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ENHANCING CARBON (IV) OXIDE ADSORPTION FROM FLUE GAS MIXTURE AT ELEVATED TEMPERATURE USING COMPOSITE OF NANOPARTICLES

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ABSTRACT

Chitosan/clay materials from periwinkle shells and clay soil at a 50:50 ratio was made adsorbent and characterized, used for the adsorption of CO_2 from flue gas at elevated temperatures (50 ^oC – 500 ^oC) in a fixed bed column (length 1.5m, and internal diameter 0.02m). Flue gas with composition of Methane (0.003), Ethane (0.002), Hydrogen (0.05), CO_2 (0.15), Water Vapour (0.02), and Nitrogen (0.76), of pressure 49KPa, temperature of 500 ^oC, and flow rate of 75min/L from the exhaust tank; enters the fixed bed column for the adsorption process where the adsorbent is already placed. The results of the characterization of the adsorbent showed that 5.283nm, 2.64nm, 434.7m^2/g, 704.2m^2/g, 0.202cc/g, and 56.73% were best the values for the adsorbent' pore width, pore diameter, microspore surface area, pore volume, and porosity, obtained using Dubinin-Raduskevich (DR), density functional theory (DFT), hydraulic diameter (DH), Langmuir, DH, and scanning electron microscope (SEM) analysing techniques respectively. The Fourier transform infrared (FTIR) Spectrum showed the presence of halogen (C-Cl), 2^0 alcohol (C-O), Nitro (N-O), and amine (N-H) compounds in the nanoparticles, revealing a strong affinity for CO_2 particles in the flue gas. Another analysis showed the presence of elements (Ca, Si, Al, and Sr) in high compositions (0.470, 0.202, 0.186, and 0.092, respectively), revealing that the adsorbent is resistant to high temperatures. X-ray diffraction (XRD) analysis of the adsorbent gave Ca $(OH)_2$, $CaCO_3$, and TiO_2 with compositions of 0.78, 0.19, and 0.026, respectively which revealed the strong affinity of the adsorbent for CO_2. The Surface morphology of the adsorbent revealed that the surface was very rough and contains variety of pores or holes with wide capacities, indicating that more CO_2 was captured and accommodated within the surface. Thermal analysis using the Barrett-Joyner-Halenda (BJH) method revealed that the adsorbent could withstand high temperatures up to 900^0C, at this temperature, the adsorbent is only about 18% of the amount that enters the fixed-bed column for adsorption, but 100% of it can remain in the process for temperatures ranging from 0 ^oC – 300 ^oC. Finally, it was revealed that 95% of CO_2 was adsorbed at the maximum value for the temperature (50 ^oC – 350 ^oC), time (0.5 - 5hr), and bed height (1 - 6cm).

Keywords: *Adsorption, CO_2, flue gas mixture, elevated temperature, chitosan/clay nanoparticles.*

1. INTRODUCTION

Carbon nanotubes and activated carbon have been studied to promote pollutants adsorption, but there are some limitations on their use as adsorbents (Dadet *et al*., 2024), since the choice of its usage is dependent on the exceptional adsorption efficiency and the technique applied, especially locally sourced materials that are converted to adsorbent(s). Adsorption process using activated carbon from neat chitosan is relatively expensive, and microporous, although efficient, but limited, because of the relatively large size of some molecules, weak mechanical properties, low specific gravity, swells and floats when dissolved in water, and has low stability in acidic media (Breck, 2018). Similar to activated carbon and carbon nanotubes, chitosan/clay nanoparticles contain zeolites that are easily obtained from the environment because they are locally sourced from soil (Ruthven, 2012) and the zeolites adsorbent can easily be regenerated and the solute can be separated from the gaseous solution after the adsorption process is completed (Younas *et al*., 2016). Nanoparticles are discrete particles or clusters with dimension between 10-100 nm, but metallic nanoparticles exhibit size-and-shape-dependent properties that are of interest for applications ranging from catalyst and sensing to optics, antibacterial activity, and data storage (Thambimuthu *et al*., 2019). The particle size, shape, and morphology of nanoparticles are checked and controlled; because the catalytic activity of nanoparticles is dependent on their size, structure, shape, size distribution, and chemico-physical environment (Kanniche *et al*., 2021). A nanocomposite is made up of a blend of two or more materials in which at least one of the components is nanosized (Yang *et al*., 2018), comprises of different physicochemical properties and apparent interface, advantageous to individual components, including higher toughness, higher stiffness, high specific strength, gas

barrier characteristics, flame retardancy, corrosion, and resistance (Wang *et al*., 2021). Nanocomposites have diverse applications in the biological sciences, drug delivery systems, and wastewater treatment, for instance, nanocomposite materials are incorporated into functional materials like carbon nanotubes, activated carbon, reduced graphene oxide, and different polymeric matrices for numerous applications, including the efficient handling of water pollutants and removal of other gases from gas mixtures (Bonenfant *et al*., 2018). Polymer-clay nanocomposite materials have attracted great interest owing to their improved properties such as elasticity, strength, hardness, flame retardancy, dimensional stability, electrical conductivity, solubility, heat resistance, wettability, and dyeability, depending on the type and content of the material used for the catalytic adsorption of gases such as carbon dioxide (Montalvo *et al*., 2021). Chitosan-based composites have also been reported for their improved mechanical, thermal, and adsorption properties, and have received a great deal of attention in recent years, with several studies conducted on the development of composite materials as adsorbents for non-ionic and anionic pollutants, organic pollutants, and herbicides (Triebe, 2017). For Carbon capture systems (CCS) to be implemented on a global industrial scale, it is of paramount importance that more suitable capture technologies, such as adsorption, that are both cost-effective and efficient are developed, and CCS will only gain public acceptance and implementation in industry once it has been confirmed to be economically viable. Many factors affect the economic viability of CCS, and one of these factors is the lack of inexpensive technology and high-performance materials for selective removal of CO_2 from flue gas. Therefore, various novel materials for post-combustion CO_2 capture have been developed and studied (Khelifa *et al*., 2021; IEA, 2016).

Several studies conducted in this area of research have been revisited, and it was found that the most recent and established technologies for CO_2 capture are chemical absorption using liquid amine-based solvents using monoethanolamine (Dadet *et al*., 2024), which can pose health risks when released into air from CO_2 capture plants, as well as an efficiency penalty, and the huge costs associated with the regeneration of spent amine based liquid solvents. Activated carbon produced from agricultural waste via chemical or physical activation, has gained wide attention as a brilliant adsorbent for the removal of pollutants owing to its high surface area, stability, array of functional groups and excellent pore structures (Afshin *et al*., 2019). Chemical activation enhances its specific surface area and porosity (Piriya *et al*., 2021) and (Silva, 2015) explored the use of activated char obtained from the pyrolysis of a mixture of non-recyclable plastics for the adsorption of CO_2 in fixed-bed columns in which 15 ^oC – 45 ^oC, 10% - 40% by volume, and 1g - 2g of adsorbent loaded in the bed, were the input temperature, and amount of CO_2 and adsorbent, respectively. (Schumann *et al*., 2021) applied a type 4A zeolite produced from clay mineral as an adsorbent to adsorb CO_2 from flue gas present in power-fuelled plants, and the synthesized materials were characterized by X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), N_2 adsorption–desorption at 196 ^oC and CO_2 adsorption at 60^0C (up to 10 bar) isotherms, and Nuclear Magnetic Resonance (NMR). In addition, the adsorption capacity of CO_2 was evaluated using CO_2 adsorption–desorption isotherms at 25 ^oC up to atmospheric pressure, with the synthesized zeolite 4A successfully prepared from natural kaolinite (via meta kaolinization) at 100 ^oC for 48h under alkaline conditions, revealing the physicochemical properties similar to those of the commercial 4A zeolite. It has been reported that CO_2 was captured successfully at low temperatures with locally sourced adsorbents, such as zeolite types made from activated basolites/clay, palm shell immersed in chitosan solution, biochar synthesized from chitosan at 50:50 material ratios (Ruthven, 2012; Ho *et al*., 2017; Pham *et al*., 2018), and synthetic adsorbents such as ethanolamine base solution and amine modified and moisture- swing nanoparticles (Dadet *et al*., 2024; Hudson *et al*., 2017).

Limited or no studies have been reported on the use of locally sourced adsorbents to capture CO_2 from flue gas at elevated temperatures. Therefore, this study is the first attempt to formulate and characterize composites of chitosan (periwinkle shells) and clay materials (clay soil), combined at a 50:50 ratio, to serve as an adsorbent for the removal of CO_2 from flue gas at elevated temperatures.

2. MATERIALS AND METHOD

2.1 Materials

Periwinkle shells and clay soil were obtained from Creek town (Obio Oko), located in Odukpani local Government Area of Cross River of Nigeria (Nair, 1977), situated about 8miles Northeast from Duke town (Hallett, 1964), and is one of the city-states that comprise of old Calabar region (Aye, 2000; Daniell, 1848). Flue gas from cracked natural gas with composition of methane (0.3%), ethane (0.7%), hydrogen (5%), CO_2 (15%), water vapour (2%), N_2 (78%) (IEC & FL, 2016), and distilled water (Chemical/Petrochemical Engineering laboratory, Port Harcourt). Instruments used are analytical balance (Scout Pro, Ohaus, London, UK), pH meter (pH ep® pocket-sized pH meter, Hanna Instruments, Inc., United States of America (USA), grinding mill (Biocotek, China), shaker (Ro-tap, England), stop watch (Quartz, China), Thermometer (Pyrex Technico, England), Fourier transform infrared (FTIR) spectrometer (Thermo Scientific, Nicolet ISI 10, USA), scanning electron microscope (SEM)/ energy dispersive analysis of x-ray (EDX) spectrophotometer (Karl Zeiss, Germany), Brunauer-Emmett-Teller (BET) surfer machine (Thermo Scientific, USA), thermogravimetric analyzer (Orton Simultaneous DTG/TGA, USA), UV-Vis spectrophotometer (Angstrom Advanced Inc, model 752,

Massachusetts, USA) A multi-gas detector/analyser, and muffle furnace (TT-EF-12, Techmel, USA).

2.2 Method

Chitosan was extracted and composite nanoparticles was prepared from chitosan and clay materials.

2.2.1 Extraction of Chitosan

Periwinkle shells were washed and dried in an electric air-drying oven for 6h at 105 ℃. The completely dried shells were ground using a mechanical grinding machine and then sieved through a 100µm mesh size. Deproteinization was conducted by heating approximately 300g of grounded periwinkle shell powder, add 1000 ml 2M NaOH placed to a water bath set to a constant temperature of 70 ˚C for 4 h. The product was neutralized by washing with tap water until the pH reaches 7. The solid was collected, washed again with distilled water, and the solid product dried in an air-dry vacuum oven. The dried product underwent demineralization through treatment with 1000 ml solution of 3.25M HCl at an ambient temperature of approximately (30±3) ℃. The mixture was stirred intermittently at 30-minute intervals for 4 h and the solid product was collected and rinsed with distilled water until it reached a pH of 7, after which it was dried. The demineralized sample was subjected to deacetylation by treating it with a 500 ml solution of 8.75M NaOH. The sample was then placed on a constant temperature magnetic stirrer and heated at 100 ℃ for 12 h. Subsequently, the sample was deacetylated, filtered, and washed with distilled water and it was subsequently dried in a vacuum oven, and the dried powder was sieved through 0.45µm mesh size and kept as nanosized particles in an air-tight container until use.

2.2.2 Preparation of Clay Soil for nanoparticles/Composite

Clay soil collected from Calabar creek was filtered and the filtrate was placed in a beaker, where it was calcinated into nanoparticles after extraction of the clay sample at 800 ºC.

2.2.3 Characterization of chitosan/clay adsorbent

The surface functional groups of the chitosan/clay mixture of the 50:50 ratio nanoparticle adsorbent samples were determined using an FTIR analyzer in the wavenumber range 4000-500 cm^{-1}. Textural properties were measured using a surface area analyzer (Thermo Scientific, USA), and SEM images of the adsorbent surface and texture were obtained using a Karl Zeiss instrument (Germany). Thermal decomposition of the adsorbent sample was determined using a standard Orton simultaneous DTG/TGA analyzer. The elemental composition of the adsorbent was obtained using EDX, as the individual fluorescent energies detected were specific to the elements were present in the sample.

2.2.4 Adsorption Experiment

The CO_2 adsorption was conducted in a fixed bed comprising a cylindrical column made of Pyrex glass with a total length of 150cm and an internal diameter of 2.01cm. The column was packed at various heights of adsorbents between 1cm and 6cm and placed within a high-temperature chamber with dimensions of 30cm x 40cm which helped to maintain a temperature range of 50 – 250°C. Flue gas of Pressure 0.5kg/cm^2.G, flow rate of 75L/min and temperature of 185^0C enters the adsorber where the chitosan/clay nanoparticles were placed inside the column for the adsorption process.

3. RESULTS AND DISCUSSION

3.1. Result of Characterization of the Chitosan/Clay Composite Nanoparticles Chitosan/clay nanoparticles prepared from locally sourced periwinkle shells and clay soil were characterized using a gas chromatography (GC) analyzer to obtain the results presented in Table 1. Characterization of the nanoparticles from chitosan/clay showed that it is a weakly acidic material with high porosity and large surface and micropore areas. This indicates that the chitosan/clay material is a good adsorbent for the adsorption of pollutants (CO_2) from flue gas. The large surface and micropore areas proved this reason, as these are properties that determine the adsorbent performance. A larger pore volume allows more adsorption of CO_2 particles onto the surface of the adsorbent and with nanosized particles, indicating that the adsorbent material is a nanoparticle and composite, which is specific and targeted for its functionality. Different methods were used for the characterization of the adsorbent, among them, DR gave the best pore width of the adsorbent of 5.283nm and best pore surface area value of 400.6m^2/g, pore size determination (DA) analysis gave the best result of pore diameter value of 2.64nm, hydraulic diameter (DH) method of cumulative adsorption pore volume analysis gave the best value of pore volume of 0.2015cc/g, and finally, the Langmuir surface area gave the best value of surface are as 704.2m^2/g.

Table 1: Characterization of Adsorbent

Property	Value
Bulk density (g/cm^3)	1.473
Ph	6.74
Porosity (%)	56.73
Surface area (m^2/g)	704.2
Micropore area (m^2/g)	400.6
Pore volume (cc/g)	0.2015

Pore width (nm)	5.283
Pore diameter (nm)	2.64

3.1.2 Result for the Physiochemical Analysis of the Adsorbent

The chitosan/clay composite particles (adsorbent) were determined based on the different analyses performed. functional group present (see Figure 1). The analysis showed the presence of an olefin alkene functional group (C-double bond), indicating a strong affinity for the addition reaction process, such that the attraction of the pollutant to the adsorbent is very strong, and hence a good adsorbent. In addition, the halogen compound (C-Cl), 2^0 alcohol compounds (C-O), nitro compound (N-O), and 1^0 amine compounds (N-H), with their functional groups having excess lone pairs of electrons at the surface, are capable of undergoing the reaction process, indicating that there is a strong energy within the adsorbent pores and surface areas that are created to have a very strong affinity for capturing CO_2 from the flue gas.

The FTIR method was the best method to determine the functional group present in the adsorbent, as shown in Table 2, depicts FTIR analysis result showing the wave number, nature of frequency, bond type and the type of

Table 2: Functional Group Analysis of Adsorbent with FTIR

Wavenumber (cm^{-1})	Nature of frequency	Assignment	Comment
712.65	Strong	C=C bending	Alkene disubstituted (cis)
856.57	Strong	C-Cl stretching	halo compound
1095.60	Strong	C-O stretching	Secondary Alcohol
1500.73	Strong	N-O stretching	nitro compound
3436.29	medium	(N-H stretching)	Primary amine

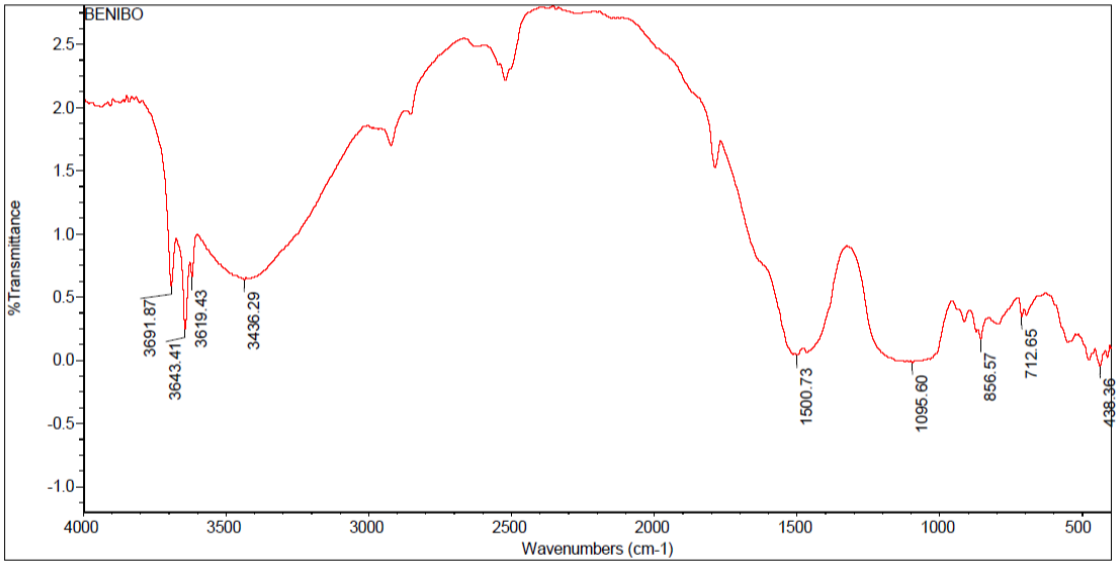


Figure 1 Functional Group Analysis of Adsorbent with FTIR

3.1.3 Elemental Composition of the Adsorbent

The chitosan/clay nanoparticles were also characterized to determine their elemental composition as shown in Table 3. The elemental analysis of the adsorbent, as shown in Table 3, indicates that Ca, Si, Al, and Sr have higher concentrations by weight, meaning that the adsorbent is electron affinity or electrovalent in nature. The presence of these elements proved that the adsorbent could withstand high-temperature applications. Other elements, such as Ti, Mg, Sb, and K, were present at very low concentrations by weight. This adsorbent is very rich, as it may have diverse applications in chemical engineering, with the lowest concentration by weight being Pb, a very good indication of the essentiality of the nanoparticle because Pb is poisonous at high concentrations (see Figure 2 for more clarification).

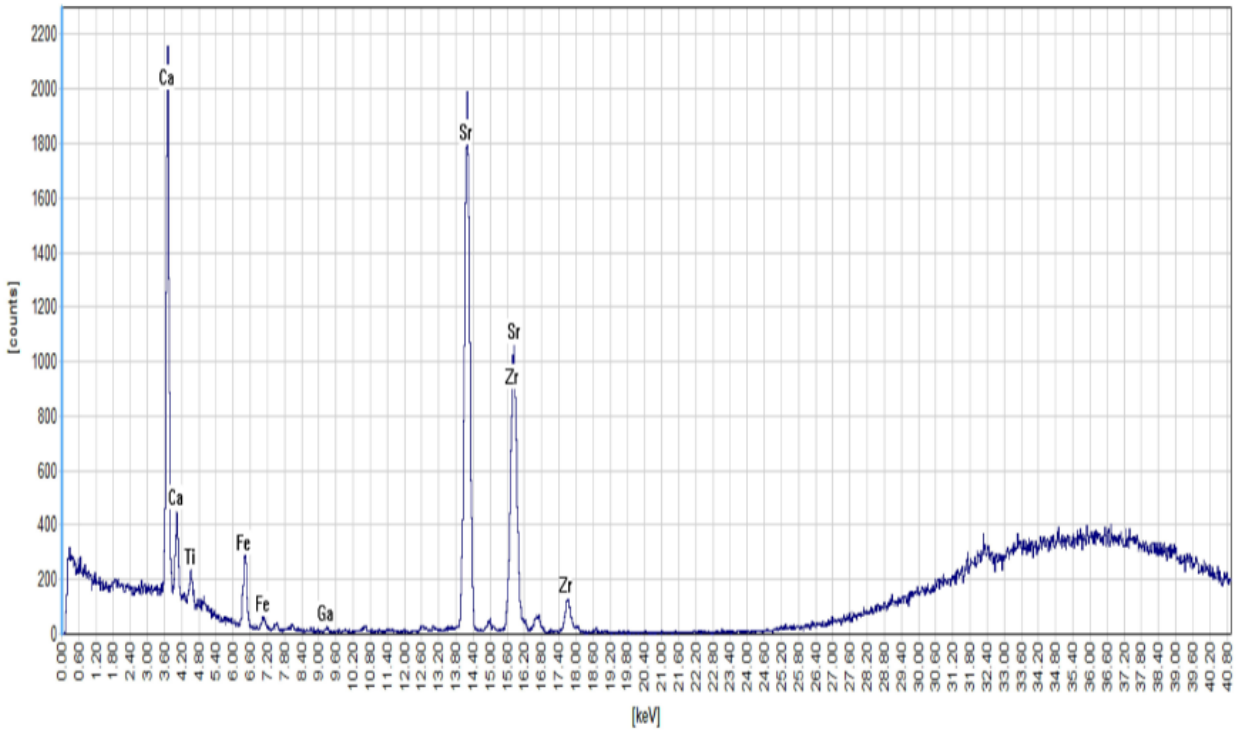


Figure 2 Elemental Composition of the Adsorbent

Table 3: Elemental Analysis of the Adsorbent

Element	Concentration (wt%)
Calcium (Ca)	47.0388
Silicon (Si)	20.2151
Aluminum (Al)	18.5732
Strontium (Sr)	9.17707
Titanium (Ti)	1.08093
Magnesium (Mg)	1.51206
Antimony (Sb)	0.88979
Potassium (K)	0.54609
Iron (Fe)	0.42161
Niobium (Nb)	0.18649
Zirconium (Zr)	0.08452
Sulphur (S)	0.08219
Phosphorus (P)	0.07948
Chlorine (Cl)	0.02590
Manganese (Mn)	0.02125
Vanadium (V)	0.01812
Lead (Pb)	0.01584

Based on the compound made up of the adsorbent using XRD analysis, it showed from the pie-chart of Fig. 3 that slake lime have the highest presence in the adsorbent with 78%, followed by limestone of 19% and oxide of Ti with 2.62%.

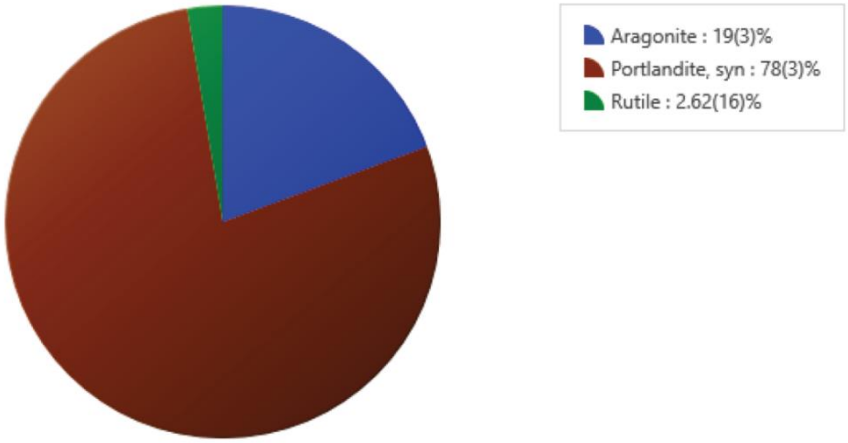


Figure 3 The Composition of the Compounds Present in the Adsorbent using XRD Analysis

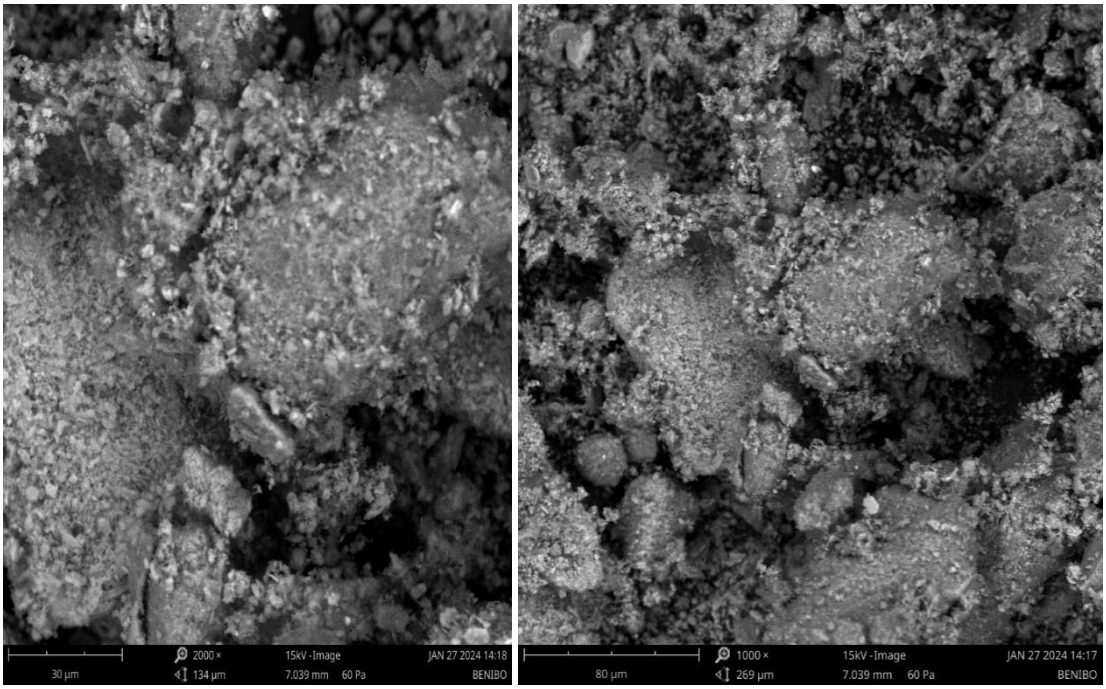
Figure 3 depicts the compounds present in the adsorbent and its percentage spread within the make up of the adsorbent. Ca $(OH)_2$, $CaCO_3$ and TiO_2 were present after XRD analysis. Their compositions were 78%, 19% and 2.62% respectively. The presence of slake lime, which has a strong affinity to react with CO_2 showed selective adsorption of the adsorbent to attract CO_2 from the stream of flue gas; hence, maximum removal of the pollutant from the mixture was achieved. Ca can retain heat; hence, at elevated temperatures, the adsorbent can still perform adsorption without denaturation.

3.1.4 Results of XED-EDS Analysis

The XED and energy dispersion X-ray spectrometry (EDS) analysis of the adsorbent provided the elemental composition of the make-up of the nanoparticles, and the surface analysis results are presented in Table 4 and Figure 4. The elemental composition of the adsorbent, as discussed earlier in Table 4, indicates the presence of Ca, Al, and Si with the highest weight concentrations of 42.98%, 23.91%, and 22.04% respectively, whereas, Na, Ti, Mg, P, Fe, K, S, and Cl have low weight concentrations of 3.51%, 1.95%, 1.35%, 1.21%, 1.03%, 0.92%, 0.56%, and 0.52%, respectively, and the atomic concentration by percentage is also in the same order. As shown in Table 4, the presence of these elements is indicative of the ability of the adsorbent to withstand high-temperature adsorption of the pollutant from the flue gas mixture.

Table 4: Elemental Composition of the Adsorbent showing Atomic and Weight Concentration in %

Element Number	Element Symbol	Element Name	Atomic Concentration	Weight Concentration
20	Ca	Calcium	34.53	42.98
13	Al	Aluminum	28.53	23.91
14	Si	Silicon	25.27	22.04
11	Na	Sodium	4.92	3.51
22	Ti	Titanium	1.31	1.95
12	Mg	Magnesium	1.80	1.36
15	P	Phosphorus	1.26	1.21
26	Fe	Iron	0.59	1.03
19	K	Potassium	0.75	0.92
16	S	Sulfur	0.56	0.56
17	Cl	Chlorine	0.47	0.52



(a) **(b)**

Figure 4 Surface Morphology of the Adsorbent at: (a) 2000X Magnification, and (b) 1000X magnification

Figure 4 shows the surface morphology of the chitosan/clay nanoparticles used as adsorbent for the adsorption of CO_2 from flue gas, which is very rough with pores, indicating that the adsorbent is very good for the adsorption of pollutants, as many active sites are present on the surface for the attraction of the pollutant or CO_2 onto the surface, which can accommodate more pollutants for efficiency. The image scanned produce 15kV of dimension 7.039mm and pressure of 60Pa.

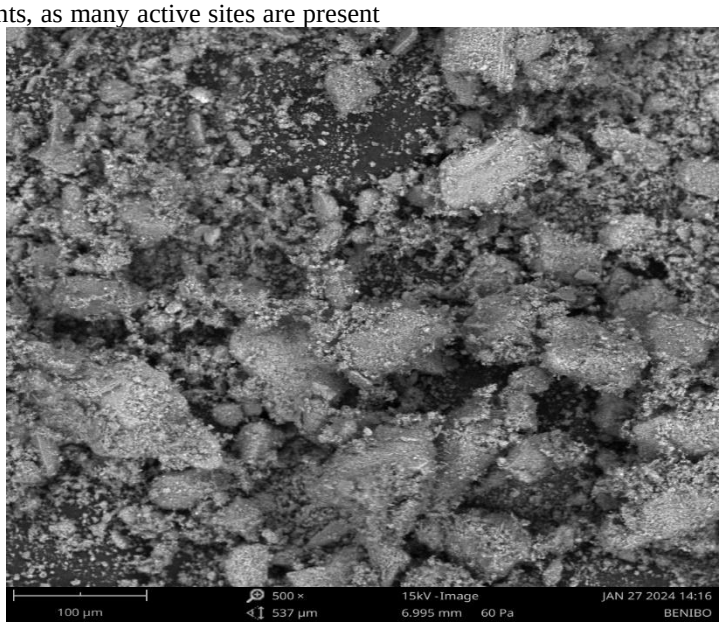


Figure 4c Surface Morphology of the Adsorbent at 500X Magnification

Figure 4c shows the surface morphology of the chitosan/clay nanoparticles used as adsorbents for the adsorption of CO_2 from flue gas, with lengths and diameter of the adsorbent sampled for analysis as 100µm and 537µm respectively. The surface morphology showed that it is very rough with pores, indicating that the adsorbent is very good for the adsorption of pollutants as many active sites are present on the surface for attraction of the pollutant or CO_2 into the surface. This surface can accommodate more of the pollutants into it for efficiency, with the scanned image produce 15kV of dimension 6.995mm and pressure of 60Pa.

3.1.5 Thermal Analysis of the Adsorbent

Thermal analysis of the adsorbent determined the temperature range in which the adsorbent could withstand adsorption without destruction. PerkinElmer thermal analysis and the BJH method were the best methods to check the adsorbent capacity as shown in Figure 6.

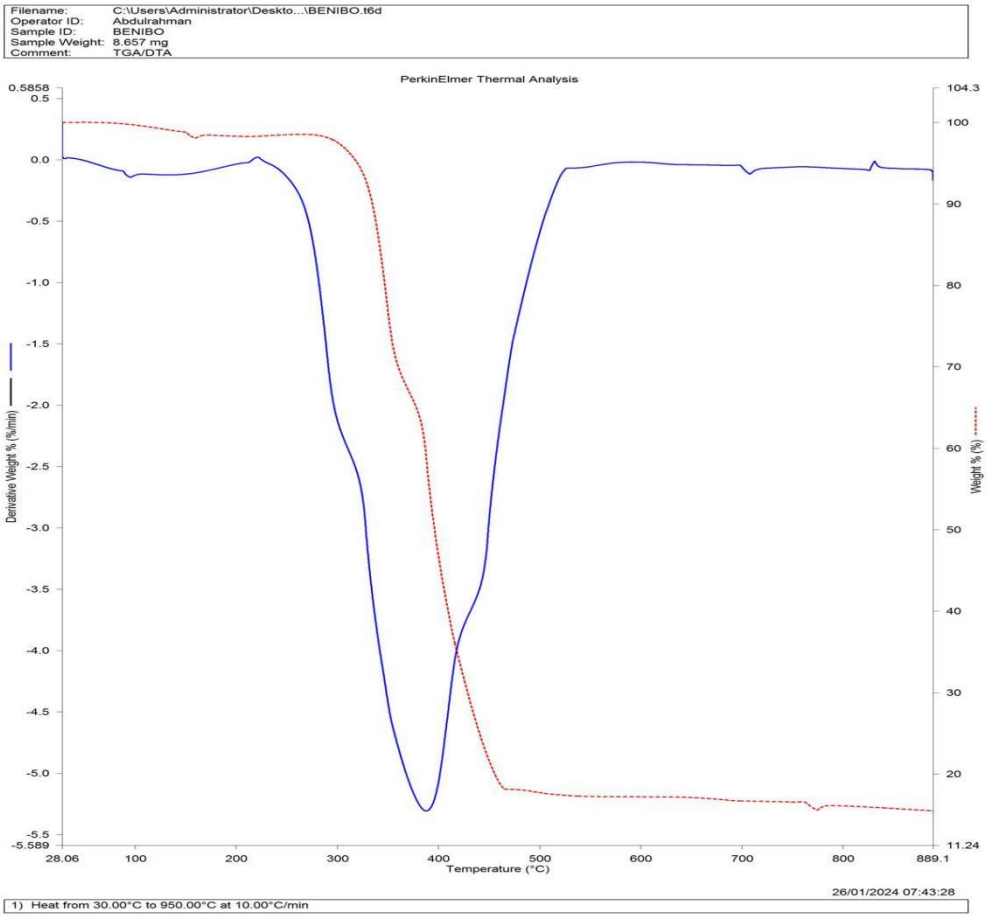


Figure 5 Effect of Temperature on the Weight and Derivative Weight of the Chitosan/Clay Nanoparticles

The adsorbent produced from chitosan/clay materials, as shown in Figure 5, is very effective and capacitated in the sense that it can withstand temperatures up to 800 ^{o}C and above, but without destruction, the adsorbent can withstand 100% temperature upto 400 ^{o}C, meaning that, at this temperature, the amount of adsorbent present remains intact without reducing, but as the temperature further increases above 400 ^{o}C, the 100% by weight of adsorbent in the absorber column drops to approximately 20% by weight of the absorbent and until its weight drops further to approximately 18% at a temperature of approximately 850 ^{o}C. This indicates that the adsorbent made up of chitosan/clay materials is useful for adsorption at elevated temperatures, as it proved that the choice of adsorption of CO_2 from the stream of flue gas at elevated temperatures is successful, as upto 95% of CO_2 is captured from the flue gas at such temperatures.

4. CONCLUSION

Chitosan/clay nanoparticles were successfully produced as adsorbents than can resist thermal degradation up to 400^{0}C as it was noticed in the BJH analysis of the adsorbent, where 100% of the adsorbent was maintained in the temperature range of (0 ^{o}C to 300 ^{o}C) and 18% of the adsorbent from 100% was able to withstand high temperatures up to 900^{0}C. Chitosan/clay nanoparticles are highly effective and efficient for the removal of CO_2 from flue gas at elevated temperatures. The 95% CO_2 captured at the surface of the particles is evidence, and the presence of pores, large surface areas, and rough surfaces of the adsorbent proved this claim.

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Ethical Compliance
All procedures performed in studies involving human participants were in accordance with the ethical standards of the University of Calabar.

Data Access Statement
Research data supporting this publication are confidential and only available on request

Conflict of Interest Declaration: The authors declare that they have NO affiliations with or involving in any organization or entity with any financial interest in the subject matter or materials discussed in this manuscript.

Author Contributions
Ojong, O.E. conceived the original concept and the writing of the manuscript, Osha, O.A. contributed to the design and implementation of the research, Abam, F.I. edited and supervised the project, S.S. Shamaye conducted the experiment and the analysis of the results.

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