



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). Fourier Transform Infra-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.

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1. Introduction

One of the biggest environmental issues is toxic heavy metal contamination [1]. The metals are particularly problematic because they are persistent and do not degrade readily. Because of their limited surface area, water solubility, and poor recovery, these metals remain difficult to remove using pure natural polymers. The fact that the chemical structure of chitosan can be altered is one of its benefits as an adsorbent [2]. Chitin can be completely or partially N-deacetylated to form the natural polymer Chitosan [3]. It is made up of (1 4)-2-amino-2-deoxy-D-glucopyranose and (1 4)-2-acetamido-2-deoxy-D-glucopyranose, which are scattered randomly (with the ratio depending on the degree of deacetylation).

Natural biopolymer shows high biocompatibility and antibacterial properties. Chitosan is biodegradable and non-toxic polymer. It has been widely used as an adsorbent and in medical applications because of its low cost [4]. 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 [5]. 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[6]. 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[7] 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[8] that the use of toxic materials in removal of metal ions contributed to the secondary pollution problem especially from their by-products. Due to its non-toxicity, biodegradability, polyelectrolytic, and transformational potential, chitosan can be regarded as a natural biopolymer with a variety of applications in effluent removal [9]. However, there are some limitations that prevent its practical use, such as low mechanical strength, low solubility in acidic medium, low adsorption capacity, and lack of sensitivity. The hydroxyl and amino-groups of chitosan have been modified in order to enhance its physicochemical properties for metal uptake. Chitosan's hydroxyl and amino groups are subject to physical or chemical alteration. Physical alterations enhance sorption abilities, gel formation, and suggest an increase in the porosity network. Chitosan's sorption capabilities are enhanced through chemical modification, which also prevents it from dissolving in strong acids. Cross-linking [10] 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.

2. Materials and Methods

2.1. 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.

3. Experiments

3.1. 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 $425\mu\text{m}$.

4. Preparation of sample

a. Deproteinization

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 [11]

4.1. 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.

4.2. 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.

4.3. 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) [12]

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

5. Effect of initial metal ion concentration on the removal of Cd^{2+} and Ni^{2+} 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 Ni^{2+} ions.

These were shaken for 30mins using a magnetic stirrer. Their absorbances were analyzed for metal ion [13] 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 Cd^{2+} in aqueous system. The adsorption efficiency of each adsorbent was then calculated using the equation;

$$\% \text{ sorption} = \frac{Co - Ce}{Co} \times 100$$

Where Co = initial concentration of Ni^{2+} and Cd^{2+} before adsorption

Ce = Equilibrium concentration of Ni^{2+} and Cd^{2+} after adsorption

5.1. Effect of Temperature

The adsorption of the metal ions on chitosan and Acetic Anhydride chitosan was studied at various temperatures (20^0C , 40^0C , 60^0C and 80^0C). 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 20⁰C for 30 minutes.

The experimental set up was repeated for 40⁰C, 60⁰C and 80⁰C 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

$$Q_e = \frac{C_0 - C_e}{m} \times V$$

where Co and Ce 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)

5.2. 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 Cd²⁺ or Ni²⁺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

$$Q_e = \frac{C_0 - C_e}{m} \times$$

Where Co and Ce 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)

6. 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

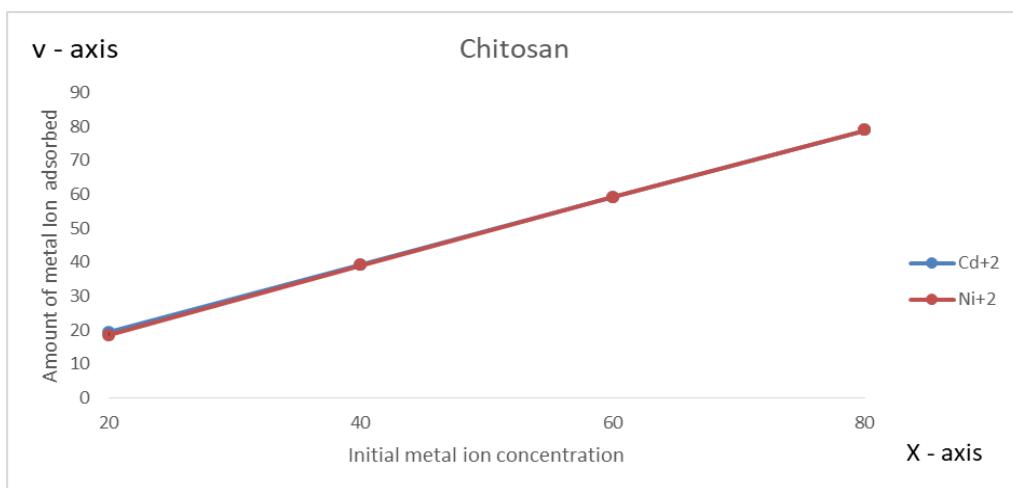


Figure 1: Graph of Initial Metal Ion Concentration for chitosan.

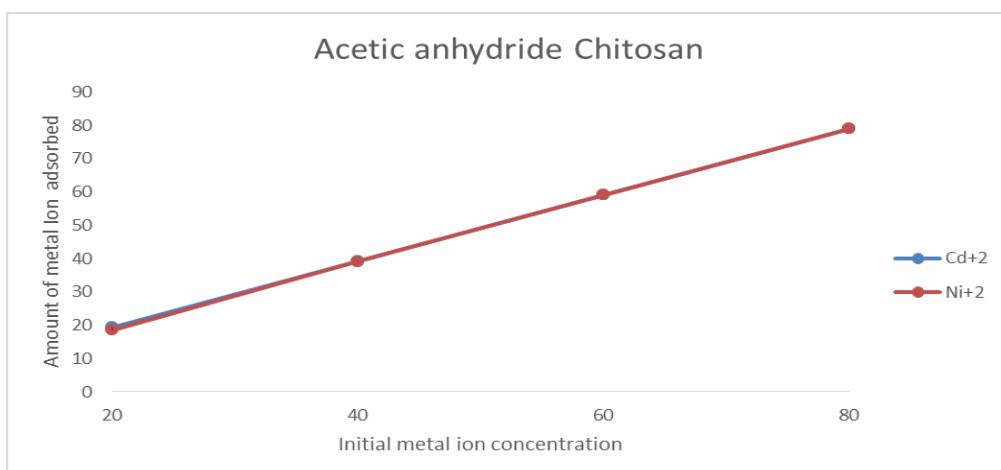


Figure 2: Graph of Initial Metal Ion Concentration for acetic anhydride chitosan.

6.1. 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 figures 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 [14]. 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 unto 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

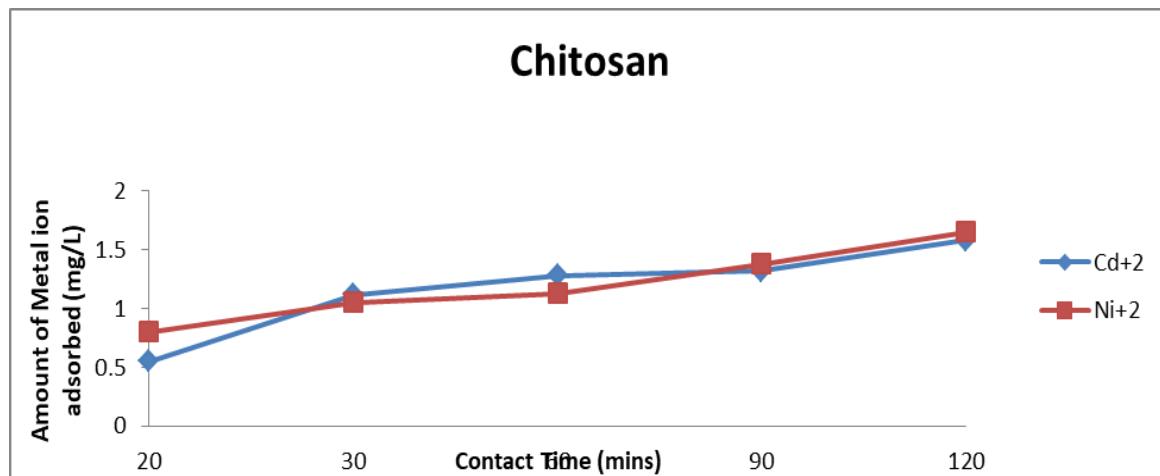


Figure 3: Graph of contact time For chitosan.

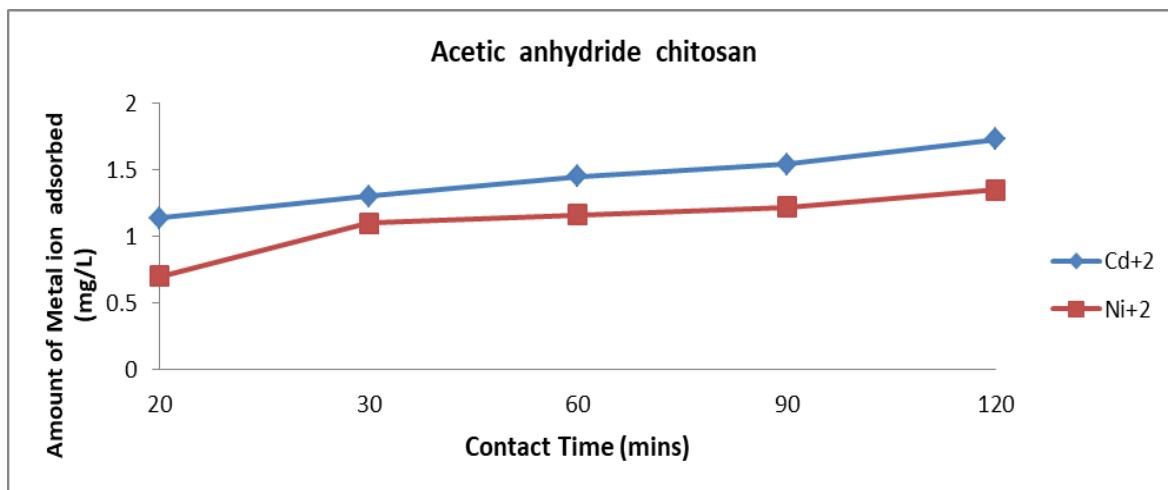


Figure 4: Graph of contact time For Acetic Anhydride chitosan.

The result from table 2 and figures 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 [15] 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 oC	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

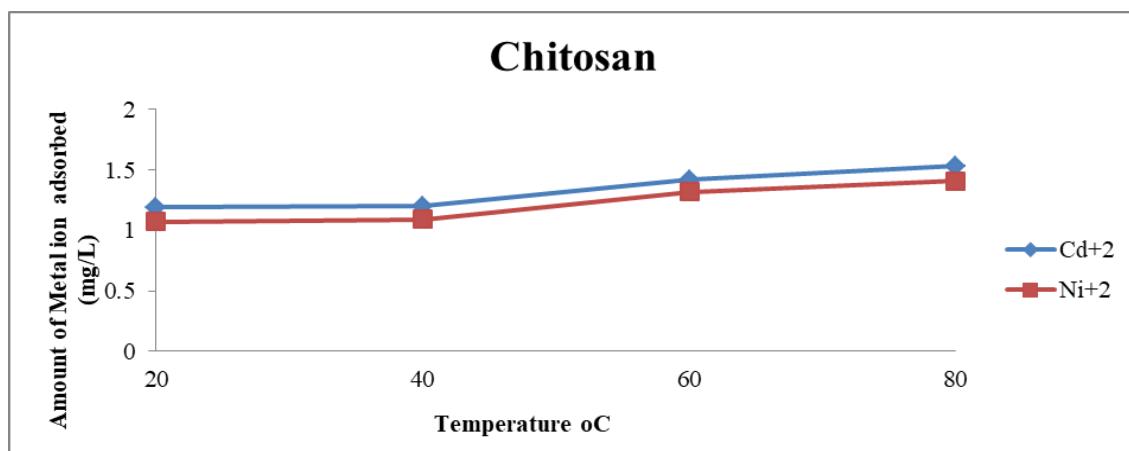


Figure 5: Graph of Effect of Temperature for chitosan.

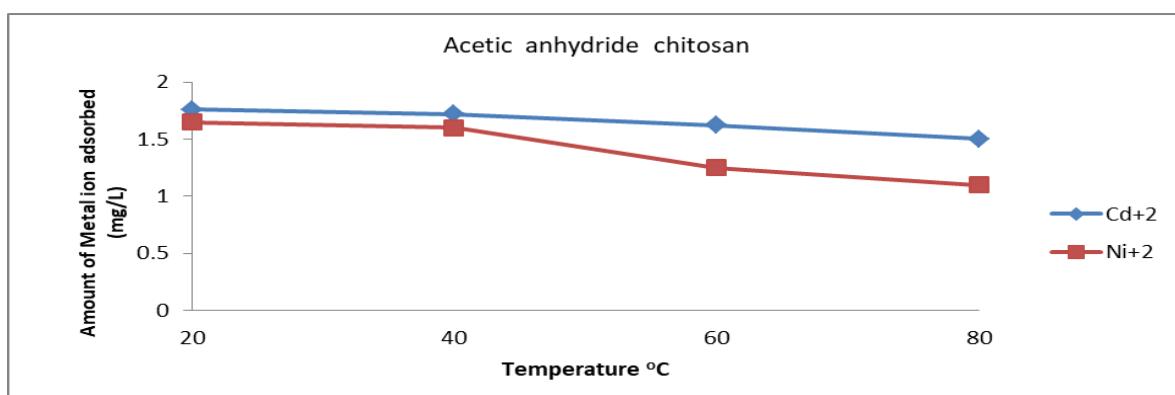


Figure 6: Graph of Effect of Temperature for acetic anhydride chitosan.

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 [16]. 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.

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

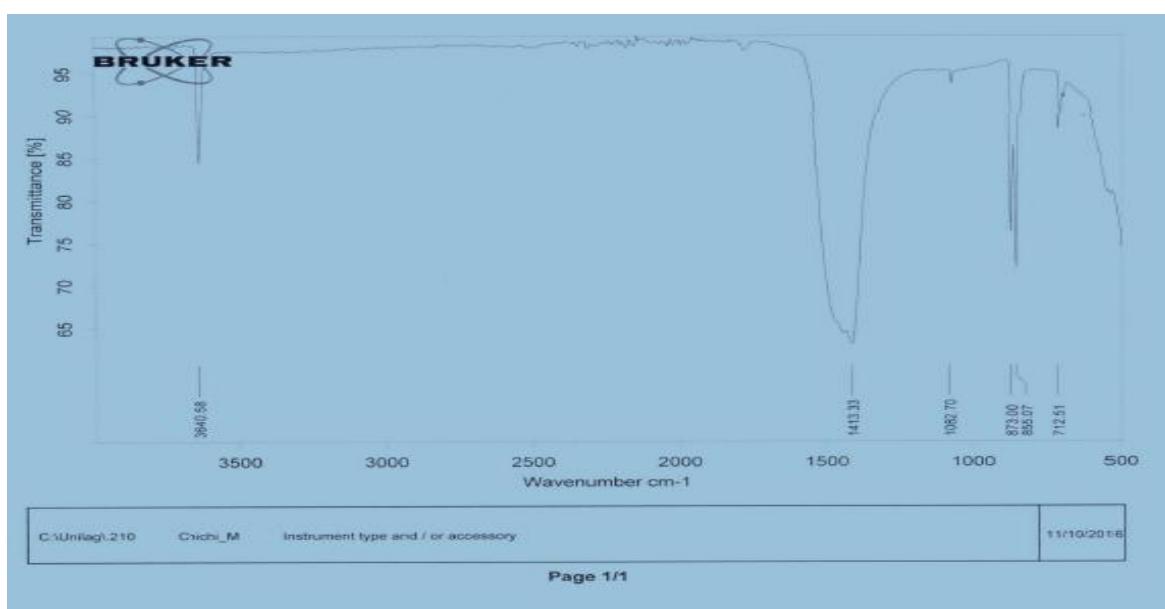


Figure7: Spectral Sheet of Unmodified Chitosan.

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 3640cm⁻¹ for O-H stretching, the band at 1413cm⁻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 CH₂ bending due to pyranose ring.

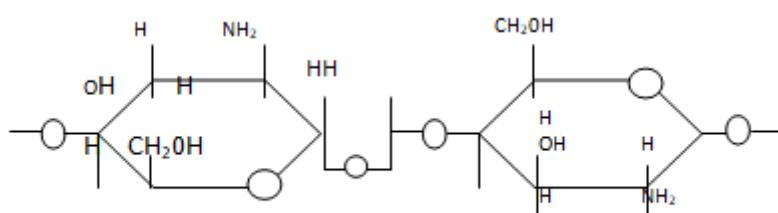


Figure 8: Structure of unmodified chitosan.

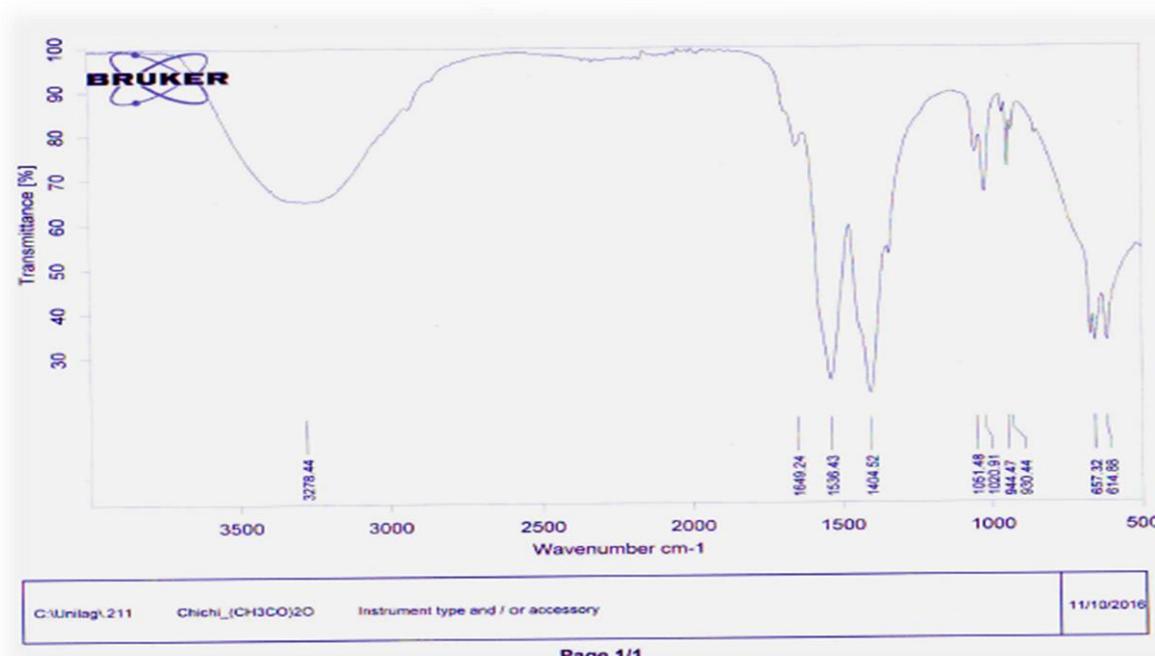


Figure 9: Spectra of Acetic Anhydride Chitosan.

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, 1536.43cm⁻¹ C=C stretch, 14045.52 cm⁻¹ C-H bend for alkyl group, 1051.48cm⁻¹ C-O stretching for primary alcohol, 944.47cm⁻¹ C-H bend of CH₂ = CH for vinyl group, 930.44 cm⁻¹ for C-H bend of RCH= CR₂ for acyl groups. The band at 1649.24cn⁻¹ also corresponds to C=O stretch for Anhydrides (RCO)₂O.

The difference in the spectra in fig 3.5 and fig 3.6 is that acetic anhydride chitosan has a strong absorption at 1536.43cm⁻¹ and 1404.52cm⁻¹ relating to C – O stretching and C-H bend for alkyl group and a new band at 1649.24cm⁻¹ and 930.44cm⁻¹ which correspond to C=O for anhydride and RCH = CR₂ for acyl group confirms that the chitosan has been modified to acetic anhydride chitosan.

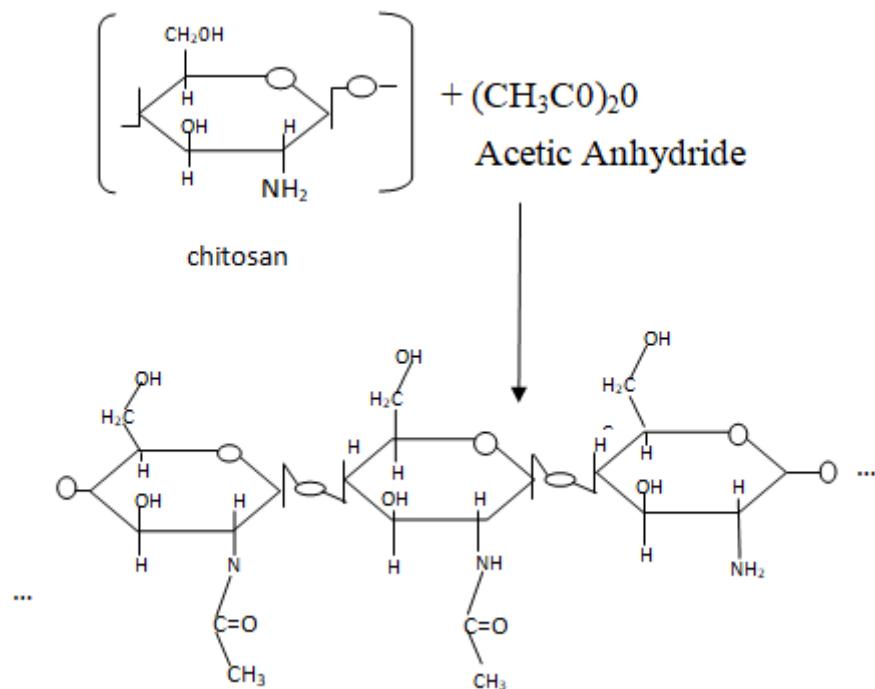


Figure 10: Structural formula of acetic anhydride chitosan.

7. 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.

For initial metal ion concentration

Table 4: Freundlich Isotherm Parameter for Modified Chitosan and Acetic Anhydride Chitosan.

Co (PPM)	Log Co	Chitosan (log qe)		Acetic anhydride chitosan (log qe)	
		Cd^{2+}	N_1^{2+}	Cd^{2+}	N_1^{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 $\log C_o$ gave a strength line for freundlich isotherm

8. Conclusion

Based on the results, it can be concluded that Acetic Anhydride chitosan is an effective adsorbent for the removal of Cd²⁺ and Ni²⁺ 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.

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