10.51975/25400102.som
Journal of the Nigerian Society of Chemical Engineers, 40(1), 2025

EVALUATION OF PHENOL REMOVAL FROM WASTEWATER WITH NANO-CHITOSAN AND ITS REGENERATION POTENTIAL

[*]Abubakar Abubakar Ibrahim[1], Abdulfatai Jimoh[2], Ismail Babatunde Adefeso[3], Fatima Muhammad Abubakar[4] and Ibrahim Shaba Mohammed[5]

[1,3,4]Department of Chemical and Petroleum Engineering, Faculty of Engineering, Bayero University Kano, PMB 1033, Kano, Kano State, Nigeria

[2]Department of Chemical Engineering, Faculty of Engineering, University Abuja, PMB 117, Airport Road, Abuja, Nigeria

[5]Department of Agricultural and Bioresources Engineering, School of Engineering and Engineering Technology, Federal University of Technology Minna, PMB 65, Minna, Nigeria

**Corresponding author: Tel: +2348032670719; E-Mail: aaIbrahim.cpe@buk.edu.ng*

ABSTRACT

Phenol is considered to be a very toxic pollutant in refinery wastewater which poses danger to man and its environment. This study target was to establish the effective assessment of phenol removal using chitosan, nano-chitosan obtained from crab shells and their generative potentials. The crab shells were prepared and converted to chitin. The experiment conducted was at different conditions for both chitosan (CTS) and nano-chitosan (NCTS) to achieve basic polysaccharide of low molecular weight chitosan (LMWC) and low molecular weight nano-chitosan (LMWNC) for removal of phenol from the refinery wastewater. Various techniques were used to characterize both chitosan, nano-chitosan and refinery wastewater, such as Double beam UV- spectrophotometer, Fourier Transforms Infrared Spectroscopy (FTIR), X-Ray Fluorescence (XRF) and Dynamic Light Scattering (DLS). The characterization of obtained chitosan and nano-chitosan absorbents showed good surface area, high pore sizes, effective size reduction yield of over 80% with good content of macro elements and good molecular weight. The values of calcium were 6.6972%, 5.6422% for CTS and NCTS respectively. The results of interaction revealed at factors of 35% sodium hydroxide, 3 h and 75 ^{o}C gives the degree of deacetylation (DD) to be 81.75%. The percentages of phenol removal were 87.88% and 98.77% for both CTS and NCTS respectively. The maximum regeneration obtained was 93.65 % which occurred at 50 mins. Hence, this showed that the synthesized nano-chitosan polysaccharide from white shrimp shells had the potential for phenolic compounds removal from refinery wastewater and the NCTS enhances the adsorption capacity due to higher surface areas.

Keywords: *chitosan; nano-chitosan; phenol; wastewater; refinery; regeneration.*

1.0 INTRODUCTION

Wastewater from industrial sources such as refinery has been reported as the nuisance of life-threatening contaminating ecosystem (Ibrahim et al., 2022a, Ibrahim et al., 2022b). Every year, about 140 billion tons of industrial and agricultural wastes are generated of which 13 billion tons are from plant biomass waste, only 3% are used for making goods (Ibrahim et al., 2022b, Apollon et al., 2024, Khader et al., 2024). The study of Mohammad et al. (2014) reported about 30 million tons/year of waste generated from the aquatic processing are thrown into the sea or remain on the land causing environmental contaminants and public health concerns, because of their high perishability and high pollution effect (Kesari et al., 2021). The contaminants are characterized by the presence of high concentrations of toxic organic hydrocarbon like phenols (Khader et al., 2024).

Phenol is among the most common organic pollutants and is present in wastewater from petroleum industries (Mohammad et al., 2014, Radha Thirumalaiarasu and Mahalakshmi, 2022). Phenol is the 11th of the 126 chemical priority pollutants by United State Environmental Protection Agency (USEPA) with odour threshold limit of 0.04 ppm (Ibrahim et al., 2022a, Panigrahy et al., 2022). The work of Soto et al. (2011) reported that as a result of toxic and inhibitory characteristics, phenols are very difficult to remove by biological processes (Panigrahy et al., 2022, Filipowicz et al., 2020). The removal of the phenol from wastewater can be achieved through several techniques such as physical, chemical, and biochemical processes (Panigrahy et al., 2022, Oliveira et al., 2021, Radha Thirumalaiarasu and Mahalakshmi, 2022).

The techniques used for phenol removal from wastewater are adsorption, which depends on adsorbents with high adsorption capacity, good mechanical resistance, and simple restoration (Khader et al., 2024, Zhou et al., 2023). Other methods used are membrane separation (Chen et al., 2019, Lee et al., 2022), electrocoagulation (Sadeghi et al., 2019), Fenton oxidation (Fu et al., 2020), and catalytic reduction (Gabris et al., 2022, Abdelfattah and Ismail, 2023, Salahuddin et al., 2020) theirs associated problems hinder the effective usage (Ibrahim et al., 2022b, Ibrahim et al., 2017). These identified challenges make

it very necessary to focus more on eco-friendly methods of getting rid of this toxic constituent of effluent before being discharged into water body (Ibrahim et al., 2022a). The needs for a more efficient method for synthesizing adsorbents containing natural polymers have received reorganization, in particular polysaccharides. Nano-chitosan, a natural biopolymer derived from chitin, has gained attention due to its biocompatibility, biodegradability, and excellent adsorption properties (Ibrahim et al., 2022a). Therefore, the major focus of this research is using more abundant aquatic waste like crab shells.

The valorization of aquatic wastes through CTS and NCTS preparation is to avoid the negative influences on human health and the environment (El Kaim Billah et al., 2023). CTS and NCTS are new polymeric materials and have demonstrated many good applications (Ibrahim et al., 2017). CTS is a semi-crystalline cationic polysaccharide that attracts positively charged molecules and enhances bonding due to the presence of the -NH_2 group. In addition, the -OH group is also present in the structure and helps to increase the adsorption capacity (Kou et al., 2022). Due to their large specific surface area, small size, and structures, CTS and NCTS have been proven to possess a great potential as superior adsorbents for removing many kinds of organic and inorganic contaminants from natural water and wastewater (Ibrahim et al., 2017, Sivakami et al., 2013). Also, studies have shown that this adsorbent (CTS/NCTS) is low cost which is yet to be exploited with phenol removal from refinery wastewater. This research work deems it fit to assess effectiveness of phenol removal capacity on CTS and NCTS. The main aim of the research is to evaluate the effectiveness of phenol removal capacity by CTS and NCTS.

2.0 MATERIALS AND METHODS

2.1 Chemicals and Materials

Crab shells was obtained from Dukun, Mokwa Local Government of Niger State and wastewater obtained from Kaduna Refinery, were stored in a cleaned container, put into the freezer and later transported to the laboratory for necessary analysis (Ibrahim et al., 2013). Chemical used include hydrogen sulphate (H_2SO_4), cupric sulphate ($CuSO_4$), sodium hydroxide (NaOH), lactic acid ($CH_3CH(OH)CO_2H$), sodium tripolyphosphate (STPP), acetone $(CH_3)_2CO$ and hydrogen peroxide (H_2O_2) all of which were analytical grades manufactured by Analar BDH. The apparatus and instruments used were weighing balance (Scout pro SPU), Fourier Transform Infrared spectrometer (Parkin Elmer 200). Dynamic Light Scattering (DLS) - Malvern, Double beam UV - spectrophotometer - G5-UV61PC, Shaking Water Bath - 030S and Viscometer - NDJ - 5S.

2.2 Deacetylation of Chitin to Chitosan

The removals of acetyl groups from chitin were done with the aid of 35% of NaOH, temperature 75 $^{\circ}$C and time 3 h. Then centrifugation was carried out for 20 mins at 2000 rpm after each washed with distilled water until the pH values reached neutral value. The supernatant was filtered and residues were oven dried at 60 $^{\circ}$C for 6 h. The obtained chitosan was ground to small particle size of 250 micrometer and stored for further analysis. Also, about 7% H_2O_2 was added to the obtained CTS and heated at 60 $^{\circ}$C for 1 h and filtered. The distilled water was used to neutralize it and about 5 ml of ethanol was added to the solution, for 6 h, after which it was filtered, dried and weighed (Ibrahim et al., 2017).

2.3 Nano-chitosan Synthesis

About 5 g of milled CTS were primed at various concentrations of 2% sodium tripolyphosphate (STPP), 2% acetic acid solution and time of 2.5 h. The STPP were added dropwise and mixed at 450 rpm. The formed nano-chitosan (NCTS) washed several times with distilled water, filtered and oven dried at 60 $^{\circ}$C (Ibrahim et al., 2022a) for 6 h (Wijesena et al., 2017, Vijayalakshmi et al., 2017). The average of particle size distribution was calculated with the aid of dynamic light scattering (DLS).

2.4 Characterization of Chitosan and Nano-chitosan

The surface functional groups of chitosan and nano-chitosan were determined by Fourier Transform Infrared (FTIR) spectroscopy. The regeneration capacity of nano-chitosan was obtained by Fourier Transform Infrared (FTIR) spectroscopy. The data obtained were plotted with the aid of essential Fourier Transform Infrared software (Ibrahim et al., 2022a, Ibrahim et al., 2024). The structural analysis of the samples was conducted using PAN analytical X' Pert PRO MPD X-ray diffraction system PW3040/60 machine. The average of particle size of nano-chitosan distribution was obtained with the aid of Dynamic Light Scattering (DLS)-Malvern.

2.5 Digestion of Refinery Wastewater

About 350 cm^3 of wastewater samples were distilled to obtain 300 cm^3 of distillate which was transferred to a separating funnel. Also, about 10 cm^3 of buffer solution with 2 cm^3 each of 4aminiantipyrine and potassium hexacyanoferrate were added to separating funnel respectively, allowed for 10 mins. The collected phenol was dried with sodium sulphate and double beam spectrophotometer (G5 - UV61PC) was used to determine concentration of phenol at wavelength of 460 nm.

2.5.1 Phenol removal by both LMWC and LMWNC

Certain amounts of both low molecular weight chitosan (LMWC) and low molecular weight nano-chitosan (LMWNC) were added to different conical flasks (250 ml), filled with the same various volume of known phenol concentration in wastewater as shown in Figure 2.1. Each of the adsorbents and adsorbate (phenol), were mixed with aid of oscillating shaker.

The amounts of phenol removed from Refinery wastewater (RWW) by the adsorbents were obtained.

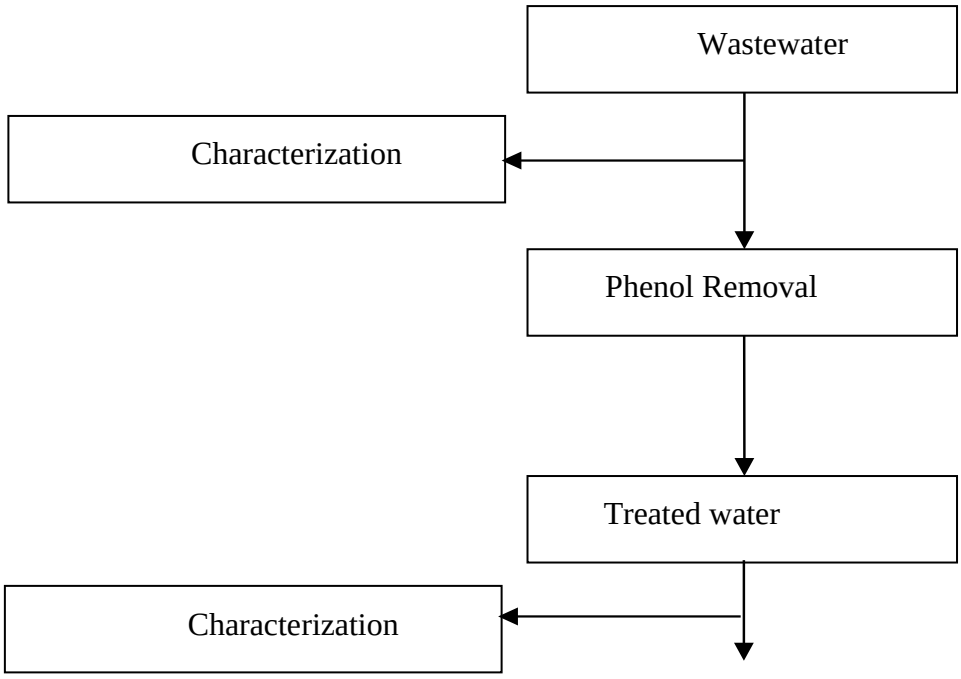

Figure 2.1: Sketch Diagram of Phenol Removal (Ibrahim et al., 2024).

2.5.2 Regeneration of nano-chitosan for phenol removal

The economy and environmental importance of adsorption depends on efficiency of regeneration. Problems associated with adsorption processes are disposal of adsorbent after usage. The regeneration can reduce the need of new adsorbent and also reduce the problem of disposal of used adsorbent. Various regeneration methods have been used with different degrees of success. These methods include washing, thermal and chemical regeneration with their respective parameters.

3.0 RESULTS AND DISCUSSION

3.1 Mineral Composition of Chitosan and Nano-chitosan

The results of mineral composition of the CTS and NCTS were shown in Table 3.1.

Table 3.1: Mineral Composition of Chitosan and Nano-Chitosan

Element	CS (%)	NCS (%)
K	0.0052	0.0034
Ca	7.4132	6.1321
Mn	LOD	LOD

***Note**: LOD: low detection, CS: Chitosan, NCS: Nano-chitosan*

Table 3.1 shows that the species are good sources of macro elements such as calcium, potassium while phosphorus was obtained from XRF analysis. After each stage of preparation, the values of calcium were 7.4132, 6.1321 (%) for CTS and NCTS respectively.

The decrease was due to demineralization carried out. This is supported by the findings of (Fawole, 2007) and (Abdulkarim et al., 2013). Nevertheless, the very low values recorded may be due to the fact that the aquatic animal needs the micro elements in trace amounts and perhaps the concentrations in the water body is very low (Sunday et al., 2012).

3.2 Chitosan and Nano-chitosan Synthesis

The results revealed at factors of 35% sodium hydroxide, 3 h and 75 $^{\circ}$C gives the degree of deacetylation (DD) to be 81.75%. These values were higher than 60.69% degree of deacetylation reported by (Abdulkarim et al., 2013). The deacetylation degree showed that the percentage of acetyl groups can be removed from the chitin to produce CTS, which play a vital role in determine the quality of produced CTS (El Knidri et al., 2020, Kou et al., 2022). From the experiment carried out, degree of deacetylation and molecular weight of CTS produced from waste crab shells were 81.76% and 74334.19 Da.

The results of interaction shows that the 2% STTP, 2.5 h and 2% Acetic acid gives 82% for the percentage size reduction.

It was observed from experiment that the particle size of NCTS was 82% yields which may be due to the accumulation of polymer molecules and intermolecular cross linking through TPP spanning (Khorram and Fallah, 2018). Surface area of the samples used plays a vital role in influencing the application and performance of the adsorbent. Increase in surface area of the samples was due to the outcome of the treatment processes such as demineralization, deproteination, deacetylation and nano sizing chitosan. The larger the surface area, the better the performance of adsorbent (Choorit et al., 2008).

3.3 Fourier Transform Infrared (FTIR)

The surface functional groups of the chitosan and nano-chitosan were determined by Fourier Transform Infrared (FTIR) spectroscopy. The data obtained were plotted with the aid of essential Fourier Transform Infrared Software as were presented in Figure 3.1.

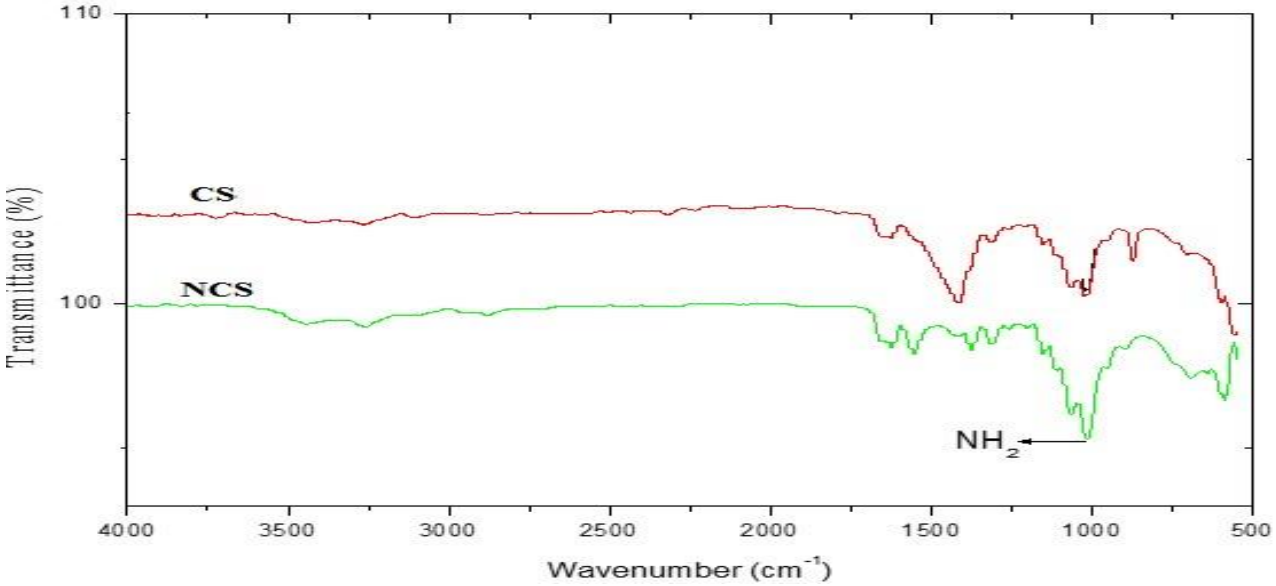

Figure 3.1: Infrared Spectra of the Chitosan (CS) Nano-Chitosan (NCS) Obtained from Waste Crab Shells

Table 3.2: Functional Group and their Respective Peak Using FTIR

Functional Group	CS	NCS	Standard
C – O	1009.03	1026.09	1300 – 1000
N – H	3216.03	3261.36	3500 – 3100
Amide II	1591.13	1620.72	1640 – 1550
C = O	1587.11	1656.86	1750 – 1625
O – H	2912.13	2934.64	3400 – 2400
NH_2	1001.31	1026.09	1030 – 1050
Amide I	1621.15	1621.72	1670 – 1600
C O	2030.37	2139.30	2200 – 2100

The FTIR studies of the CTS and NCTS were compared with standard commercial species. The major absorption band represents the free amino group ($-NH_2$) at C_2 position of glucosamine, were observed as shown in Table 3.2. The absorption bands which represent the -C-O stretching of primary alcoholic group ($-CH_2$ - OH) were observed for CTS and NCTS. Also, the main vibration values obtained were compared with standard that indicated the N-H stretching, symmetric CH_3 stretching and asymmetric CH_2 stretching, CH stretching, C=O stretching in secondary amide (amide I) and C-N- stretching in secondary amide (amide II) confirms with their structure as shown in Table 3.2 and Figure 3.1.

The broad and weak absorption bands were due to the combined effect of NH_2 and OH groups. The absorption band of each sample could be attributed to the N-H secondary amine stretches. The weak absorption band in the region was due to the presence of methylene and methyl groups in each sample structure and originates due to the C-H bond. The absorption peak at 3216.03 cm^{-1} and 3261.36 cm^{-1} for CTS and NCTS were due to the presence of N-H of amide II bond structure in the polymer. These spectra values were within the standard for CTS and NCTS and thus are similar to vibration patterns reported by (Ibrahim et al., 2022a, Ibrahim et al., 2024, Pereira et al., 2014) with insignificant changes in the positions and intensities which were due to the differences in the method of synthesized polymer.

3.4 Assessment of Wastewater and Treated Water

For this study, the wastewater collected from Kaduna Refining and Petrochemical Company (KRPC) was analyzed before treated with the developed adsorbents as shown in the Table 3.3 and post analysis was also carried out.

Table 3.3: Analyzed Wastewater and Treated Water from Kaduna Refining Plant

Parameter	Wastewater	NCTS	CTS	WHO
pH	6.79	7.00	6.70	7.50
Temperature (^{o}C)	28.20	27.00	28.00	<35.00
Total Solids (mg/l)	140.71	57.40	80.30	30.00
Total Dissolved Solids (mg/l)	380.07	241.23	310.51	500.00
Suspended Solids (mg/l)	89.26	22.51	48.57	>10.00
Dissolved Oxygen (mg/l)	12.31	8.41	10.22	8-10.00
Biochemical Oxygen Demand (mg/l)	15.94	9.42	11.56	9.42
Chemical Oxygen Demand (mg/l)	208.72	67.28	124.26	67.28
Phenol (mg/l)	7.18	0.033	0.40	0.001
Chloride (mg/l)	57.89	25.08	33.06	250.00
Sulphate	250.00	125.00	160.00	400.00
Ammonia (mg/l)	10.75	3.25	6.35	0.20
Conductivity	733.00	366.00	424.00	200.00

Wastewater sample was collected from KRPC Ltd, Kaduna State. The wastewater sample was analyzed for general characterization and treated with both CTS and NCTS to determine the presence and level of pollutant as shown in the Table 3.3. The values of the pollutant before and after treatment with the adsorbents observed that pH of wastewater increased after treatment from 6.79 to 7.00 and 6.70 for both NCTS and CTS respectively. The electrical conductivity was observed to be reduced after treatment from 733 to 366 and 424.00 for both NCTS and CTS respectively, reduction of chemical oxygen demand was observed after treatment within the range of 208.72 to 67.28 and 124.26 mg/l for both NCTS and CTS respectively and after treatment, the biochemical oxygen demand was observed to be reduced from 15.94 to 9.42 and 11.56 mg/l for both NCTS and CTS respectively. This indicates that the low-cost adsorbent has better adsorption capacity in wastewater treatment, which could be attributed to the modified CTS. However, NCTS has higher adsorption capacity of pollutants compared to CTS. Consequently, this NCTS from waste crab shells could be employed in multi-component wastewater treatment.

3.4.1 Influence of contact time

The influences of contact time between adsorbate on the adsorbents (CTS and NCTS) are presented below (Figures 3.2 and 3.3) It shows that adsorption process was faster at start but get slower as time progresses. This could be as result of vacant active site on the adsorbents at first stage which later got saturated as the time progressed. Also, low mass transfer was observed at lower concentration compared to high mass transfer in the higher initial concentration. The adsorption capacity of the adsorbents increased with an increase in contact time, which paves way to the determinant factor in evaluating the adsorption capacity and percentage removal of an adsorbent as shown in Figures 3.2 and 3.3.

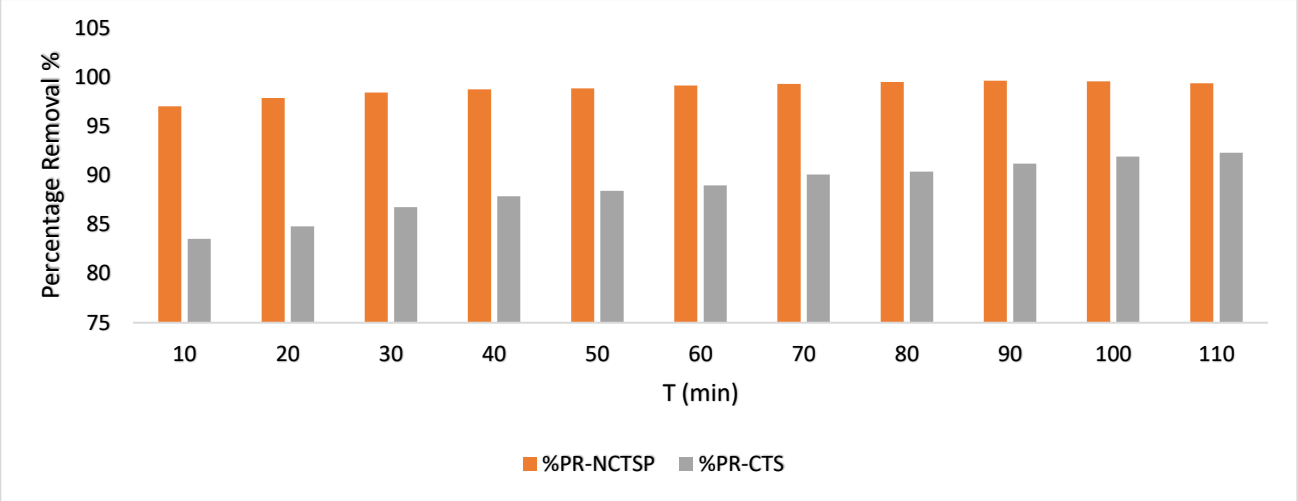

Figure 3.2: Percentage Phenol Removal by Nano-Chitosan and Chitosan

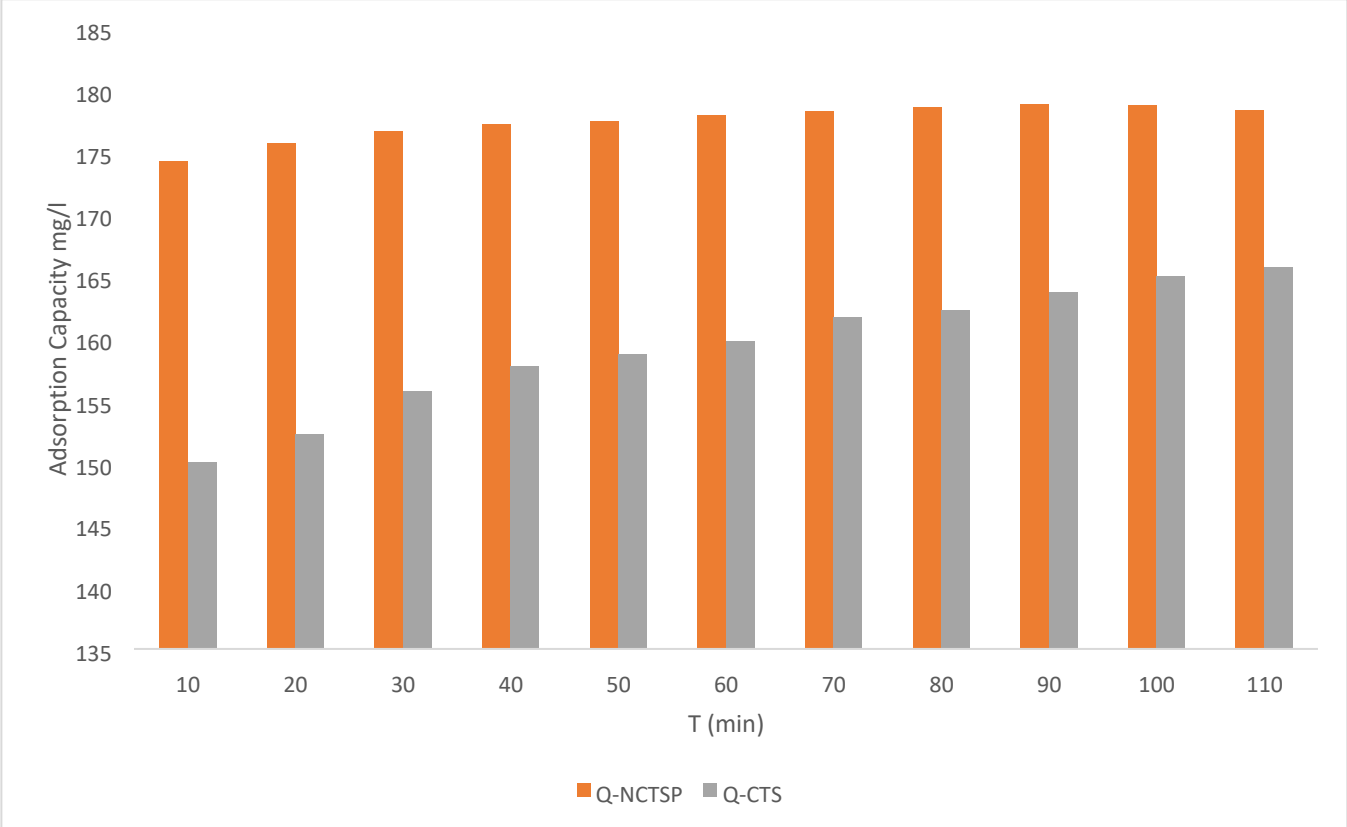

Figure 3.3: Phenol Adsorption Capacity by Nano-Chitosan and Chitosan

Figures 3.2 and 3.3 showed that adsorption capacity and removal efficiency of NCTS were 177.30 mg/g and 98.77% and that of CTS were 87.88 mg/g and 87.88% all within 10 to 40 mins. It was also deduced that large amount of phenol was adsorbed in the first 10 - 40 mins of contact time. This initial fast rate of adsorption may be a consequence of the availability of several binding sites for solute uptake. The large amount of phenol removal in the first few minutes of contact time between solute and adsorbent may be due to increased surface area resulting from the influence of improved surface reactivity from the influence of chemical pretreatment. Similar observation of large removal in less than 20 mins was reported by (El Jamal and Awala, 2011).

3.4.2 Influence of temperature

The influent of temperature on phenol adsorption on CTS and NCTS were presented as the adsorbents witnessed an increase in adsorption removal percentage and no significant change with further increase of temperature. A rapid increase in adsorption was observed within initial time at different temperatures

and then a gradual increment was observed. At higher temperatures the rate of diffusion of solute within the pores of the adsorbent increases (Ibrahim et al., 2022a).

3.4.3 Influence of adsorbent dosage

The influence of adsorbent dosage on adsorption of phenol using NCTS and CTS were carried out as different doses of adsorbents ranging from 1.36 - 4. 68 mg/l. The maximum percentage removal of phenol was observed as shown in Figure 3.3 and compared to the value reported by (Auta et al., 2012). The low adsorption percentage can be ascribed to the fact that all the adsorbents have a limited number of active sites that would have achieved saturation above a certain adsorbate concentration (Barkat et al., 2009). Effective utilization of synthesis NCTS cum further research to domesticate the NCTS adsorbent will contribute to SDG goals - SDG 3 (good health and wellbeing) and SDG 6 (clean water and sanitations).

3.5 Regeneration Effectiveness of Nano-chitosan for Phenol Removal

The following results were obtained after carried of regeneration procedure to ascertain the effectiveness of reuse of NCTS in phenol removal. However, about 20% EDTA solution was found to be effective in desorbing phenol and recovering the adsorption. From the results obtained, maximum regeneration was 93.65, 92.16, 91.49, 91.11, 90.11, 86.49 and 80.65% from first to seventh cycles which occurred at 50 min intervals as presented in Table 3.4. The results indicated that the batch gets saturated early and the regeneration efficiency increases slightly. The material was tested in seven cycles of sorption/desorption and it demonstrated reproducible performance, similar results were obtained by (Vijayalakshmi et al., 2017).

Table 3.4: Regeneration Data of Phenol Adsorbed on Prepared NCTSP

S/N	Time (min)	10	20	30	40	50
	Cycles	Percentage Regenerations of Nano-chitosan %				
1	Cycle 1	80.81	84.04	85.39	92.31	93.65
2	Cycle 2	78.57	81.93	83.82	89.47	92.16
3	Cycle 3	73.91	79.01	84.62	89.29	91.49
4	Cycle 4	71.91	80.26	83.87	88.46	91.11
5	Cycle 5	65.91	79.17	80.7	87.23	90.00
6	Cycle 6	62.2	77.05	76.92	82.93	86.49
7	Cycle 7	60.81	76.92	70.21	77.78	80.65

3.6 Fourier transform infrared (FTIR) of Adsorbent after Regeneration

The surface functional groups of the based adsorbent were determined by Fourier Transform Infrared (FTIR) spectroscopy. The data obtained were plotted with Origin Software as presented in Figure 3.4.

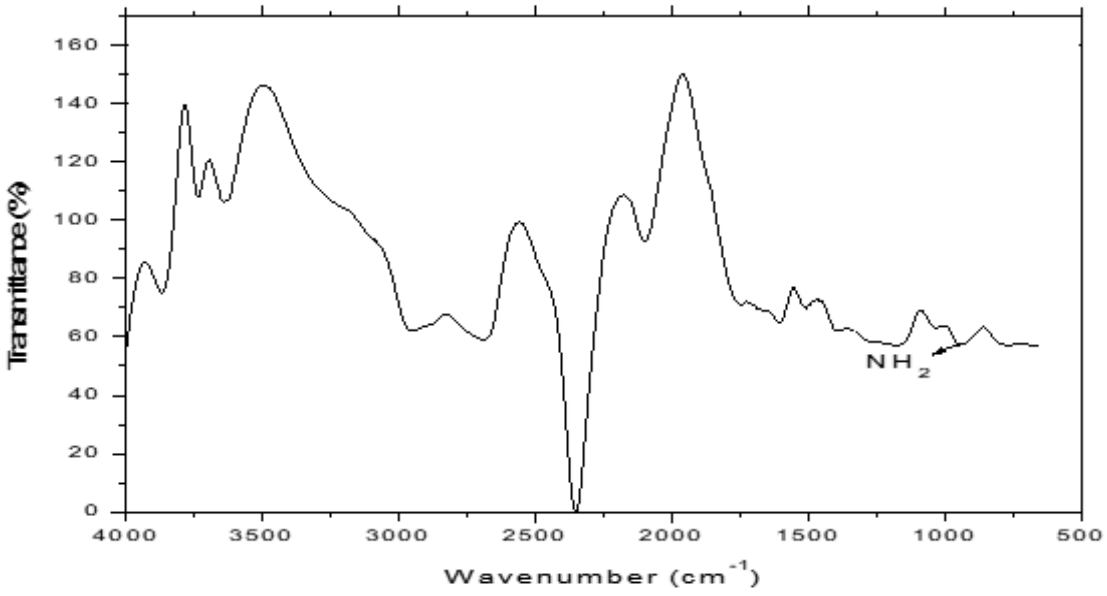

Figure 3.4: Infrared Spectra of the Adsorbent after Adsorption

The FTIR studies of the adsorbents were compared with standard commercial species. The broad and weak absorption bands were due to the combined effect of -NH_2 and -OH groups. The absorption band of each sample could be attributed to the N-H secondary amine stretches. The weak absorption band in the region were due to the presence of methylene and methyl groups in each sample structure and originates due to the C-H bond. These spectral values obtained were within the standard and are similar to vibration patterns reported by (Pereira et al., 2014) with insignificant changes in the positions and intensities which was due to the differences in the method of synthesized polymer.

4.0 CONCLUSION

The results of interaction revealed at factors of 35% sodium hydroxide, 3 h and 75 °C gives the DD to be 81.75%. This may be accredited to the procedures applied during the preparation. The standard quality of chitosan is also determined through molecular weight. It was observed from experiment that the particle size of NCTS was 82% yields as results of interaction of 2% STTP, 2.5 h and 2% Acetic acid. The value obtained may due to the accumulation of polymer molecules and intermolecular cross linking through TPP spanning. The percentages of phenol removal were 87.88% and 98.77% for both chitosan and nano-chitosan respectively.

Acknowledgment

The author would like to thank the Petroleum Technology Development Fund Nigeria.

Declaration of competing interest

The authors declare that they do not have any competing interest in the preparation and submission of this manuscript.

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