



## COMPARISON OF THE ADSORPTION CAPACITY OF CHITOSAN AND CINNAMALDEHYDE MODIFIED CHITOSAN IN THE REMOVAL OF NICKEL AND CADMIUM FROM AQUEOUS SOLUTION

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### ABSTRACT

**Background and Aim:** Chitosan can also be used in toothpaste, mouth washes, and chewing gum. They freshen the breath and prevent the formation of plaque and tooth decay. Salts of chitosan added to toothpaste, mask the unpleasant taste of silicon oxide and bind powders so that they maintain their granular shapes. The aim of this study is to modify chitosan with some aldehydes and the obtained product characterized and tested towards their metal ion uptake application.

**Materials and methods:** Chitosan was produced by complete deactivation of chitin from crustacean shells (snail shells). The chitosan produced was used to prepare cinnamaldehyde chitosan and Acetic Anhydride chitosan. Fourier Transformed Infrared Spectroscopy (FTIR) analysis of the pure chitosan and cinnamaldehyde chitosan were carried out. The FTIR spectrum of unmodified chitosan had strong peaks observed at  $3640.58\text{cm}^{-1}$  due to O-H stretching, the bands at  $1413.33\text{cm}^{-1}$  for C-H bending and the band at  $1632\text{cm}^{-1}$  was assigned to N-H bending.

**Results/ Discussion:** After the chemical modification, some changes were observed in the spectra of cinnamaldehyde chitosan. The two products: chitosan and cinnamaldehyde chitosan were applied for the adsorption of Cadmium and Nickel from aqueous solution and their percentage sorption were compared. Cinnamaldehyde chitosan gave 99.56% at an optimum concentration of 80ppm while unmodified chitosan gave 98.61% at an optimum concentration of 80 ppm

**Conclusion:** From this investigation, we can infer that the chemical modification of chitosan with the different organic compounds can lead to promising materials in the light of their application directions. The modified chitosan products showed good ability to uptake metal ions from their aqueous solutions.

**Keywords:** Chitosan, Chemical modification, FTIR spectroscopy, Characterization, metal ion removal.

## INTRODUCTION

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. The use of toxic materials in removal process contributed to the secondary pollution problem especially from their by-products (Kandile *et al.* 2013).

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 effluents removal (Ngah *et al.* 2006).

Physical or chemical modification can be performed to modify hydroxyl and amino groups of chitosan. Physical modification improve the sorption properties, gel formation and implicated an expansion of the porous network. Chemical modification, improved the sorption properties of chitosan while hindering the dissolution of chitosan in strong acids (Yang *et al.* 2014). It also enhances the mechanical

strength of chitosan and enhances superficial area of the beads.

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. Solution properties of chitosan depend on its average degree of acetylation (DA) and the distribution of the acetyl groups along the main chain in addition to the molecular weight (Kubota and Eguchi, 1997). 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 and hydrochloric acid on solubility is shown by the dependence of the degree of ionization on pH and PK of the acid.

Chitosan is compatible with lots of biologically active components incorporated in cosmetic products composition chitosan and its derivative offer uses in three areas of cosmetics: in cosmetic products hair care, skin care and oral care. Chitosan and hair are complementary to each other owing to the fact that they carry opposite electrical charges: chitosan is positive and hair is negative. A clear solution that contains chitosan forms a clear elastic film on hair, thereby increasing its softness, smoothness, and mechanical strength. The material can also form a gel when added to mixtures of alcohol and water. Chitosan can be used in shampoos, rinses, permanent wave agents, hair colorants, styling lotions, hair sprays and hair tonics.

Several derivatives of chitosan have potential applications in hair care. They include glyceryl chitosan, an adduct of an oligomer of hydrolyzed chitosan. n-hydroxypropyl chitosan quaternary

hydroxypropyl-substituted chitosan, chitosan oligosaccharides etc.

Chitosan and its derivations have two advantages that make it good candidate for skin care: one being their positive charge and the other is that the molecular weights of most chitosan products are so high that they cannot penetrate the skin. Thus chitosan can function as a moisturize for skin. Because of its lower costs, it might compete with lyaluronic acid in this application. Chitosan is already found in creams, pack material, lotions, and nail enamel: nail lacquers, foundation, eye shadow, lipstick, cleaning materials, and bath agents.

Chitosan can also be used in toothpaste, mouth washes, and chewing gum. They freshen the breath and prevent the formation of plaque and tooth decay. Salts of chitosan added to toothpaste, mask the unpleasant taste of silicon oxide and bind powders so that they maintain their granular shapes. Chitosan can also be applied as a dental filler material where it absorb candida like thicans, a fungus that sticks to teeth, making it candidates to clean false teeth. The aim of this study is to modify chitosan with some aldehydes and the obtained product will be characterized and tested towards their metal ion uptake application.

## MATERIALS AND METHODS

### Collection of samples

African giant land snail shells (*Archarchatinamarginata*) were collected 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 $\mu$ m

### Preparation of sample

Chitosan was prepared according to the following deproteination, decalcification, decolouration and deacetylation

**Deproteination:** A total of 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<sup>0</sup>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 deioned water to neutral pH, air dried and weighed.

**Decalcification:** About 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 deioned water to a neutral pH, filtered and air-dried.

**Decoloration:** 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 mins, washed to neutral pH and air-dried to give chitin.

**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<sup>0</sup>c for 80 mins, the excess sodium hydroxide solution was decanted. The residue was washed to neutral pH with deionised water and air-dried to give chitosan powder.

**Preparation of Cinnamaldehyde Chitosan:**

Chitosan (1.0g) was suspended 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 complete solubility was obtained. Five (5) ml of Cinnamaldehyde was added drop-wise while stirring. The mixture was stirred for a further 3 hours. A pale yellow material was formed and separated by filtration. The obtained product was dried in vacuum at 40°C for 24 hours (Tariq *et al.* 2010)

### Preparation of Aqueous solution of Nickel and Cadmium

The adsorbates of Ni<sup>2+</sup> and Cd<sup>2+</sup> was prepared from analytical grade Ni(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O and 2.10g of Cd(NO<sub>3</sub>)<sub>2</sub> by weighing out 4.79g of Ni(NO<sub>3</sub>)<sub>2</sub> and 2.10g of Cd(NO<sub>3</sub>)<sub>2</sub> respectively, dissolving in distilled water before making it up to mark with distilled water to get the stock Solution. This stock solution where diluted with distilled water to obtain the working standard solutions required for the analysis.

### Characterization of the unmodified chitosan and modified chitosan

Unmodified chitosan and chitosan modified with cinnamaldehyde were characterized using FTIR spectroscopic analysis.

### Treatment of the unmodified chitosan and cinnamaldehyde modified chitosan with solution of the metal ion

### Effect of initial metal ion concentration on the removal of Cd<sup>2+</sup> and Ni<sup>2+</sup> using chitosan and Cinnamadehyde 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<sup>2+</sup> ions. These were shaken for 30mins using a magnetic stirrer. Their absorbances were analyzed for metal ion

content using AAS (Atomic Adsorption Spectrophotometer). The differences between the initial and residual concentrations was recorded as the amount of metal ions adsorbed onto the adsorbent. The experiment was repeated separately using cinnamaldehyde chitosan. The two samples were also to absorb Cd<sup>2+</sup> in aqueous system. The adsorption efficiency of each adsorbent was then calculated using

$$\% \text{ sorption} = \frac{C_0 - C_e}{C_0} \times 100 \text{ (Jideonwo et al .2013)}$$

C<sub>0</sub>

Where C<sub>0</sub> = initial concentration of Ni<sup>2+</sup> and Cd<sup>2+</sup> before adsorption

C<sub>e</sub> = Equilibrium concentration of Ni<sup>2+</sup> and Cd<sup>2+</sup> after adsorption

### Effect of Temperature

The adsorption of the metal ions on chitosan and Cinnamaldehyde chitosan was studied at various temperature (20°C, 40°C, 60°C and 80°C). 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°C for 30 minutes.

The experimental set up was repeated for 40°C, 60°C and 80°C 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

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

m

Where C<sub>0</sub> and C<sub>e</sub> are the concentration of metal ions before and after absorption (mg/L)

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 study. In a typical experiment, 0.5g of chitosan, were added to 50ml of  $\text{Ni}^{2+}$  or  $\text{Cd}^{2+}$  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 cinnamaldehyde chitosan. The two samples were also used to absorb  $\text{Cd}^{2+}$  or  $\text{Ni}^{2+}$  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 absorbed 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 absorption (mg/L)

$V$  = Volume of metal ion used (ppm)

$m$  = weight of the adsorbent (grams).

### RESULTS AND DISCUSSION

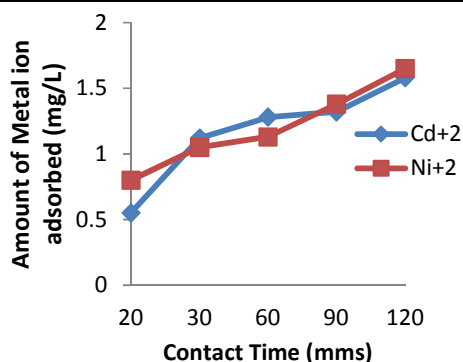
The effect of initial metal ion concentration is shown in Table 1. The percentage removal of  $\text{Cd}^{2+}$  and  $\text{Ni}^{2+}$  increased with increasing concentration of the metal ion due to the greater availability of binding sites. The variation in the adsorption of these metal ions might be 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. This is in

line with the work of Okiemen and Onyenkpa (1989). The modified chitosan showed good ability for metal ion uptake. Cinnamaldehyde modified chitosan had the highest percentage sorption (99.56%). This high percentage adsorption of the materials may be due to the different functional groups present in the various samples.

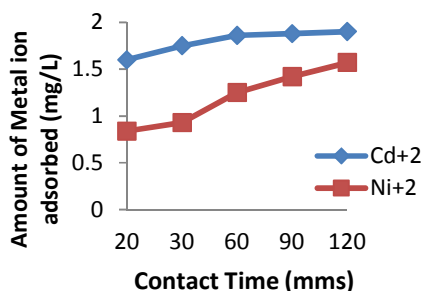
In the unmodified chitosan, the functional groups present were the hydroxyl and primary amino group. On the other hand, Cinnamaldehyde chitosan had the phenyl group, alkene and aldehyde as functional groups. The functional groups present in the modified chitosan must have affected adsorption because the presence of the additional functional group onto chitosan probably led to a decrease in the swelling ability of chitosan and thus enhancing its mechanical strength as a result of increase in the superficial area of the chitosan matrix. A decrease in swelling of chitosan led to an increase in absorption and also created more active site for the metal ions to be absorbed. The extent of adsorption was rapid in the initial stages before attaining equilibrium. The amount of  $\text{Cd}^{2+}$  and  $\text{Ni}^{2+}$  adsorbed was found to increase with time. The rate of adsorption consisted of two phases, an initial rapid phase and a slow second phase until equilibrium was accomplished (Fig 1 & 2). The first phase occurred instantaneously which is related to the exterior surface adsorption. The second phase was the steady stage before adsorption reached equilibrium. The observation was found to be in line with the work of Wang *et al.* (2014) who reported the removal of  $\text{CO}^{2+}$  ion from aqueous solution by Chitosan-montmorillonite. It took about 120mins to attain equilibrium for cinnamaldehyde modified chitosan (Fig 2) at which a higher percentage sorption (95.00%) was obtained while unmodified chitosan gave (82.50%).

**Table 1:**Effect of contact time on adsorption of ions in unmodified and modified chitosan

Contact time (mins)	Residual metal ion conc (mg/l)				Amount of ion Adsorbed (mg/l)				% sorption (w/w)			
	Chitosan		Cinnamaldehyde chitosan		Chitosan		Cinnamaldehyde Chitosan		chitosan		Cinnamaldehyde chitosan	
	Cd <sup>+2</sup>	Ni <sup>+2</sup>	Cd <sup>+2</sup>	Ni <sup>+2</sup>	Cd <sup>+2</sup>	Ni <sup>+2</sup>	Cd <sup>+2</sup>	Ni <sup>+2</sup>	Cd <sup>+2</sup>	Ni <sup>+2</sup>	Cd <sup>+2</sup>	Ni <sup>+2</sup>
20	1.54	1.20	0.40	1.16	0.55	0.80	1.60	0.84	27.50	40.00	80.00	42.00
30	0.88	0.95	0.25	1.07	1.12	1.05	1.75	0.93	56.00	52.50	87.00	46.50
60	0.72	0.87	0.14	0.75	1.28	1.13	1.86	1.25	64.00	56.50	93.00	62.50
90	0.68	0.62	0.12	0.58	1.32	1.38	1.88	1.42	66.00	69.00	94.00	71.00
120	0.42	0.35	0.10	0.43	1.58	1.65	1.90	1.57	79.00	82.50	95.00	78.50



**Fig. 1.** Amount of metal ion absorbed for unmodified chitosan for the period of contact (time).

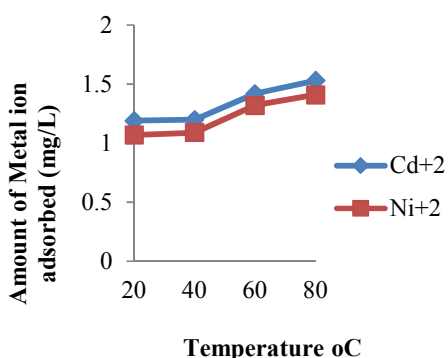


**Fig.2**Amount of metal ion absorbed for Cinnamaldehyde chitosan for the period of contact (time).

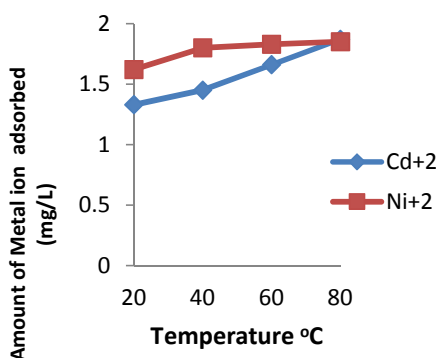
Increase in temperature from 20°C to 80°C was found to result in a steady increase in the removal efficiency (Table 2). Increased adsorption at increasing temperature is ascribed to enhanced mobility of metal ions from bulk solution (Yubinet *al.*1998). This is an indication that the adsorption capacity of the metal ion increased with temperature. This may be as a result of increase in the mobility of the adsorbent and metal ion with temperature. An increasing number of molecules may also acquire sufficient energy to undergo an interaction with active sites at the surface. Increasing temperature produce enhanced swelling effect within the internal structure of the adsorbent enabling metal ions to penetrate further (Fig 3 & 4). Hence optimum temperature was 80°C at which a higher percentage of metal ions was adsorbed (93.50%) for cinnamaldehyde modified chitosan and adsorption was very effective while unmodified chitosangave only 76.50%.

**Table 2.** Effect of Temperature on adsorption of ions in unmodified and modified chitosan

Temp °C	Residual metal ion conc (mg/l)				Amount of metal ion Adsorbed (mg/l)				% sorption (w/w)			
	Chitosan		Cinnamaldehyde chitosan		Chitosan		Cinnamaldehyde Chitosan		chitosan		Cinnamaldehyde chitosan	
	Cd <sup>+2</sup>	Ni <sup>+2</sup>	Cd <sup>+2</sup>	Ni <sup>+2</sup>	Cd <sup>+2</sup>	Ni <sup>+2</sup>	Cd <sup>+2</sup>	Ni <sup>+2</sup>	Cd <sup>+2</sup>	Ni <sup>+2</sup>	Cd <sup>+2</sup>	Ni <sup>+2</sup>
20	0.81	0.93	0.67	0.38	1.19	1.07	1.33	1.62	59.00	53.50	66.50	81.00
40	0.80	0.91	0.55	0.20	1.20	1.09	1.45	1.80	60.00	54.50	72.50	90.00
60	0.58	0.68	0.34	0.17	1.42	1.32	1.66	1.83	71.00	70.00	83.00	91.50
80	0.47	0.59	0.13	0.15	1.53	1.41	1.87	1.85	76.50	70.50	93.50	92.50



**Fig. 3** Amount of metal ion absorbed for unmodified chitosan with increase in temperature



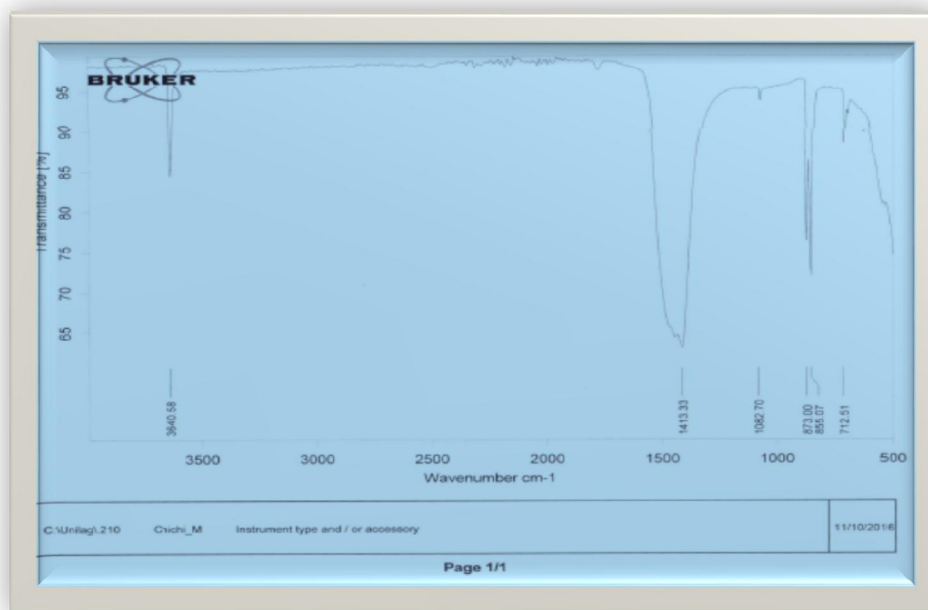
**Fig. 4.** Amount of metal ion absorbed for cinnamaldehyde chitosan with increase in temperature

The result of FTIR spectroscopy for chitosan, Acetic Anhydride chitosan and Cinnamaldehyde chitosan are presented in the spectra sheet. FT-IR spectroscopy was used for characterization to elucidate the changes that occur in the chemical structure, Plate 1 is the spectra of neat chitosan. The spectrum of neat chitosan showed a broad and sharp peak at 3640.58cm<sup>-1</sup> for O-H stretching, the band at 1413.33cm<sup>-1</sup> for C-H bending, the band at 1082.70cm<sup>-1</sup> is assigned for C-O-C bonds while the peaks at 873.00cm<sup>-1</sup>, 855.07cm<sup>-1</sup> and 712.51cm<sup>-1</sup> were assigned to CH<sub>2</sub> bending due to pyranose ring.

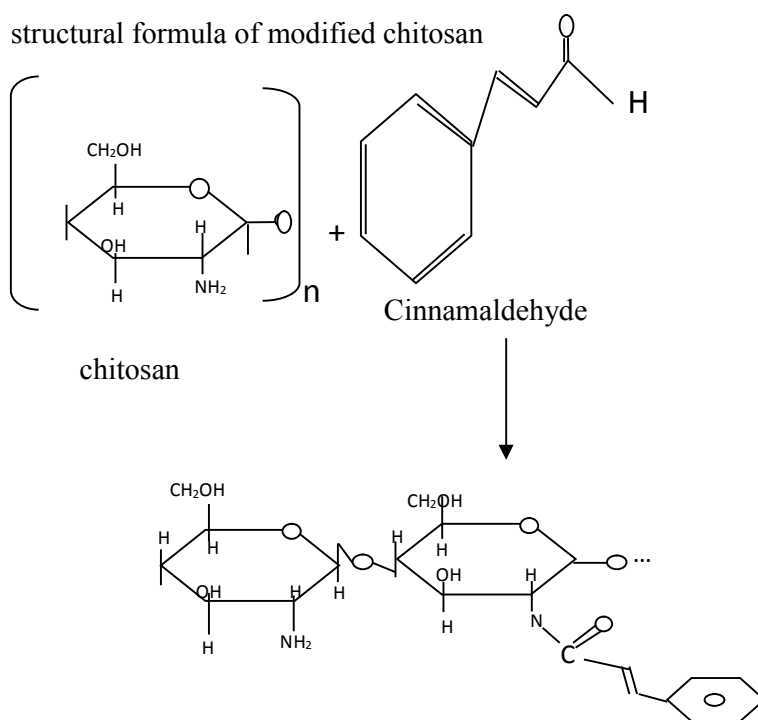
Plate 2 depicts the spectrum of Cinnamaldehyde – Chitosan. The band at 3639.55 cm<sup>-1</sup> O – H stretch for phenols, 1675.93 cm<sup>-1</sup> C=C stretch for Amides, 1605.10 cm<sup>-1</sup> for Olefinic double bonds, 972.34 cm<sup>-1</sup> C-H stretch for alkenes, 947.55 cm<sup>-1</sup> C-H stretch to CH<sub>2</sub>=CH adsorption at 747.42 cm<sup>-1</sup> represents the C-H stretch of Aldehydes. In the spectra of cinnamaldehyde chitosan some differences were observed. The peaks were sharper than that of unmodified

chitosan, the peak at  $3640.58\text{cm}^{-1}$  due to O - H stretch for unmodified chitosan shifted to a lower wave number of  $3639.55\text{cm}^{-1}$  corresponded to O-H stretch for phenols. The characteristic absorption at  $1605.10\text{cm}^{-1}$  and  $972.34\text{cm}^{-1}$  are due to olefinic

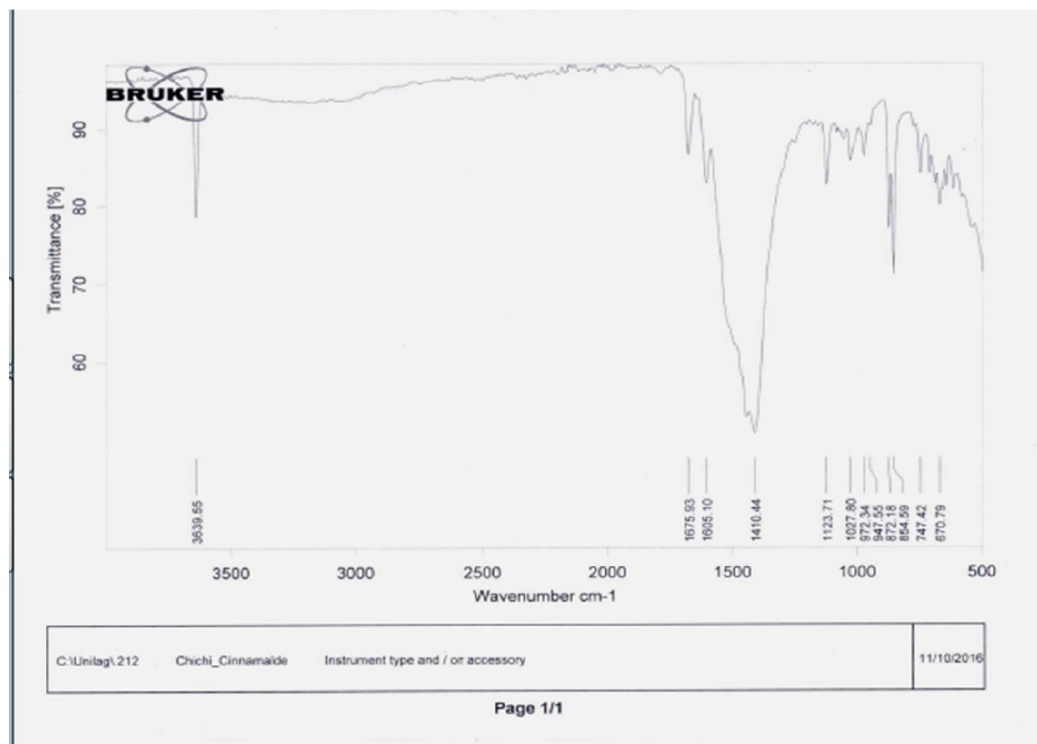
double bonds and C-H stretch for alkenes and the adsorption at  $747.42\text{cm}^{-1}$  represents the C-H stretch of Aldehydes. This confirms that chitosan has been modified to cinnamaldehyde chitosan.



**Plate 1:** Spectral Sheet of Unmodified Chitosan.







**Plate 2:** Spectral Sheet of modified Chitosan(Cinnamaldehyde Chitosan).

## Conclusion

The chemical modification of chitosan with the different organic compounds as seen from this study holds great promise in absorption of metallic ions. It was evident that the modified chitosan products showed good ability to uptake metal ions from their aqueous solutions. In addition, modifying chitosan with aldehydes reflected in obvious decrease in such capacity as the solubility and swelling ability of the chitosan decreased considerably. This behaviour can be attributed to the chain mobility restrictions caused by modification and hence the limited swelling ability of the chitosan matrix in water. FTIR analysis also suggest that the possible mechanism was the

electrostatic interaction between protonated amino and hydroxyl group with the metal ion. Based on the findings of this research we can therefore infer that cinnamaldehyde chitosan is an effective adsorbent for the removal of  $\text{Cd}^{2+}$  and  $\text{Ni}^{2+}$  from aqueous solution since a high adsorption capacity was achieved and the mechanical strength of the adsorbent was improved by this modification. We therefore recommend that natural biopolymer such as chitosan should be used for remediation of metal ions instead of synthetic chemicals.

## Author's Contributions

BCE designed the study, performed the experimental analysis and wrote the draft of the manuscript while REO,

FOA and LUO managed to literature searches and edited the final draft. All authors read and approved the final manuscript.

## REFERENCES

- Kandile N.G., A.A. (2013). New hydrogels based on modified chitosan as metal biosorbent agents. *Int. J. Biol. Macromol.* 2013; 64:328-333.
- Kubota, N., Eguchi, Y., (1997). Selective Sorption of Fe<sup>2+</sup> using modified form of chitosan beads. *Polym.J.* 29, 123-127.
- Ngah W.S.W., FatinathanS, (2006).Chitosan flakes Chitosan –GLA Beads for adsorption of P-nitrophenol in Aqueous solution” *Colloids and surfaces: Physicochemical and engineering aspects.* Vol. 277, PP. 214 - 226, 2006.
- Okieimen, F.E., Onyenkpa, and V.U. (1989): Binding of cadmium, copper, lead and nickel IVNs with melon (*Citrullus vulgaris*) seed husks. *Biol waste* 29:11-16
- Okolo P.O., Akakuru O.U., Osuji O.U., and Jideonwo, A. (2013). Studies on the properties of chitosan-starch beads and their application as drug release materials. *J. Chem. Soc. Trans.* 6: 118-126.
- Pradip Kumar Dutta, Toydeepdutta, Dripatte V.S. (2004). Chitin and chitosan Chemistry properties and application. *Journal of Science and Industrial Research* 63: 30-31.
- Tariq R.A.Shobahi, Magdy T. AbdelaalMohama S.I Makki (2010).Chemical modification of chitosan for Metal ion Removal. *Arabian Journal of Chemistry.* (2014) 7, 741-746.
- Wang H., Tang H., Liv Z., Zhang X., HaO<sub>2</sub>. (2014). Removal of CO<sup>2+</sup> ion from aqueous solution by Chitosan-montmorillonite. *J. Environ. Sci.* 26:1879-1884.
- Yang G., Tang L., Lei Z., Zeng G., Cai Y., Wei X., Zhou Y., L. S., Fang Y., Zhang Y.(2014)Cadmium (II) removal from aqueous solution by adsorption on &-ketoglutaric acid-modified magnetic Chitosan. *Appl. Surf. Sci.* 292: 710-716.