with Min-Max normalization, while the BEM model was most effective for phosphate prediction. The results confirmed that machine learning models could accurately simulate pollutant dynamics in constructed wetlands. The study recommends the use of ANN models with appropriate normalization techniques for integrated prediction of multiple water quality parameters, offering a reliable tool for enhancing the design and operation of nature-based wastewater treatment systems.

Keywords: Wastewater treatment, Modelling, Machine learning, Constructed wetland, Pollutant removal, MATLAB

1. Introduction

Water is a crucial necessity for life, yet only about 0.3% of the planet's water resources are usable (Kılıç, 2022). Requirement for water grows as the world's population does. However, anthropogenic activities have significantly contributed to the degradation, depletion, and contamination of available water sources. As a result, recycling wastewater is important because there will always be a need for more water.

Wastewater, defined as water whose physical, chemical, or biological characteristics have been altered due to contamination, is typically generated from domestic, industrial, and commercial activities (Amoatey & Bani, 2011). It is often contaminated by domestic, industrial, and commercial use. Excretory waste, food waste, oils, soaps, and chemicals are among the substances that can contaminate wastewater. Despite comprising 99.9% water and only 0.1% contaminants, untreated or inadequately treated wastewater poses

severe risks to aquatic ecosystems, public health, and water security (Tuser, 2021). The adverse impacts include eutrophication, oxygen depletion, habitat destruction, and contamination of potable water sources (Ambulkar & Nathanson, 2022).

Constructed wetlands (CWs) have been widely adopted as nature-based solutions for decentralized wastewater treatment. These engineered systems emulate the biogeochemical processes of natural wetlands, utilizing vegetation, substrates, and microbial communities to facilitate pollutant removal through sedimentation, filtration, adsorption, and biodegradation. CWs are recognized for their cost-effectiveness, low energy requirements, and operational simplicity, particularly in rural and peri-urban contexts (Domínguez-Solís et al., 2025). However, the complexity of interacting physical, chemical, and biological mechanisms within CWs has led to their characterization as “black-box” systems, complicating efforts to optimize performance and predict treatment outcomes (Biswal & Balasubramanian, 2022).

Recent advancements in computational modelling have enabled the application of machine learning (ML) techniques to simulate and predict pollutant removal efficiencies in CWs. Studies such as Kiiza et al. (2020) demonstrated the efficacy of artificial neural networks (ANNs) in modelling nitrogen and phosphorus removal in vertical subsurface flow CWs. Similarly, Zhang et al. (2020) employed genetic algorithm-assisted ML models to enhance predictive accuracy for pollutant removal under varying hydraulic and environmental conditions.

Despite these developments, limited research has focused on CWs treating domestic wastewater in tropical urban environments, particularly systems configured in series. Moreover, comparative evaluations of multiple ML algorithms such as linear regression, support vector machines (SVM), bagging ensemble models (BEM), and ANNs across different data transformation techniques remain underexplored.

This study addressed these gaps by modelling and simulating pollutant removal (dissolved oxygen, nitrate, and phosphate) in a subsurface flow constructed wetland system located at the University of Lagos. The system was designed to treat domestic wastewater using a series of horizontal subsurface flow cells. MATLAB was utilized to implement and compare the performance of various ML models under different data transformation regimes. The novelty of this research lies in its integration of real-world operational data with a robust ML framework, offering insights into model selection, transformation effects, and predictive accuracy for ecological wastewater treatment systems.

2. Materials and Methods

2.1. Location of Study

The Central Sewage Inception Chamber is located within the University's Services Area and receives residential sewage from the campus community via a network of sewers. Sewage is pumped into two oxidation tanks, which serve as the initial treatment stage.

Following this, the wetland system is designed to receive and process large particles that have been filtered out in a Grit Removal Chamber. These particles are subsequently directed to an anaerobic digester for further breakdown.

The total area of the Subsurface Flow Constructed Wetland (SSFCW) was determined based on the model proposed by Vymazal and Kropfelová (2008). The SSFCW receives an average sewage influent of 380 m³/day and spans a total area of 7,200 m².

The wetland is divided into nine (9) cells, each measuring 800 m² in area and 0.65 m in depth. These cells are subsurface horizontal flow wetland structures, planted with *Cyperus papyrus* and filled with a substrate mixture of gravel and ocean sand. The substrate has an average particle size ranging from 0.1 mm to 0.35 mm.

A schematic layout of the Constructed Wetland Sewage Treatment System is provided below.

2.2. Data

Data for this study were obtained from previous analyses of wastewater collected from sample points 1 to 11 along the longitudinal profile of the CW over several weeks during active operation of the facility. The parameters assessed in this study include dissolved oxygen, phosphate, and nitrate.

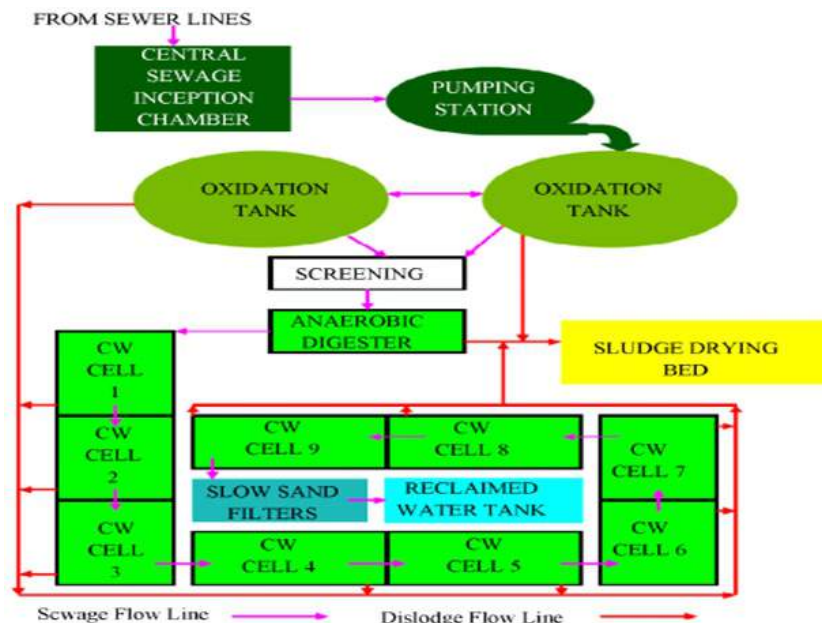


Fig. 1: Layout of Unilag constructed wetland sewage system (Adelere et al., 2014)

2.3. Model Development with MATLAB

MATLAB was employed to construct and evaluate multiple predictive models for wastewater parameter estimation. The dataset was imported from an Excel file using the `readtable` function and stored in the `dataTable` variable. To ensure reproducibility, the `rng` function was used to initialize the random number generator with a fixed seed. Predictor variables and the response variable were extracted from the dataset, and a holdout cross-validation strategy was implemented using the `cvpartition` function, with 20% of the data reserved for testing. The training and test sets were subsequently defined based on the partition indices. Three different data transformation functions were defined for the dissolved oxygen data. These functions included the logarithm to the base e (referred to as `log`), the logarithm to the base 10 (referred to as `log10`), and the identity transformation (referred to as `raw`). For the Nitrate and Phosphate data, aside from the identity transformation, two different normalization techniques were used to transform the data. These techniques included Min-Max and Z-score normalisation. The code defines 4 models based on linear regression, a support vector machine for regression, an ensemble of decision trees (bagging), and an artificial neural network (ANN), and assigns descriptive names to them. The artificial neural network architecture consisted of 3 hidden layers for the DO data, with 10, 8, and 5 neurons in each layer, and 1 hidden layer with 10 neurons for the Nitrate and Phosphate data. The neural network used the sigmoid activation function for the hidden layers and the linear activation function for the output layer. The code



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initializes arrays to store the results. The outer loop goes over each data transformation. The transformation is applied to the training and test sets. The inner loop goes over each model. The model is fitted on the transformed training data. The fitted model is used to make predictions on the transformed training and test data. RMSE and R^2 statistics are computed for the transformed training data. The RMSE and R^2 statistics are calculated for the transformed test data. The results are stored in the arrays created earlier. A table is created from the arrays containing the results. Each row of the table corresponds to a particular combination of data transformation and model. The table is then displayed in the Command Window.

2.3. Model Development for Combined Pollutants using ANN

The ANN model was selected for this study due to its proven capability to model complex, nonlinear relationships between input and output variables in environmental systems. Wastewater treatment processes, particularly in constructed wetlands, involve multiple interacting physical, chemical, and biological mechanisms that are inherently nonlinear and dynamic. Traditional statistical models often fall short in capturing these complexities, especially when multiple pollutants are involved simultaneously.

ANNs have been widely applied in environmental modelling due to their flexibility, adaptability, and ability to generalize from data. In this study, a feed-forward neural network architecture was implemented with three input variables representing the concentrations of dissolved oxygen, nitrate, and phosphate and three corresponding output targets. This configuration allowed for the simultaneous prediction of multiple pollutant concentrations, thereby improving computational efficiency and enabling integrated performance evaluation.

The ANN model was trained using data collected over a ten-week operational period from a subsurface flow constructed wetland system. To enhance model performance and stability, three data transformation techniques, such as Z-score normalization, Min-Max normalization, and raw data, were applied prior to training. The network architecture consisted of a single hidden layer with ten neurons, chosen based on preliminary sensitivity analysis and computational constraints. The sigmoid activation function was used in the hidden layer, while a linear activation function was applied at the output layer to accommodate the continuous nature of the target variables.



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3. Results and Discussions

The performance of the models varied significantly across pollutants and data transformation techniques. Root Mean Square Error (RMSE) and the coefficient of determination (R^2) were used as performance metrics. Lower RMSE values indicated better predictive accuracy, while higher R^2 values reflected stronger correlation between predicted and actual values.

Dissolved Oxygen

The linear regression and support vector machine (SVM) models demonstrated superior performance across all data transformation techniques. The linear model achieved RMSE values of 0.11654 (training) and 0.063635 (testing), with corresponding R^2 values of 0.72819 and 0.93365. The SVM model yielded similar results, with RMSE values of 0.11791 and 0.057583 for the train and test data, as well as R^2 values of 0.72819 and 0.93365 for the train and test data. These findings are consistent with Rizal et al. (2022), who reported that SVM and linear models performed well in predicting dissolved solids in river systems.

Nitrate

Model performance for nitrate prediction was highly sensitive to the data transformation applied. Both Z-score and Min-Max normalization significantly outperformed raw data across all models. The Min-Max normalized linear and SVM models achieved the lowest RMSE values of 0.13179 and 0.11258, and the highest R^2 values of 0.78029 and 0.94202, respectively.

Phosphate

The bagging ensemble model (BEM) consistently outperformed other models for phosphate prediction, regardless of the data transformation applied. It achieved the lowest RMSE and highest R^2 values for both training and testing datasets. Min-Max normalization and raw data transformations yielded better results than Z-score normalization. This supports the conclusions of Gulyani & Fathima (2017), who found ensemble models to be robust and effective in capturing nonlinear behaviours in wastewater treatment systems.

Combined Pollutants

Based on the results in Table 4.4, it is evident that the ANN model performs differently depending on the data transformation applied. For the Z-score normalized data, the ANN model achieves the highest R^2 values for

the 'DO Out' variable, which is the concentration of the outlet dissolved oxygen, with an R^2 of 0.96954 and 0.99804 for the train and test data.

Table 1: RMSE and R^2 value of ANN for dissolved oxygen, nitrate and phosphate

Data transformation	train_rmse	test_rmse	train r^2	test r^2
DO_ZScoreNorm	0.4603	0.48269	0.96954	0.99804
N_ZScoreNorm	0.34937	0.39188	0.95993	0.64357
P_ZScoreNorm	0.3659	0.42378	0.9924	0.99317
DO_MinMaxNorm	0.10734	0.14782	0.97526	0.99642
N_MinMaxNorm	0.082373	0.093688	0.95391	0.96265
P_MinMaxNorm	0.1587	0.1483	0.98625	0.90623
DO_raw	1.4038	1.487	0.98835	0.076539
N_raw	3.7136	5.7073	0.90148	0.14809
P_raw	8.4825	11.9	0.48564	0.48282

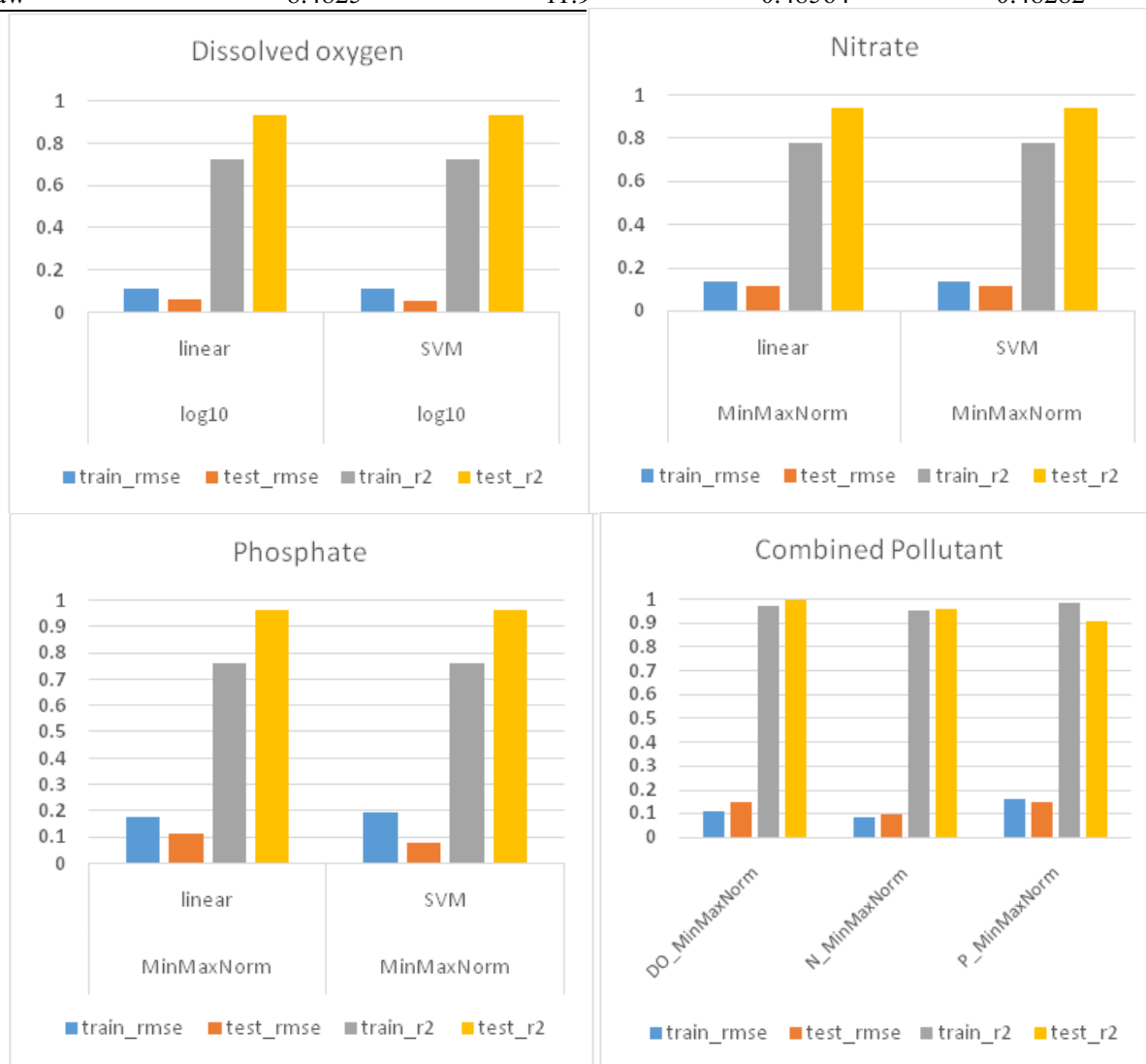


Fig. 2: Graphical representation of the results

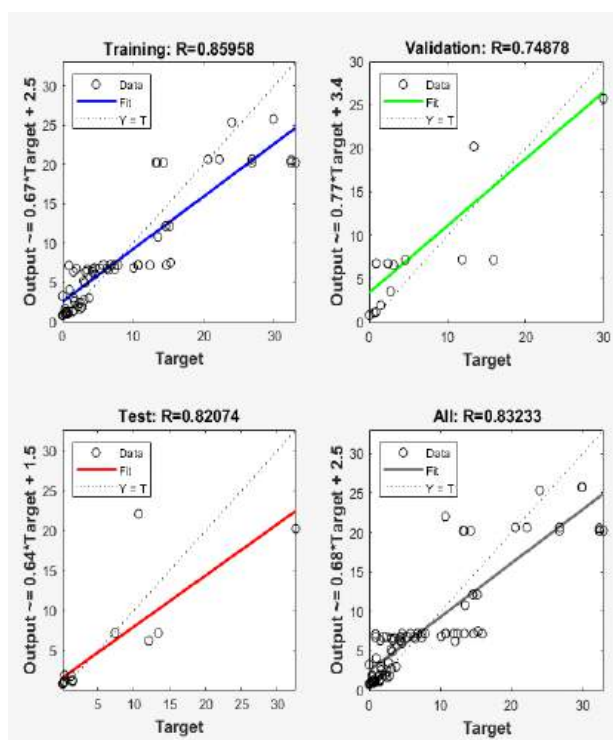
Figure 4 shows a comparison of the actual and predicted values generated by the support vector machine for the decrease in phosphate concentration along the CW.

4. Conclusion

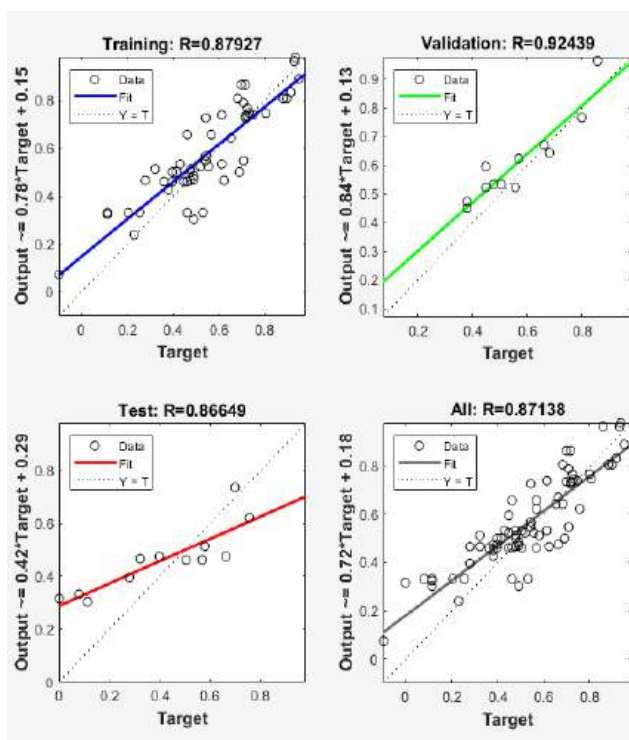
This study demonstrated the effectiveness of machine learning models in predicting pollutant concentrations, specifically dissolved oxygen, nitrate, and phosphate, in a subsurface flow constructed wetland system treating domestic wastewater. The models were trained and evaluated using operational data collected over ten weeks, with performance assessed through RMSE and R^2 metrics.

The results indicated that linear regression and support vector machine (SVM) models, when combined with Min-Max normalization, were highly effective for predicting dissolved oxygen concentrations. For phosphate prediction, the bagging ensemble model (BEM) consistently outperformed other models across all data transformation techniques. The artificial neural network (ANN) model achieved the highest predictive accuracy when applied to Z-score and Min-Max normalized data, particularly for DO_Out, where R^2 values exceeded 0.99 on the test set.

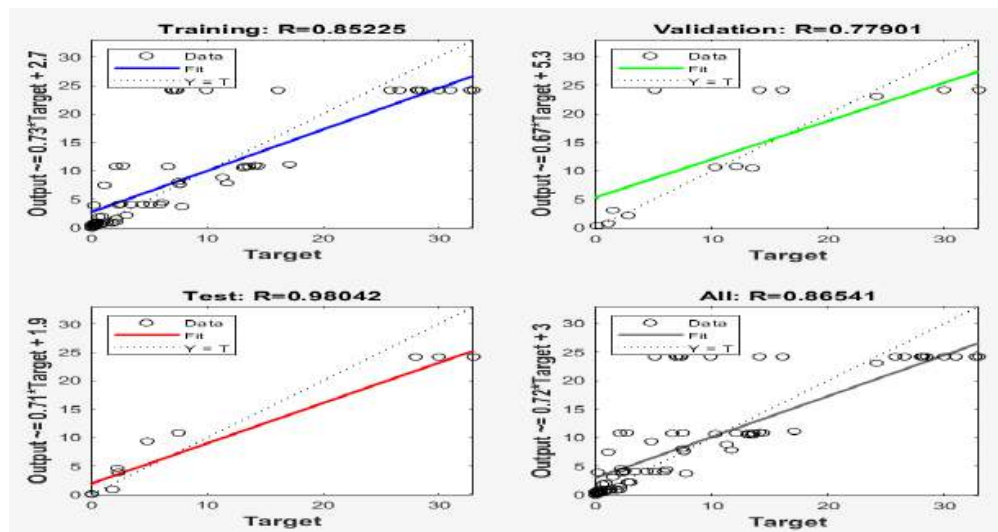
This research confirmed that pollutant concentrations in constructed wetlands could be predicted with high accuracy using machine learning models. Among the data transformation techniques evaluated, Min-Max normalization yielded the most consistent improvements in model performance. The findings support the recommendation to adopt ANN models with appropriate normalization for integrated prediction of multiple water quality parameters in ecological wastewater treatment systems.



(a) Dissolved Oxygen

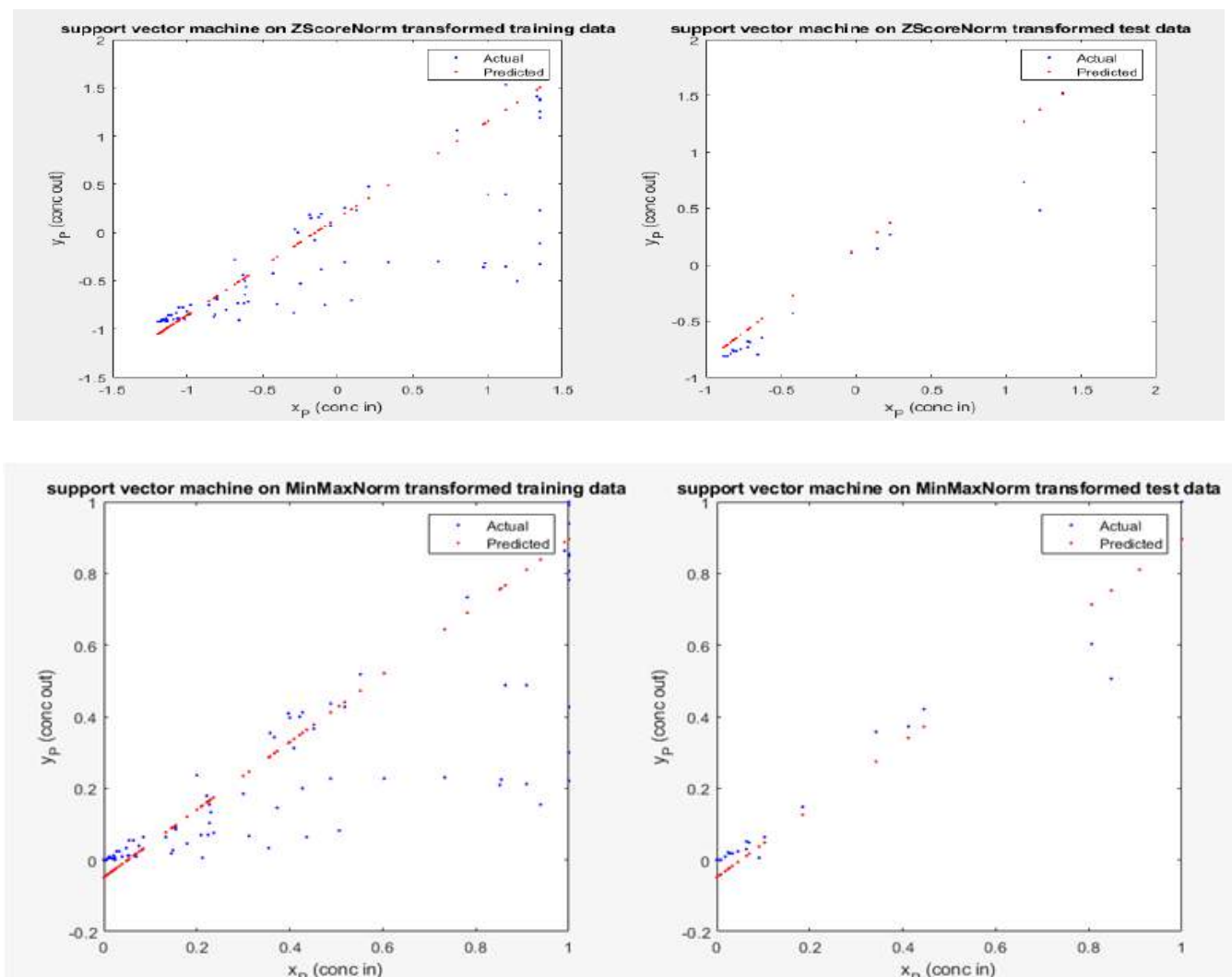


(b) Nitrate



(c) Phosphate

Fig. 3: The regression analysis of ANN for (a) Dissolved Oxygen (b) Nitrate (c) Phosphate



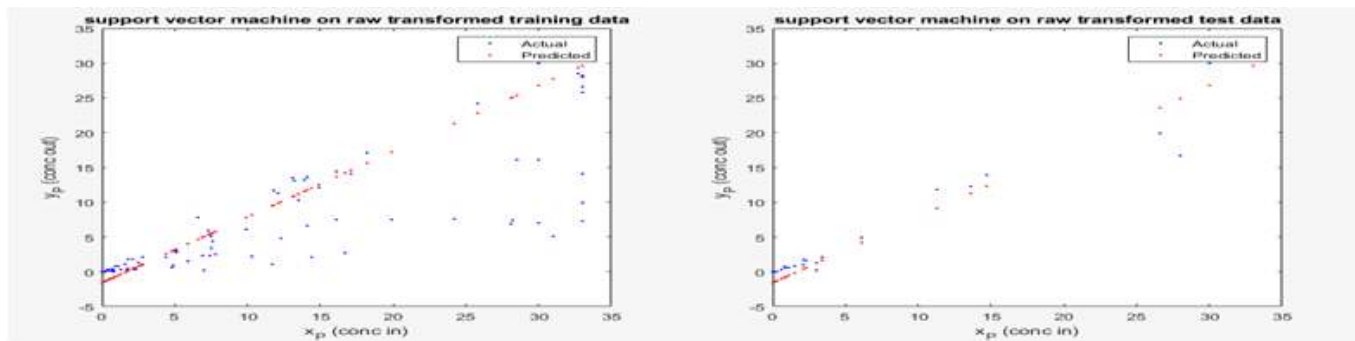


Fig. 4: The performance of SVM on phosphate ZScoreNorm, MinmaxNorm and raw transformed data



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