

Adsorption of Cadmium And Nickel from Aqueous Solution Using Chitosan And Chemically Modified Chitosan

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ABSTRACT.

Chitosan was produced by complete deacetylation of chitin from crustacean shells (snail shell). ForrierTransfomInfra-red Spectroscopy(FTIR) analysis of the unmodified chitosan and Acetic anhydride chitosan were carried out. The FTIR spectrum of unmodified chitosan has strong peaks observed at 3640.58cm^{-1} and the chemically modified acetic anhydride chitosan at 3278.44cm^{-1} . The two products: chitosan and Acetic Anhydride chitosan were applied for the adsorption of cadmium and Nickel from aqueous solution using a UV-visible Spectrophotometer (model JENWAY 6320D) and their percentage sorption was compared. It was observed that the modified chitosan with Acetic Anhydride, showed good ability for metal ion uptake.The amount Cadmium and Nickel absorbed was found to increase with time.Results also indicate that the adsorption capacity of metal ion increased with temperature. The high percentage adsorptions of the materials are due to the additional functional groups present in the samples. It took about 120 minutes for acetic anhydride modified chitosan to reach equilibrium at which a higher percentage sorption (86.50%) was obtained, while unmodified chitosan gave (82.50%).

KEYWORDS; Chitosan, Chemical modification, FTIR spectroscopy, Characterization, Metal ion removal



Introduction

Chitosan, a natural polysaccharide, is produced by the complete or partial N-acetylation of Chitin. It consists of randomly distributed β (1-4)-2-amino-2-Deoxy-D-glucopyranose and β (1-4)-2-acetamido-2-deoxy-D glucopyranose (with the ratio depending on the degree of deacetylation).

Natural biopolymer shows high biocompatibility and antibacterial properties. It is biodegradable and non-toxic polymer, thus it can be widely used in medical application. Moreover, the strong functionality of chitosan-(two hydroxyl groups and one primary amine group) which can donate a free pair of electrons, make chitosan soluble in diluted aqueous acidic solvents and allows the formations of the coordination bonds, which offers a considerable opportunity of a chemical modification[1].

In addition to the molecular weight and the distribution of the acetyl groups along the main chain, the solution properties of chitosan depend on its average degree of acetylation[2]. Deacetylation usually done in the solid state gives an irregular structure due to the semi-crystalline character of the initial polymer. The role of protonation of chitosan in the presence of acetic acid[3] and hydrochloric acid on solubility is shown by the dependence of the degree of ionization on pH and pK of the acid.

Nowadays, there has been an overwhelming growth in the production and use of synthetic chemicals. Most of these chemicals have been found to contaminate water supplies over the years. The presence of metal ions in water can cause some changes to the physical, chemical and biological properties of water, thus, can harm aquatic life and human health. Modern legislation is often compelled to enforce more restrictive regulations for effluent discharges due to the rise of public concern on health. As a result, various treatment systems have been accomplished to eliminate this type of pollutant from aqueous solutions.

The practice of using conventional materials for the removal of metal ion in wastewater treatment has become a major concern for researchers in line with their environmental impact. It was noted[4]that the use of toxic materials in removal of metal ions contributed to the secondary pollution problem especially from their by-products.

Chitosan can be considered as natural biopolymer due to the properties of non-toxicity, biodegradability, polyelectrolicity and possibility for transformation, which leads to a number of applications in effluentremoval [5].

Physical or chemical modification can be performed to modify hydroxyl and amino groups of chitosan. Physical modification improves the sorption properties, gel formation and implicated an expansion of the porous network. Chemical modification, improves the sorption properties of chitosan while hindering the dissolution of chitosan in strong acids. It also enhances the mechanical strength of chitosan and enhances superficial area of the beads. Chitosan is known to have good complexing capacity through specific interactions of the amino (-NH₂) groups with heavy metals (Muzzarelli, 1973). Analysis of complex formation mechanism with copper in dilute solution proposed two different complexes depending on pH and copper content (Rhazi et al, 2002).

Chitosan depends on the physical state of chitosan (powder, gel, fiber or film) and adequate Chelation is attained for greater degrees of deacetylation of chitin. Therefore Chelatan is related to the content and distribution of the amino groups (Kurita et al, 1979).

Chitosan differs from cellulose where chitosan has -NH₂ group in C-2 position instead of OH group in cellulose. The main reaction easily performed involving the C-2 position in chitosan is the quaternization of the amino group or a reaction in which an aldehydic function reacts with -NH₂ by reductive amination (Sashiva et al, 2003).

Cross-linking is one of the most common chemical modifications used to strengthen the stability of chitosan in acidic solutions. It can change the crystalline nature of chitosan and improves the resistance of chitosan over acid, alkali and chemicals, thus increases the sorption abilities of chitosan.

Materials And Methods

Materials

The materials used for this study include; sodium hydroxide, concentrated Hydrochloric acid, sodium hypochlorite, acetic acid, acetic anhydride, cinnamaldehyde. All chemicals were of analytical grade and purchase from BDH Germany.

Experiments

Collection of sample

African giant land snail shells (*Archachatina Marginata*) were purchased from a local market (Baleke market) in Agbor Ika South Local Government Area of Delta State, Nigeria. It was washed, sun-dried for two weeks and pulverized with grinding machine. The ground shells were later sieved with a mesh sieve of about 425µm.

Preparation of sample

a. Deproteination:

200g of the ground snail shell was put in a beaker and deproteinated by heating it in 2.5L of 1.2M

sodium hydroxide for two and half hours at a temperature of 80°C with occasional stirring at intervals. The experiment was allowed to cool and the excess sodium hydroxide solution was decanted. The residue was washed with plenty of deionised water to neutral pH of 7, air dried and weighed.

b. Demineralization (Removal of Calcium Carbonate):

180g of the deproteinated sample was put in 760.0ml of 0.7M HCL in a beaker, to remove the calcium carbonate until the bubbling stopped. The excess hydrochloric acid was decanted and the residue washed with deionised water to a neutral pH of 7, filtered and air-dried.

c. Decolouration (Colour Removal)

150g of the decalcified sample was dispersed in 1.2L of 0.32% solution of sodium hypochlorite (containing 12.5% of available chloride) in a beaker for 30 minutes, washed to neutral pH and air-dried. This gives chitin.

d. Deacetylation of Chitin to Produce Chitosan:

100g of the chitin was put into a beaker and deacetylated with 1.3L of 50% sodium hydroxide (12.5m) at a temperature of 121°C for 80 minutes; the excess sodium hydroxide solution was decanted. The residue was washed to neutral pH with deionised water and air-dried to give chitosan powder [6]

Preparation of acetic Anhydride Chitosan

1.0g of chitosan was dissolved in the least amount of distilled water (50ml) for 1 hour. Few drops (2ml) of acetic acid were added and sonicated for a further 2 hours until homogeneity was obtained. About 2ml of acetic anhydride was dropwise added while stirring and the reaction mixture was heated for one hour and then an aqueous solution of sodium hydroxide was added carefully after cooling to adjust the medium at pH ~ 8.5.

Preparation of Aqueous solution of Nickel and Cadmium

The adsorbates of Ni^{2+} and cd^{2+} was prepared from analytical grade $Ni(NO_3)_2 \cdot 6H_2O$ and 2.10g of $Cd(NO_3)_2$ by weighing out 4.79g of $Ni(NO_3)_2$ and 2.10g of $Cd(NO_3)_2$ respectively, dissolving in distilled water before making it up to mark with distilled water to get the stock Solution. These stock solutions were diluted with distilled water to obtain the working standard solutions required for the analysis.

Characterization of the unmodified chitosan and the acetic anhydride modified chitosan.

- Unmodified chitosan and chitosan modified with acetic anhydride were characterized by using Parkin-Elmer Fourier Transformed Infrared Spectrophotometer model 2000 (FTIR) [7]

Treatment of the Unmodified and Modified Chitosan with Solutions of Metal Ions

Effect of initial metal ion concentration on the removal of Cd²⁺ and Ni²⁺ using chitosan and Acetic Anhydride chitosan.

In a typical experiment, 0.5g of the adsorbent (chitosan), was weighed separately. into 100ml conical flasks containing 50ml of 20ppm, 40ppm, 60ppm and 80ppm of Ni²⁺ ions. These were shaken for 30mins using a magnetic stirrer. Their absorbances were analyzed for metal ion [8] content using a UV-visible Spectrophotometer (model JENWAY 6320D). The difference between the initial and residual concentrations was recorded as the amount of metal ions adsorbed onto the adsorbent. The experiment was repeated separately using acetic anhydride chitosan. The three samples were also to absorb Cd²⁺ in aqueous system. The adsorption efficiency of each adsorbent was then calculated using the equation;

$$\% \text{ sorption} = \frac{C_o - C_e}{C_o} \times 100$$

Where C_o = initial concentration of Ni²⁺ and Cd²⁺ before adsorption

C_e = Equilibrium concentration of Ni²⁺ and Cd²⁺ after adsorption

Effect of Temperature

The adsorption of the metal ions on chitosan and Acetic Anhydride chitosan was studied at various temperatures (20^oC, 40^oC, 60^oC and 80^oC). The kinetic sorption studies were carried out using 50ml of each metal ion solution of initial concentration of 2ppm. The metal ion solutions were measured into conical flask containing 0.5g of the adsorbent. The mixtures were uniformly agitated at 20^oC for 30 minutes.

The experimental set up was repeated for 40^oC, 60^oC and 80^oC respectively. At the end of each contact time, the mixture was analyzed for residual metal ion content using AAS and the amount of metal ion adsorbed was calculated using

$$Q_e = \frac{C_o - C_e}{m} \times V$$

where C_o and C_e are the concentration of metal ions before and after adsorption (mg/L) respectively

V= Volume of metal ion used (ppm)

m= weight of the adsorbent (grams)

Effect of Contact Time

Different contact time of 20, 30, 60, 90 and 120 minutes were used for this research work. In a typical experiment, 0.5g of chitosan, were added to 50ml of Ni²⁺ or Cd²⁺ solution at concentration of 2ppm in different conical flask and allowed to agitate at room temperature for 20, 30, 60, 90 and 120 minutes respectively using a magnetic stirrer at 120 rpm. The experiment was repeated separately using acetic

anhydride chitosan. The two samples were also to absorb Cd^{2+} or Ni^{2+} in aqueous system. At the end of each contact time the suspension were filtered using Whatman filter paper and the filtrate analysed with AAS. The amount of metal ion adsorbed was calculated using

$$Q_e = \frac{C_o - C_e}{m} \times V$$

Where C_o and C_e are the concentration of metal ions before and after adsorption (mg/l) respectively

V = Volume of metal ion used (ppm)

m = weight of the adsorbent (grams)



RESULTS AND DISCUSSION

Table 1: Result of the effect of initial metal ion concentration

Initial metal conc. (Ppm)	Residual metal ion conc (mg/l)				Amount of metal ion adsorbed (mg/l)				% sorption (w/w)			
	Chitosan		Acetic anhydride chitosan		Chitosan		Acetic anhydride chitosan		chitosan		Acetic anhydride chitosan	
	Cd ⁺²	Ni ⁺²	Cd ⁺²	Ni ⁺²	Cd ⁺²	Ni ⁺²	Cd ⁺²	Ni ⁺²	Cd ⁺²	Ni ⁺²	Cd ⁺²	Ni ⁺²
20	0.60	0.54	0.58	0.21	19.40	19.50	19.42	19.79	97.40	97.30	97.10	98.95
40	0.80	0.98	0.69	0.25	39.20	39.02	39.31	39.75	98.00	97.55	98.28	99.36
60	0.90	0.99	0.80	0.85	59.10	59.10	59.01	59.70	98.50	98.35	98.67	99.50
80	1.10	1.11	0.93	0.35	78.90	78.90	78.90	79.05	98.60	98.61	98.84	98.81

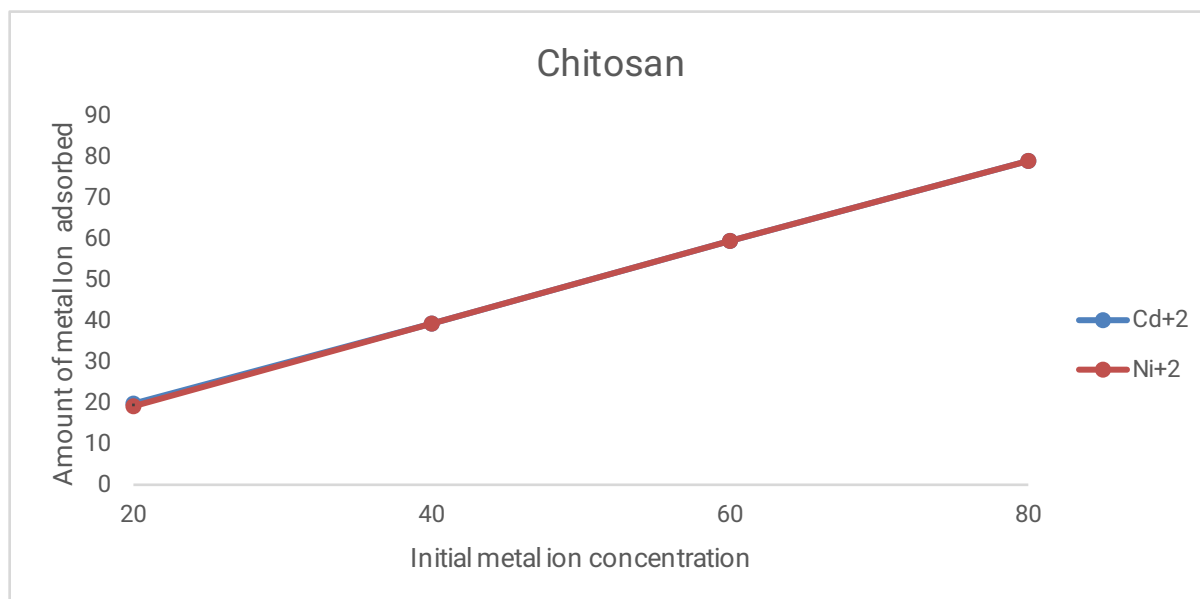


Figure 1 Graph of Initial Metal Ion Concentration For chitosan

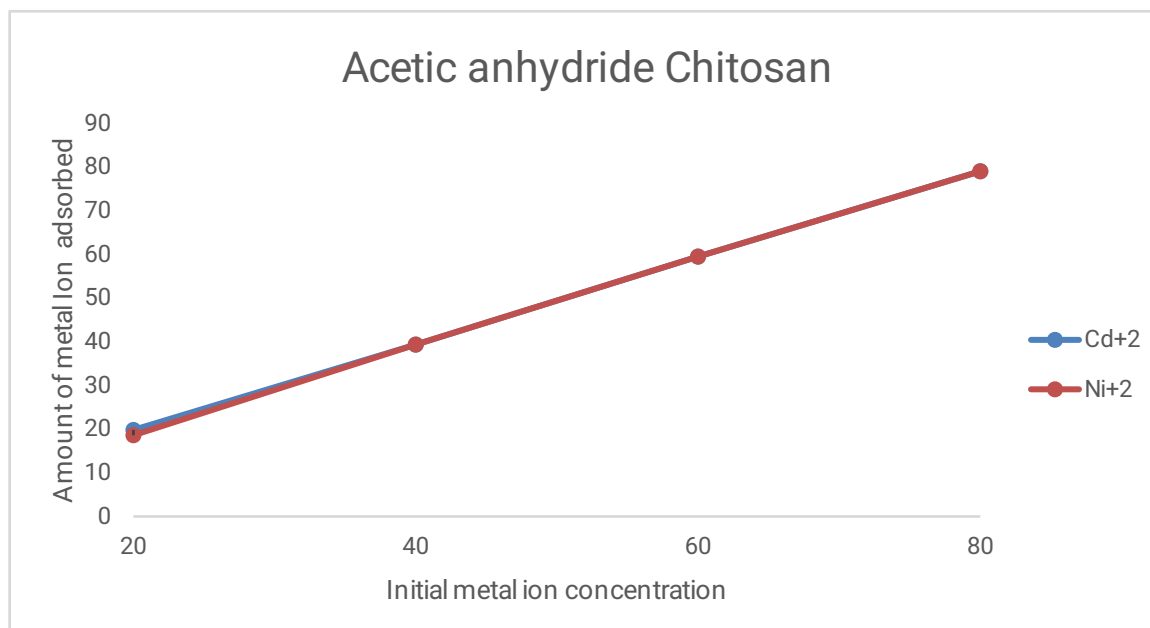


Figure 2 Graph of Initial Metal Ion Concentration For acetic anhydride chitosan

The Result of the Effect of Initial Metal Ion Concentration

The result of the effect of initial metal ion concentration is shown in Table 1 and fig 1 and 2. The percentage removal of Cd^{2+} and Ni^{2+} increased with increasing the concentration of the metal ion due to the greater availability of binding sites. The variation in the adsorption of these metal ions might be due to differences in the chemical properties of the adsorbate, particularly hydration energies and ionic sizes. The variation may have also occurred because increase in concentration of the adsorbate brings about increase in competition of the adsorbate molecules for the few available binding sites on the surface of the adsorbent, hence increasing the amount of metal ions removed[9]. From Table 1, it was observed that

the modified chitosan with Acetic Anhydride, showed good ability for metal ion uptake. The high percentage adsorptions of the materials are due to the additional functional groups present in the samples.

In chitosan, the functional group present is hydroxyl and primary amino group while in acetic anhydride chitosan, the functional groups present are carboxyl group and acyl group. The functional groups present in the modified chitosan affect adsorption because the presence of the additional functional group onto chitosan led to a decrease in the swelling ability of chitosan. It also enhances its mechanical strength and increases the superficial area of the chitosan matrix. A decrease in swelling of chitosan led to increase in adsorption and also create more active site for the metal ions to be adsorbed.



Table 2 Result of the Effect of Contact time

Contact time (mins)	Residual metal ion conc (mg/l)				Amount of metal ion Adsorbed (mg/l)				% sorption (w/w)			
	Chitosan		Acetic anhydride chitosan		Chitosan		Acetic anhydride chitosan		chitosan		Acetic anhydride chitosan	
	Cd ⁺²	Ni ⁺²	Cd ⁺²	Ni ⁺²	Cd ⁺²	Ni ⁺²	Cd ⁺²	Ni ⁺²	Cd ⁺²	Ni ⁺²	Cd ⁺²	Ni ⁺²
200	1.54	1.20	0.86	1.30	0.55	0.80	1.14	0.70	27.50	40.00	57.00	35.00
30	0.88	0.95	0.70	0.90	1.12	1.05	1.30	1.10	56.00	52.50	65.00	55.00
60	0.72	0.87	0.55	0.84	1.28	1.13	1.45	1.16	64.00	56.50	72.50	58.00
90	0.68	0.62	0.46	0.78	1.32	1.38	1.54	1.22	66.00	69.00	77.00	61.00
120	0.42	0.35	0.27	0.65	1.58	1.65	1.73	1.35	79.00	82.50	86.50	67.50

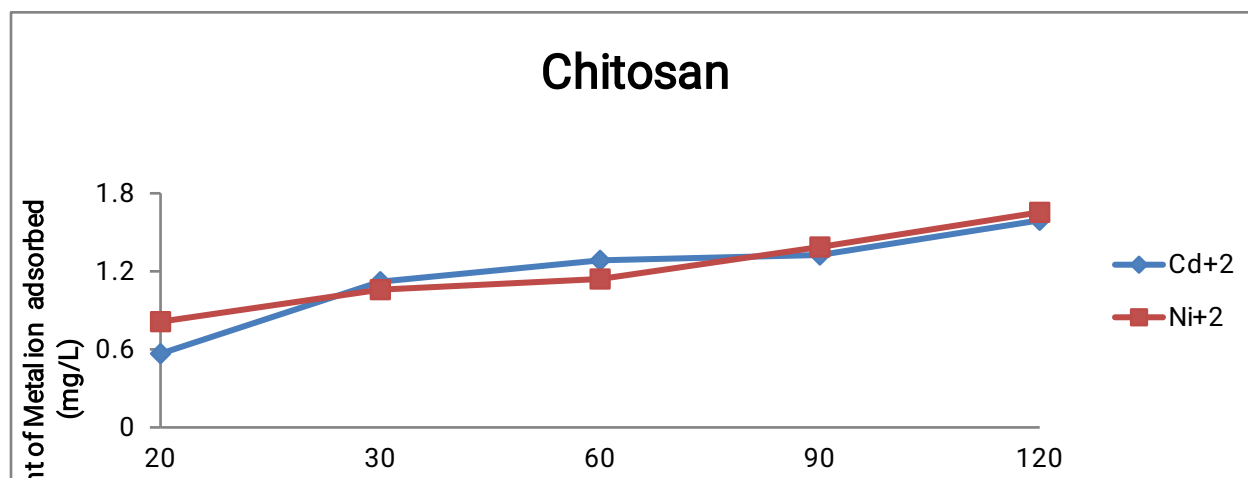


Figure 3 *Graph of contact time For chitosan*

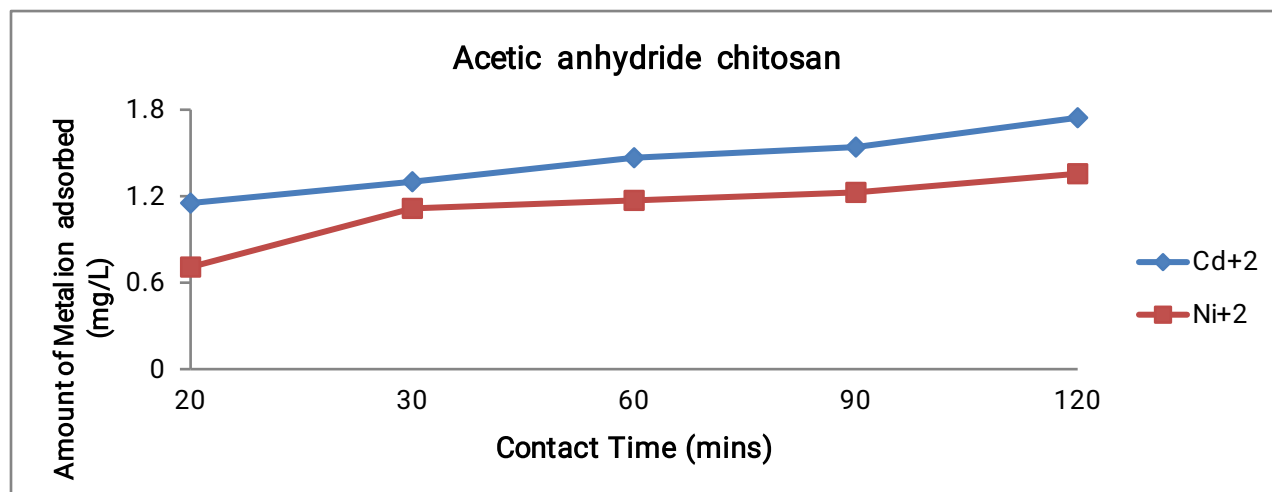


Figure 4 *Graph of contact time For Acetic Anhydriden chitosan*

The result from table 2 and fig 3 and 4 shows that the extent of absorption is rapid in the initial stages before attaining of equilibrium. The amount Cadmium and Nickel absorbed was found to increase with time. The rate of absorption consists of two phases: an initial rapid phase and a slow second phase until equilibrium is accomplished. The first phase occurred instantaneously which is related to the exterior surface adsorption. The second phase is the steady phase before adsorption reaches equilibrium. This result is in line as reported [10] earlier. It took about 120 minutes for acetic anhydride modified chitosan to reach equilibrium at which a higher percentage sorption (86.50%) was obtained, while unmodified chitosan gave (82.50%)

Table 3. The Result of the Effect of Temperature

	Residual metal ion conc (mg/l)	Amount of metal ion Adsorbed (mg/l)	% sorption (w/w)

Temp o/°C	Chitosan		Acetic anhydride chitosan		Chitosan		Acetic anhydride chitosan		chitosan		Acetic anhydride chitosan	
	Cd ⁺²	Ni ⁺²	Cd ⁺²	Ni ⁺²	Cd ⁺²	Ni ⁺²	Cd ⁺²	Ni ⁺²	Cd ⁺²	Ni ⁺²	Cd ⁺²	Ni ⁺²
20	0.81	0.93	0.24	0.35	1.19	1.07	1.76	1.65	59.00	53.50	88.00	82.50
40	0.80	0.91	0.28	0.40	1.20	1.09	1.72	1.60	60.00	54.50	86.00	80.00
60	0.58	0.68	0.39	0.75	1.42	1.32	1.62	1.25	71.00	70.00	80.50	62.50
80	0.47	0.59	0.50	0.90	1.53	1.41	1.50	1.10	76.50	70.50	75.00	55.00

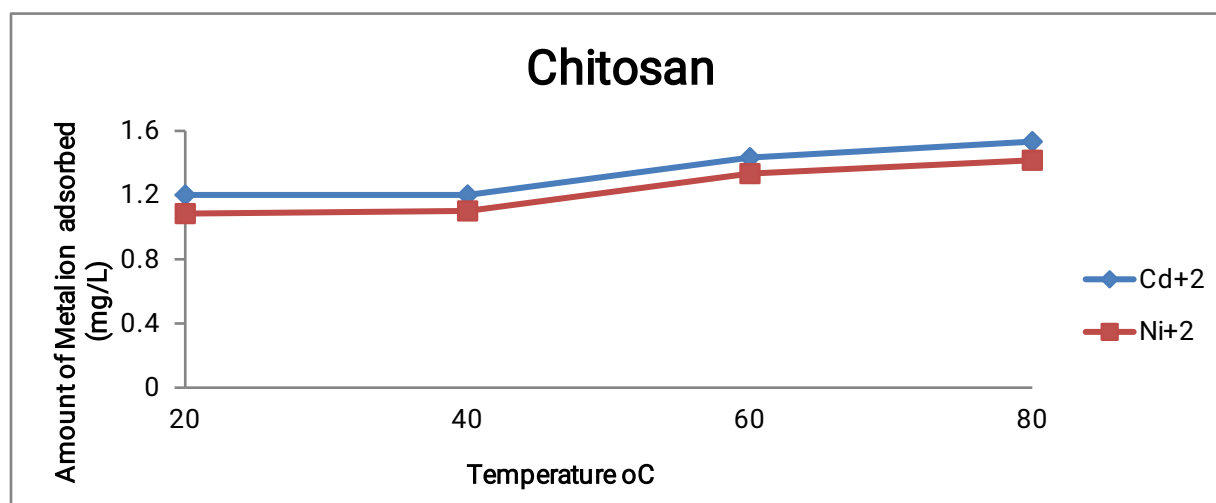


Figure 5 Graph of Effect of Temperature For chitosan

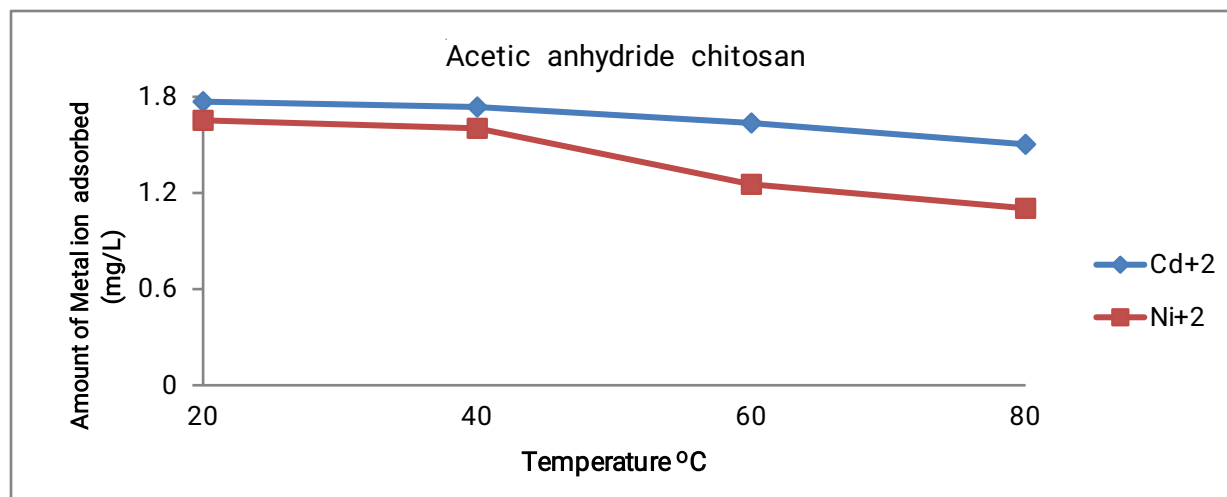


Figure 6 Graph of Effect of Temperature For acetic anhydride chitosan

From the result in Table 3 and figure 5 and 6, Increase in temperature from 20 to 80°C was found to result in the steady increase in the removal efficiency. Increase adsorption at increasing temperature is ascribed to enhanced mobility of metal ions from bulk solution [11]. Results indicate that the adsorption capacity of metal ion increased with temperature. This may be as a result of increase in the mobility of the adsorbent and metal ions with temperature. An increasing number of molecules may also acquire sufficient energy to undergo interaction with active site at the surface. Increasing temperature produces enhanced swelling effect in the internal structure of the adsorbent enabling metal ion to penetrate further. Hence optimum temperature was 80°C.

The result of the FTIR spectroscopy for chitosan, Acetic Anhydride Chitosan

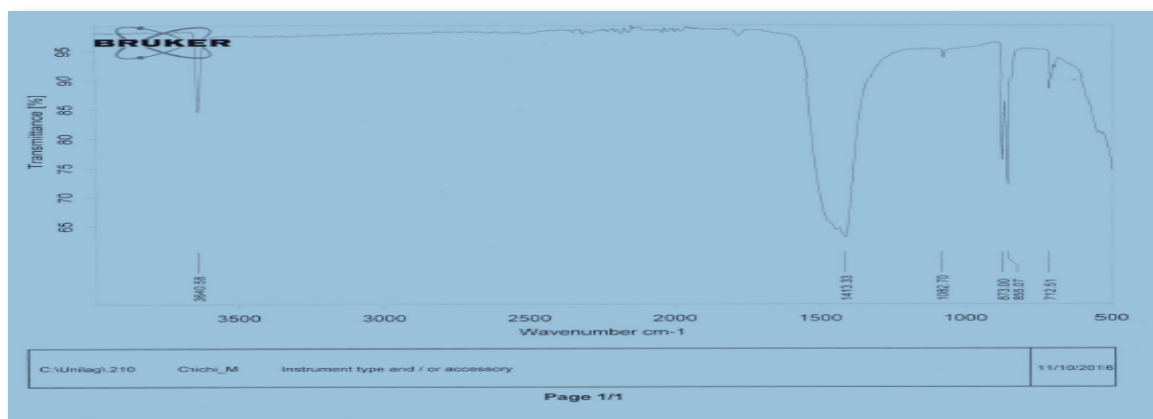


Figure 7 *Spectral Sheet Of Unmodified Chitosan*

The result of FTIR spectroscopy for chitosan and Acetic Anhydride chitosan are presented in the spectra sheet. FT-IR spectroscopy was used for characterization to elucidate the changes that occur in the chemical structure, figure 7 is the spectra of unmodified chitosan. The spectrum of unmodified chitosan shows a broad and sharp peak at 3640.58cm^{-1} for O-H stretching, the band at 1413.33cm^{-1} for C-H bending, the band at 1082.70cm^{-1} is assigned for C-O-C bonds while the peaks at 873.00cm^{-1} , 855.07cm^{-1} and 712.51cm^{-1} are assigned to CH_2 bending due to pyranose ring.

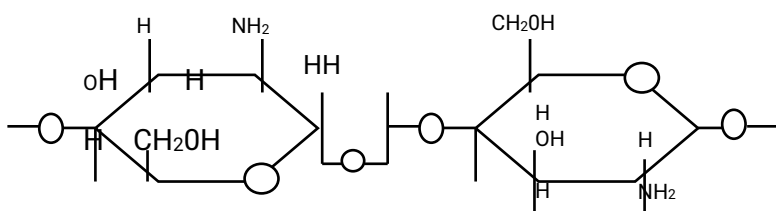
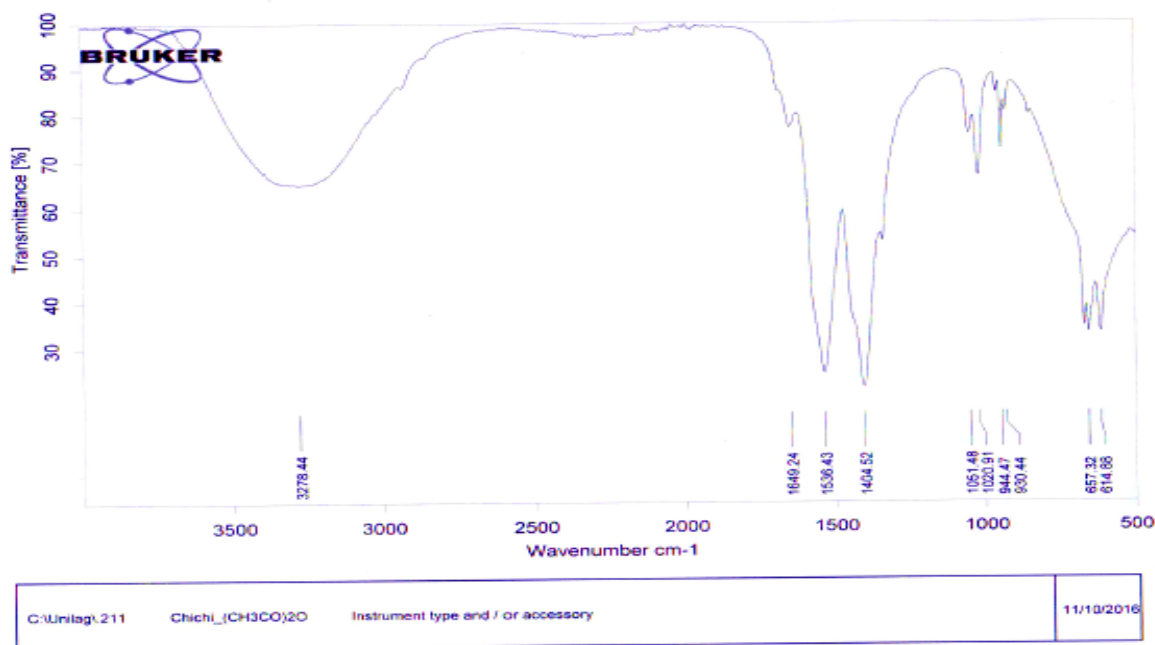


Figure 8 *Structure of unmodified chitosan*



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Figure 9 *Spectra of Acetic Anhydride Chitosan*

Figure 9 shows the spectrum of Acetyl-chitosan (Acetic Anhydride chitosan). The broad band at 3278.44 cm^{-1} for O – H stretching of secondary amines and carboxylic acid, 1649.24 cm^{-1} N – H bend for primary amines, 1536.43 cm^{-1} C=C stretch, 14045.52 cm^{-1} C-H bend for alkyl group, 1051.48 cm^{-1} C-O stretching for primary alcohol, 944.47 cm^{-1} C-H bend of $\text{CH}_2 = \text{CH}$ for vinyl group, 930.44 cm^{-1} for C-H bend of $\text{RCH} = \text{CR}_2$ for acyl groups. The band at 1649.24 cm^{-1} also corresponds to C=O stretch for Anhydrides $(\text{RCO})_2\text{O}$. The difference in the spectra in fig 3.5 and fig 3.6 is that acetic anhydride chitosan has a strong absorption at 1536.43 cm^{-1} and 1404.52 cm^{-1} relating to C – O stretching and C-H bend for alkyl group and a new band at 1649.24 cm^{-1} and 930.44 cm^{-1} which correspond to C=O for anhydride and $\text{RCH} = \text{CR}_2$ for acyl group confirms that the chitosan has been modified to acetic anhydride chitosan.

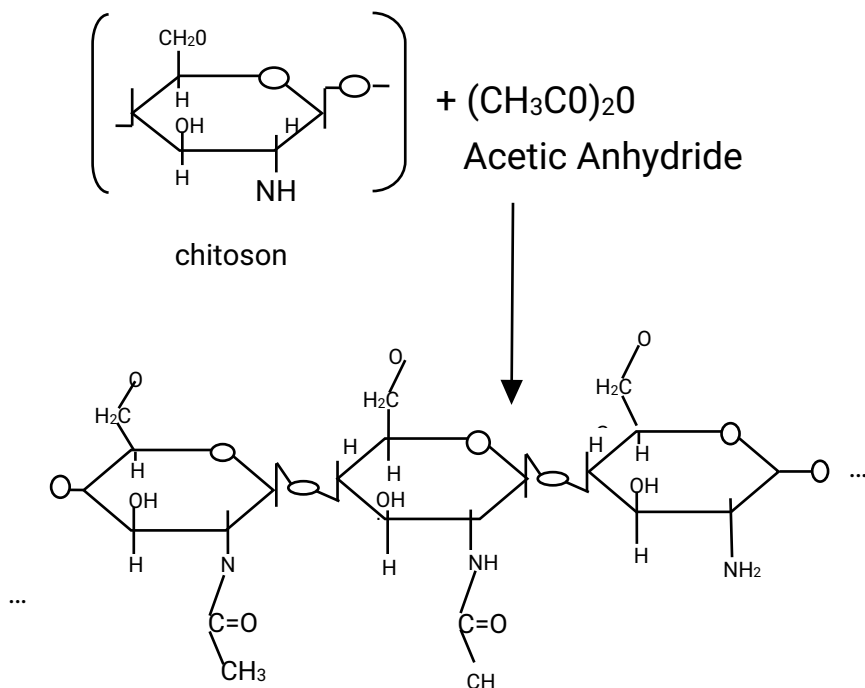


Figure 10 Structural formula of acetic anhydride chitosan

Langmuir Isotherm Versus Freundlich Isotherm

The values for the absorption isotherms (freundlich and Langmuir) on the adsorption of Cd^{2+} and Ni^{2+} by unmodified Chitosan and Acetic Anhydride Chitosan are presented in Table 4.

Table 4 Freundlich Isotherm Parameter For Modified Chitosan and Acetic Anhydride Chitosan For initial metal ion concentration

Co (PPM)	Log Co	Chitosan (log qe)		Acetic anhydride chitosan (log qe)	
		Cd^{2+}	Ni^{2+}	Cd^{2+}	Ni^{2+}

20	1.30	1.288	1.2900	1.289	1.296
40	1.60	1.593	1.591	1.594	1.599
60	1.78	1.772	1.771	1.772	1.776
80	1.90	1.897	1.897	1.898	1.901

A Plot of $\log q_e$ against $\log C_0$ gave a straight line for Freundlich isotherm

Conclusion

Based on the results, it can be concluded that Acetic Anhydride chitosan is an effective adsorbent for the removal of Cd^{2+} and Ni^{2+} from aqueous solution since a high adsorption capacity was achieved and the mechanical strength of the adsorbent was improved by this modification. Chemical modification of chitosan with different organic compounds can lead to promising materials in the light of their application.

- 1) The derivatives of chitosan have been analysed to be used for metal ion adsorption using $Cd(NO_3)_2$ and $Ni(NO_3)_2$ aqueous solutions as representative examples for metal ions. The results from the experiment shows that the modified derivatives of chitosan are of higher capacity than the unmodified derivatives.
- 2) This can be elucidated by the certainty that the modification process hinders the chain mobility and consequently the matrix swelling ability.
- 3) That the high uptake of metal ion with the modified chitosan derivatives was higher than the unmodified chitosan
- 4) The addition functional groups in the modified derivatives of chitosan increases the efficiency of metal ion uptake as they are capable of decreasing transition metal ion concentrations.
- 5) Natural polymeric adsorbents are eco and environmentally friendly and low cost.

Limitation

A major constraint to this study was the constant power interruption during the course of the experiment. Another constraint encountered during the research work was the non-availability of snail shell that was used for the preparation of the adsorbent. Further researches should make use of other more available materials for the preparation of the adsorbent. This can be overcome if future researchers can provide a sizeable standby generator that can power most of the equipments used during the course of the study.

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