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Removal of Heavy Metal from Contaminated Water by Biopolymer Crab Shell Chitosan

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Abstract: The study focuses on potential of using crab shell chitosan as a low-cost adsorbent, for heavy metals removal from aqueous solutions in an adsorption filtration system. Chitosan was synthesized from chitin by the treatment of strong alkali solution under reflux condition and chitin was extracted from crab shell followed by decalcification and deproteinization treatment. Spectrometric (AA and UV) method was employed to detect the heavy metals concentration. Prepared 10 mg L⁻¹ solutions of zinc, lead, cadmium, cobalt, nickel, chromium, manganese and iron were passed through the 5 g of chitosan separately and it was found that chitosan was excellent adsorbent in removing mentioned heavy metals. The removal efficiency of chitosan was in the following order Mn>Cd>Zn>Cu>Co>Ni>Fe>Pb>Cr. The result also showed that the time required for 100% breakthrough of prepared chitosan for Mn and Zn was approximately 27 and 23 h whereas it was only 16 h for both Cr and Pb, respectively. The research revealed that prepared chitosan showed better removal performance for Mn, Cd, Zn whereas the removal efficiency was satisfactory for Co, Ni and Fe but it exhibited relatively least performance for Pb and Cr.

Key words: Bioremediation, environmental pollution, metal chelating agent, toxic materials, sorption mechanism

INTRODUCTION

Contamination of diverse water resources by heavy metal is a great concern because of their detrimental effect on human, animal and plants (Li and Bai, 2006; Sharma et al., 2008). Heavy metals are very harmful because of their non-biodegradable nature, long biological half-lives and their potentiality to be accumulated in different body parts (Manaham, 2005; Wilson and Pyatt, 2007). It is well known that some heavy metals which are essential component in metabolism are toxic when present in high concentration (Gazzo, 2001). Trace metal like iron, copper, zinc, cobalt and manganese are essential metals since they play important role in biological systems (Mashi et al., 2004; Garcia et al., 2005). However, some research also confirmed that heavy metals such as Cd, Pb, Cu, Zn and Ni have carcinogenic or toxic effects on human beings and environment (Trichopoulos, 2001; Turkdogan et al., 2003; Kocasoy and Sahin, 2007). Heavy metals enter in the environment through a wide variety of sources, including combustion, wastewater discharges and manufacturing facilities (Jarup, 2003; Singh et al., 2004). Mining and processing of metal ore can be a significant source of heavy metal contamination of the environment (Dudka and Adriano, 1997; Navarro et al., 2008). One of the major routes of the excessive accumulation of heavy metals in agricultural soil is wastewater irrigation that adulterates the soil and later affects the food quality and safety (Muchuweti et al., 2006). Other potential sources of entering the heavy metals to the human body are inhalation and ingestion through the plants produced in contaminated areas (Tripathi et al., 1999; Mendil, 2006). It is observed that serious systemic health problems can develop as a result of excessive dietary accumulation of heavy metals such as Cd and Pb in human body (Oliver, 1997).

In recent years, biosorption by biologically originated materials in removing heavy metals has drawn more and more attention, largely due to the unique properties of these biomaterials being environmentally benign, low cost, effective at low metal concentrations and easily reusable. Chitosan attracted particular consideration because of its capability to adsorb various heavy metal ions chemically or physically (de Castro Dantas et al., 2006).
The nitrogen in the amino group of the chitosan molecule acts as an electron donor and is presumably responsible for selective chelation with metal ions (Bassi et al., 1999; Prachan et al., 2005). Chitosan can be produced easily from Chitin, poly-β-(1, 4)-N-acetyl-D-glucosamine and it is the most common polysaccharide after cellulose found in the nature extracted from crustacean shells, such as prawns, crabs, insects and shrimps (Xu et al., 2008; Xu-fen et al., 2007; Rinaudo, 2006).

Several processes have been developed and used for removing metals dissolved in industrial wastewater over the years. The techniques are: chemical precipitation, ion exchange, membrane filtration, solvent extraction, or adsorption (Chiron et al., 2003; Gupta and Ali, 2004; Molnari et al., 2004). Conventionally, precipitation is the most common technique for removal of metals, but this method leads to the production of toxic sludge. On the other hand, solvent extraction technique is not suitable for effluents containing less than 1 g L\(^{-1}\) of targeted heavy metals and ion exchange processes are too expensive due to the high cost of synthetic resins (Selatnia et al., 2004). In consequence, new separation methods are required to reduce heavy metal concentrations to environmentally acceptable levels at affordable cost (Klimmek et al., 2001; Han et al., 2006). Adsorption filtration method is preferred for heavy metals removal in small-scale treatment system because of its simplicity, ease of operation and handling, regeneration capacity and sludge free operation (Thirunavukkarasu et al., 2003; Nurul et al., 2006).

Although, a number of researchers are available on removal of heavy metals by chitosan from other sources but very few researches have been reported on crab shell chitosan. Therefore, the current study examines the capability of chitosan obtained from crab shell for removing toxic heavy metals by adsorption filtration method.

**MATERIALS AND METHODS**

**Preparation of chitosan from crab shell:** The research project was conducted from February, 2006 to November, 2007, in the Department of Chemistry, Jahangirnagar University, Dhaka, Bangladesh. The raw materials i.e., crab shell was collected from Bio-Chemical and Seafood Export Co., Dhaka, Bangladesh. It was then dried, crushed and decalcified by treatment with 10% HCl, the acid being changed everyday. The dorsal cover of the shell was peeled off on the third day. Its inner layer was removed by rubbing it away with the fingers. Thereafter, the rest of bone was broken into smaller bits. Decalcification was completed in about four days which can be represented in the following reaction.

\[
2\text{HCl} + \text{CaCO}_3 = \text{CO}_2 + \text{Ca}^{2+} + 2\text{Cl}^- + \text{H}_2\text{O}
\]

The resulting chitin protein complex of the dorsal cover was deproteinized by the treatment of 10% (w/v) NaOH at 103 to 105°C in an autoclave. The septa region was deproteinized in 6 h treatment under similar conditions.

Several studies confirmed that chitosan, a poly-N-acetylglucosamine, is obtained by the deacetylation of chitin (Crini and Badot, 2008, Orrego and Valencia, 2009; Dambies et al., 2000). To follow this process chitin shells collected from crab shell were dried and again crushed and boiled successively with 5% HCl for several hours then it was filtered in a Buchner funnel. The solid was added to sodium hydroxide (20% aqueous solution) and refluxed for 4 h and was filtered. The reaction mass was finally added to the deionized water and was again boiled for several hours. After cooling and washing, it was finally dried at 105°C. The powder thus obtained was boiled with 3 N acetic acid and the solution was cooled and filtered. The resulting slurry was neutralized with 15% KOH solution in a large beaker and the precipitate was then filtrated and thoroughly washed with hot water and deionized water. This resulting chitosan precipitates was dried at 105°C and ground to pass through a US standard 40-mesh screen. The individual particle size of this material ranges between 0.32 and 2.0 mm. The IR spectrum of prepared chitosan was taken in KBr disc.

**Chemicals used for metal solution:** Different metal solutions were prepared for passing through the column packed with crab shell chitosan and mother solution of 100 mg L\(^{-1}\) of zinc, nickel, iron, lead, cadmium, manganese and 200 mg L\(^{-1}\) chromium were prepared from zinc chloride, nickel chloride, iron (III) chloride, lead chloride, cadmium chloride, manganese (II) sulphate and chromium (III) sulphate, respectively. All chemicals used were Mark analytical grade including standard stock solution of known concentrations of different heavy metals.

**Column preparation and calculation of adsorbed amount:** Eight columns were made with 5 g uniformly grained prepared Chitosan and the prepared 10 mg L\(^{-1}\) each heavy metal solution was passed through the columns until the break through volume as well as saturation volume of the materials was reached. Water samples that passed through the columns were collected in the sample bottles after several times interval. The flow rate of the columns
were measured 3.5 mL min\(^{-1}\). The amount of metal adsorbed in each volume interval was calculated from the following equation:

\[
\text{Total amount adsorbed} = X_p + (10-C) \times V \times 10^{-3}
\]

where, \(X_p\) is the previous absorbed amount, \(C\) is the concentration in volume (V) and V is the volume interval that passed through the column.

**Heavy metal analysis:** Heavy metals (Fe, Zn, Cd, Pb, Cr, Ni and Co) analyses were carried out using Atomic Absorption Spectrophotometer (SHIMADZU AA-6800). The AAS was calibrated for all the metals by running different concentrations of standard solutions. Average values of three replicates were taken for each determination. Quantitative estimation of Mn in the digested samples was carried out using UV Spectrophotometer (Sequoia-Tuner, Model-390) following permanganate oxidation method at 522 nm (Charlot, 1964). Because of its distinctive color and stability, permanganate ion is preferably used as the determination form for manganese. For the measurement of all metals in water samples, analytical conditions are very essential to get accurate result and they are summarized in Table 1.

**RESULTS AND DISCUSSION**

Infrared Spectra (IR) was taken for both chitin and chitosan. In the IR of chitin and chitosan all the stretching frequencies for the different functional groups were almost same. But the stretching frequency of C = O was missing in the spectrum of the prepared chitosan. Secondary amide in the solid state usually showed the C = O absorption near 1640 cm\(^{-1}\) but in the spectrum of prepared chitin two strongly perpendicular bands were observed near the frequency at 1652 cm\(^{-1}\).

The findings of the present research revealed that chitosan can successfully remove manganese from contaminated water. 10934.5 mg kg\(^{-1}\) of manganese was passed through the prepared chitosan composite and it was found that the amount of manganese which absorbed by chitosan was 8350.8 mg kg\(^{-1}\) and manganese removal efficiency of chitosan was 76.3% (Table 2). Similar performance was also observed with cadmium and zinc. For cadmium and zinc, 9183.9 and 9625.4 mg kg\(^{-1}\) were passed through the chitosan and the amount adsorbed by them was 6949.0 and 6301.6 mg kg\(^{-1}\) which indicates that the removal efficiency of chitosan for Cd and Zn was 75.6 and 65.4%, respectively (Table 2). The removal efficiency of chitosan for nickel, iron and cobalt was found nearly 58%. Again for passing of Ni 8164.4 mg kg\(^{-1}\), Fe 8144.3 mg kg\(^{-1}\) and Co 8032.0 mg kg\(^{-1}\) through the chitosan, the adsorption amount of metals was 4710.4, 4683.7 and 4712.4 mg kg\(^{-1}\), respectively (Table 2). Furthermore, it is found that the removal performance of Pb and Cr was relatively lower than all the other heavy metals, which were about 43.6 and 36.5% respectively. After passing 6183.3 and 6688.6 mg kg\(^{-1}\) of Pb and Cr through crab shell chitosan the study showed that the amount of Pb and Cr absorbed by chitosan was 2699.3 and 2436.8 mg kg\(^{-1}\), respectively (Table 2).

The effect of flow rate was also a significant factor on prepared chitosan. The influent (Co) and effluent (Ce) concentrations were calculated for each heavy metal (Chen and Chung, 2006). For calculating the 100% breakthrough time of chitosan for each heavy metal, the Ce/Co was plotted against different time interval in Fig. 1. It is observed in Fig. 1 that crab shell chitosan can remove 100% of Mn and Cd up to about 14 and 11 h, respectively. After 10 h the influent and effluent ratio of Mn, Cd, Zn, Co, Ni, Fe, Pb and Cr was 0.001, 0.020, 0.132, 0.322, 0.467, 0.354, 0.594 and 0.612, respectively (Fig. 1). Approximately 27 h was required to reach 100% breakthrough of prepared chitosan for Mn whereas 16 h was required for both Cr and Pb (Fig. 1). Furthermore, the complete breakthrough time for Fe, Ni and Co was nearly 20 h whereas for Zn and Cd it was 23 and 22 h, respectively (Fig. 1a-h).

The IR spectra of chitosan were compared with the IR spectra of chitin. The Infrared spectra clearly show a marked change due to the removal of acetyl groups from the amino nitrogen. The C - O stretching frequency at 1640 cm\(^{-1}\) was missing in the spectrum of chitosan which was obtained from deacetylation of the chitin but two bands occurred at 1652 cm\(^{-1}\) in chitin that is supported by the observation of Shin et al. (2001). This band is due to the antisymmetric deformational vibration due to the formation -NH\(^{+}\) because chitin is dissolved in HCl during the reaction. The band appearing at 1521 cm\(^{-1}\) may be assigned to the symmetric NH\(^{+}\) deformational mode. In addition, the IR spectrum of the prepared Chitosan was confirmed from pure Chitosan. The physical and chemical property of the prepared chitosan was compared with the original (97% pure) chitosan and it was observed that this
Table 2: Heavy metal removing performance of biopolymer chitosan

<table>
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<th>Mn (mg)</th>
<th>Conc. (mg L⁻¹)</th>
<th>Absorbed (mg)</th>
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pure chitosan is inactive in both acid and base but the prepared chitosan is slightly soluble in acid and it is basic impurity as CaCO₃ was present in a large scale.

From the present research, it is observed that the sorption capacity of crab shell chitosan was decreased in the following order: Mn>Cd>Zn>Co>Ni>Fe>Pb>Cr. There are very few studies available on the removal of heavy metal by crab shell chitosan however the chitosan produced from Fly Larva Shells (FLS) revealed that the sorption ability was decreased in order of Cu>Mn>Ni>Zn>Pb>Fe (Gyllen et al., 2002). This study also noted that chitin and chitosan produced from FLS act as sorbents for free metal ions up to 600-800 mmol kg⁻¹. Previous research by An et al. (2001) found that in case of Cd the removal capacity of crab shell of Chinonecetes opilio was considerably higher than the other sorbents such as cation exchange resin, zeolite, granular activated carbon, powdered activated carbon. Another study concluded that the chitosan prepared for crab shell has a cadmium uptake capacity (per a weight basis) greater

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Fig. 1: Effect of flow rates on each metal adsorption by crab shell chitosan packed column, (a) Mn, (b) Zn, (c) Fe, (d) Ni, (e) Pb, (f) Co, (g) Cr and (h) Cd

than porous alumina, hydrous ferric oxide and nonporous chitosan (Evans et al., 2002). For an equilibrium aqueous concentration of 10 mg kg$^{-1}$ cadmium, cadmium uptake by porous alumina ranges from 20000 to 50000 mg kg$^{-1}$ (Papelis et al., 1995) and 8000 mg kg$^{-1}$ by hydrous ferric oxide (Dzombak and Morel, 1990).

Lower removal capability of chitosan for chromium and lead might be due to relative weak chelating ability of chitosan on chromium and lead which is in good agreement with results reported earlier by Kartal and Imamura (2005). However, chitosan coated ACPS (acid treated oil palm shell charcoal) exhibited better performance on removing chromium than uncoated crab shell chitosan and it is shown that the adsorption capacity of chitosan coated ACPS for chromium was 15400 mg kg$^{-1}$ (Nomanbhay and Palanisamy, 2005). Similar trend was observed for chromium for other adsorbent (5000-12000 mg kg$^{-1}$) (Schmuhl et al., 2001).

To estimate the each adsorption amount of heavy metals on chitosan materials, influent (Co) and effluent
(Ce) concentration were calculated and it was observed that initially the adsorption amount of metals on the prepared chitosan was expectedly high and it was gradually decreased over time in Fig. 1. However, the adsorption amount was not uniformly decreased with time and a probable reason was that the passing rate of the prepared heavy metal solution through the column was not same. Surface area and contact time also played a vital role for the adsorption of heavy metals in prepared chitosan. The shape of the uptake isotherms (Fig. 1) showed that the uptake process is a complex one. Simple ion adsorption on the chitosan surface does not appear to be the dominant mechanism as is inferred from literature. It is concluded from the previous work where under moderate magnification, metal containing aggregates were observed on the polymer (Rana et al., 2009). So a possible uptake mechanism is the formation of metal-containing nodules on the polymer surface.

Furthermore, absorption presumably by diffusion of metal ions into the polymer is also playing a part in the total process. Further chitosan embedded or laced with calcium carbonate in the composite materials may create some cryptand sites of right size so that some metals are simply caged at those sites. Thus, a combination of nodular formation, cryptand site formation, ion adsorption and ion absorption account for the total uptake. The greater uptake is attributed due to the free amino group of chitosan having its lone pair electrons can act as a specific chemical bonding sites for metal ions capable of forming complex ions. Research by Guibal (2004) also confirmed that metal cations can be adsorbed by chelation on amine groups of chitosan in near neutral solutions. The present research is also strongly support the study of Pradhan et al. (2005) that the high adsorption capacity could be ascribed by the following factors: (1) the high hydrophilicity of chitosan with a large number of hydroxyl groups; (2) the large number of primary amino groups with high activity and (3) the flexible structure of the polymer chains of chitosan, which enables a suitable configuration for complexation with metal ions.

CONCLUSION

The study showed the first details study of crab shell chitosan, an abundant low-cost biopolymer, for removing hazardous trace elements. The removal performance of chitosan was not found same for all the studied heavy metals, it was better for manganese, zinc and cadmium whereas satisfactory level was not observed for lead and chromium. In addition, the study concluded that the use crab shell chitosan for heavy metals removal appears to be technically feasible, eco-friendly and with high efficacy. However, further studies are needed to unveil the complete removal mechanism of chitosan for heavy metals.

REFERENCES


