

Adsorption of Cd(II) ions by synthesized chitosan from fish shells

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Abstract

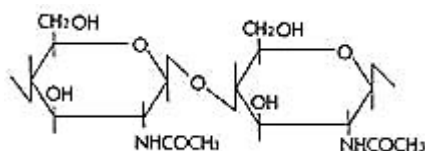
One of the major applications of chitosan and its many derivatives is based on its ability to bind strongly heavy and toxic metal ions. Chitosan is made from chitin by a chemical process involving demineralization(DM),deproteinization (DP), decolorization (DC), and deacetylation (DA). In this research natural bio polymer “chitosan” was synthesized using fish shells and adsorption of cadmium by chitosan was studied. Chitosan was characterized using Fourier Transform Infrared Spectroscopy (FTIR) and solubility in 1% acetic acid. The affinity of chitosan for cadmium was studied using CdCl₂ solution as the heavy metal solution containing Cd (II) ions. The Infra red spectroscopic study on the chitosan and the metal-chitosan complexes reveal a metal coordination based on the observed characteristic band changes. At initial cadmium concentrations of 3, 5, 8 mg/L, the adsorbed cadmium ion concentrations are 2.5, 4.2 and 7.4 mg/L, respectively.

Key words; chitosan. Chitin, aqueous solution, adsorption, deacetylation,

INTRODUCTION

Chitosan is a natural carbohydrate biopolymer derived by deacetylation (DA) of chitin, a major component of the shells of crustacean such as crab, shrimp, and crawfish. After cellulose, chitin is the second most abundant natural biopolymer found in nature (No and Meyers, 1989).

CHITIN



CHITOSAN

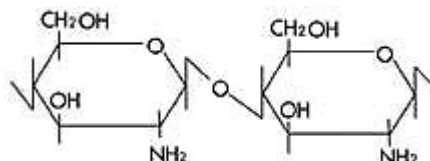


Figure 1. Structure of Chitin and Chitosan (Stephenie Akkalut 2008).

Due to increase in the world population and development of industrial applications, environmental pollution problem became important. Communities produce both liquid and solid wastes. The liquid waste-wastewater is essentially the water supply of the community after it has been used in a variety of applications. In recent years, heavy metal concentrations, besides other pollutants, have increased to reach dangerous levels for living environment in many regions.

The presence of toxic and polluting heavy metals in wastewaters from industrial effluents, water supplies and mine waters and their removal has received much attention in recent years. The amount of heavy metals that industrial wastewaters often contain is considerable and would endanger public health and the environment if discharged without adequate treatment. Cadmium does not exist in nature as the native metal but principally as the sulphide ore greenockite (CdS), which is strongly associated with zinc sulphide ore sphalerite. Cadmium enters the environment in the waste waters of industries using cadmium, but also in discharge from the iron and steel industry (Bamgbose J. T).

Various soluble forms of cadmium exist in water. It exist mainly as Cd^{2+} , but also as $[CdCO_3(aq)]^0$, $[CdCl]^+$, $[Cd(OH)]^+$ and $[CdSO_4(aq)]$. Free Cd^{2+} ion occurs at pH levels below 8. At higher pH values, $[Cd(OH)]^+$ is formed and in very alkaline solutions $[Cd(OH)_3]^-$ and $[Cd(OH)_4]^{2-}$ are formed (Dojlido and Best 1993, Serkan Keleulo).

The aim of this study is the characterization of chitin biopolymer, preparation and characterization of chitosan biopolymer from chitin biopolymer in controlled experimental condition to use these biopolymers as adsorbent materials and investigate the uptake performance for heavy metal ions (Cd^{2+}).

2. Materials and Methods

2.1 Crawfish Chitosan Production

2.1.1 Raw Material

Crawfish shell was obtained from a commercial crawfish shells were separated, and washed under running warm tap water to remove soluble organics, adherent proteins and other impurities, then they were dried and ground through a grinding mill.

2.1.2 Isolation of Chitosan

1) DP (Deproteinization)

Depending upon the production sequence, the crawfish shells or demineralized shells was deproteinized with 3 % (w/v) NaOH solution for 1 hr at b.p°C with constant stirring at a solid to solvent ratio

of 1:10 (w/v) (No and Meyers 1989). Samples were then filtered under vacuum, and the filtrate was washed with tap water for 30 minutes and oven-dried.

2) DM (Demineralization)

Depending upon the production sequence, the crawfish shells or deproteinized shells were demineralized with 1N HCl for 60 min at room temperature with a solid to solvent ratio of 1:25 (w/v) (No and Meyers 1989), then filtered under vacuum. The filtrate was washed for 30 min with tap water and oven-dried.

3) DC (Decoloration)

Crawfish shells were decolorized with acetone for 10 min and dried for 2 hr at ambient temperature, followed by bleaching with 0.315 % (v/v) sodium hypochloride (NaOCl) solution (containing 5.25% available chlorine) for 5 min at ambient temperature with a solid to solvent ratio of 1:10 (w/v), based on dry shell (No and Meyers 1989). Sample [chitin] was then washed with tap water and dried under vacuum for 2-3 hrs.

4) Deacetylation

Deacetylation is the process to convert chitin to chitosan by removal of acetyl group. It is generally achieved by treatment with concentrated sodium or potassium hydroxide solution (40- 50%) usually at 90°C or higher for 30 min or longer to remove some or all of the acetyl groups from the polymer (No and Meyers, 1989). The N-acetyl groups cannot be removed by acidic reagents without hydrolysis of the polysaccharide, thus, alkaline methods must be employed for N-deacetylation (Muzzarelli, 1977).

2.1.3 Sorption of cadmium ions on chitosan

20mg/L cadmium solution was prepared by dissolving 4 mg analytical grade CdCl₂ powder in distilled water. This solution was kept as stock solution and 3, 5 and 8 mg/L solutions were prepared by diluting stock solution.

50ml of 3mg/L CdCl₂ solution was taken and 50mg of chitosan was added. Then the mixture was continuously stirred using magnetic stirrer for 2 hours at (30 °C). After that solution was filtered and filtrate and 3mg/l CdCl₂ solution were analyzed using atomic adsorption spectroscopy to determine amount of cadmium absorbed by chitosan. The same steps were repeated to the other dilute solutions.

Finally uptake of cadmium by amine groups (-NH₂) on chitosan was investigated using FTIR spectroscopy (Bruker Alpha-T) in the range of 400 to 4000 cm⁻¹.

Results and Discussion

Table 1 amount of cadmium adsorbed after adding 50mg of chitosan with 30° C and neutral pH.

Total Cd ²⁺ in original solution (ppm)	Total Cd ²⁺ after addition of chitosan (ppm) (adsorb)
3	2.5
5	4.2
8	7.4

FT-IR analysis

The spectra of chitin, chitosan and chitosan-Cr polymeric complexes are shown in Figure 2. The band amide (C=O) around 1637 cm⁻¹ stretching frequency, characteristic of chitosan with acetylated units is present in all the spectra. However, in chitosan-metal complexes, a new band around 1625-1635 cm⁻¹ appears. These bands correspond to the bending in plane of N-H which also appear as a shoulder at around 1605 cm⁻¹. This observed red shift is due to interaction of chitosan with the metal ions. The broad bands in the region 3000-3600 cm⁻¹ could be attributed to the stretching of OH groups of the chitosan and overlapping stretching bands of NH. With the chitosan-metal complexes, the bands are unfolded and the stretching of O-H is observed between 3418 and 3450 cm⁻¹ while the stretching of N-H is observed between 3260 and 3266 cm⁻¹. In addition, a significant change is observed in the region from 1000 to 1200 cm⁻¹. In the free chitosan heteropolymer, a broad band around 1068 cm⁻¹ appears which could be associated with the stretching of C-O bond. In the presence of metal ions, the band shifted and appear between 1113 and 1116 cm⁻¹ which correspond to the stretching of C-O bond of C3 from chitosan (secondary OH, Figure 1) as well as the band between 1025 and 1030 cm⁻¹ corresponding to the stretching of C-O bond of C6 from chitosan (primary OH) verifying the complexation of the chitosan to Cr not only via the amine groups, but also through the OH groups. Also in this region, two important bands were identified in the chitosan-metal polymeric complexes. The stretching frequencies between 1064 and 1075 cm⁻¹ correspond to the asymmetric stretching of C-O bonds (Lima and Airoidi 2004).

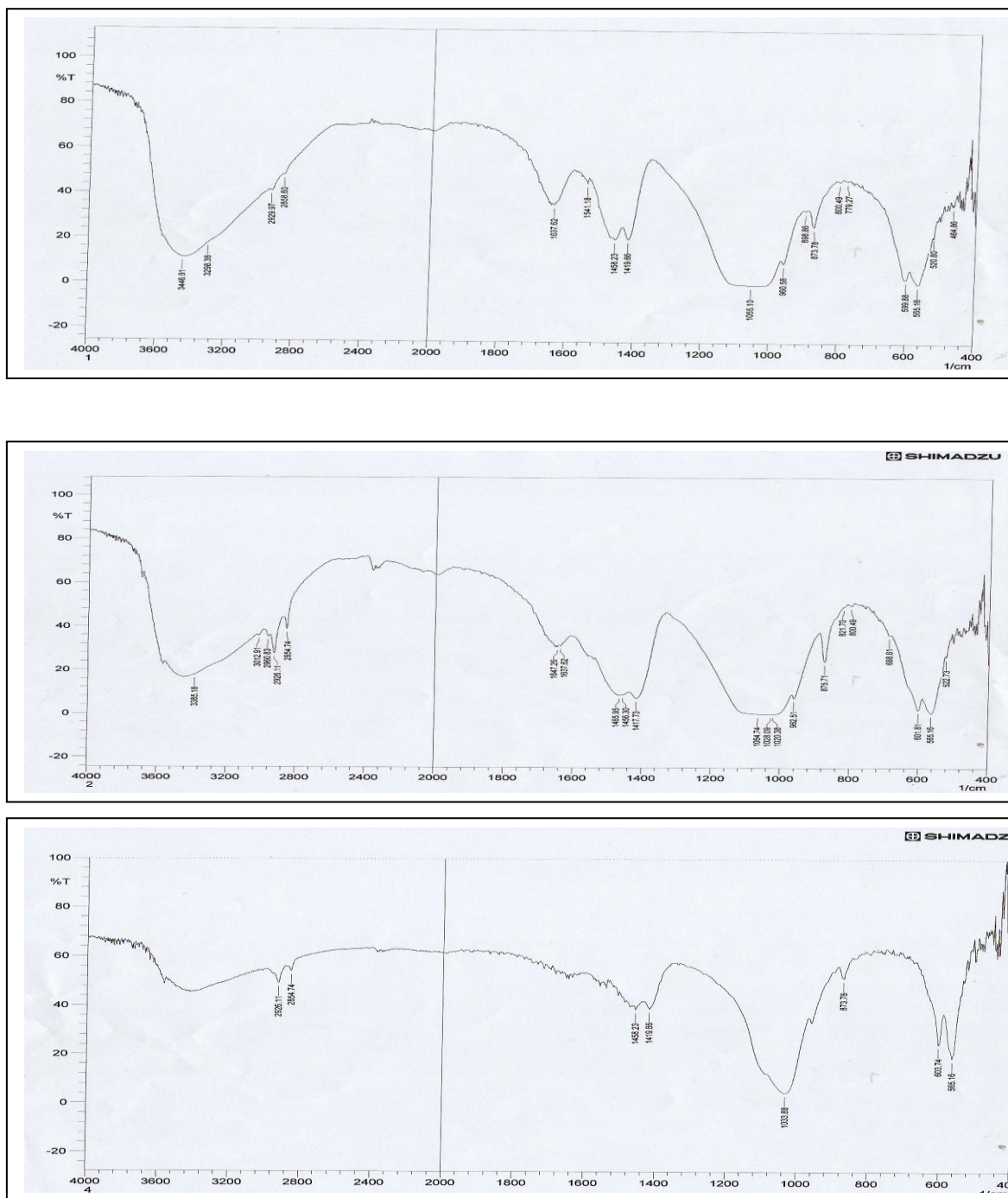


Figure 2. FT-IR Spectra of a: Chitin, b: Chitosan and c: Chitosan-Cd complex

Conclusions

• This study showed that chitosan adsorbs heavy metals, in particular Cd (II) ions. Chitosan as a result of its bioavailability would be economically useful for the treatment of wastewater containing heavy metals.

References

1. No, H.K., Meyers, S.P. Lee, K. S. 1989.' Isolation and Characterization of Chitin from Crawfish hell Waste. *Journal of Agricultural and Food Chemistry*.. Vol.37(3) p.575-579.
2. Stephenie Akkalut, 2008'Enhancement of degree of deacetylation of chitin in chitosan', thesis,.
3. Bamgbose J. T. 2010 'Adsorption kinetics of cadmium and lead by chitosan', *African Journal of Biotechnology* Vol. 9 (17), pp. 2560-2565, 26 April,.
4. Dojlido, J.R. and Best, G. A. 1993. *Chemistry of Water and Water Pollution*. pp. 65-69, 84-91, 108-114, 201-205 ..
5. Serkan Keleolu, 1977'Comparative adsorption studies of heavy metal ions' thesis,2007.
6. Muzzarelli, R.A.A. Chitin; *Pergamom*: Oxford,.
7. Lima, I.S. and Airoidi, C. 2004. "A thermodynamic investigation on chitosan", *Thermochimica Acta*. Vol. 421, pp. 133-139..