

EXTRACTION OF CHITOSAN FROM CRAB SHELL AND ITS COMPETENCY FOR THE REMOVAL OF CHROMIUM

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Abstract

The removal of heavy metals from industrial wastewater has become a challenge of the days to the researchers. This paper deals with the extraction of chitosan from crab shell through a simple digestion in alkaline medium. The extracted chitosan seems suitable for its application for the removal of aqueous chromium by adsorption filtration method. Experimental results demonstrate that this extraction method could be efficient compared to the other conventional techniques. The mechanistic details for chromium binding on chitosan material have also been discussed.

Keywords: Chitin, chitosan, chemisorptions, biopolymer

Introduction

Chitin is one of the most abundant natural polysaccharides produced by many living organisms (Tokura *et al.*, 1995; Zaku *et al.*, 2011) and is found usually as a component in the shell of shrimps, crabs, lobstars (Jeuniaux, 1978; Franco *et al.*, 2005; Roberts, 1992). This biopolymer consists of a linear chain of poly- β -(1 \rightarrow 4)-N-acetyl-D-glucosamine; first identified by the end of nineteenth century (Dutta *et al.*, 2004; Rinaudo, 2006). Because of its insolubility in some common laboratory solvents, its chemical modification to chitosan is usually carried out to increase its applicability (Patil *et al.*, 2002). Chitosan is derived from the deacetylation of chitin in alkaline medium (Rojas *et al.*, 2005). The term chitosan usually refers to chitin that has been deacetylated to more than 60%. Due to its bioavailability, biocompatibility, biodegradability and the non-toxic nature, the material is widely being used in a range of value added products (Muzzarelli, 1997; Varma *et al.*, 2004).

The deacetylated product chitosan with amine functional groups can be expected to exhibit higher affinity towards metal ions than the acetamide groups in chitin do (Yang *et al.*, 1984). The degree of deacetylation controls the content of glucosamine and therefore the fraction of free amine groups available for metal binding. The interaction of metal ions with chitosan amino groups could be possible in different ways; chelation or electrostatic attraction depending on some other system parameters. At neutral pH or in deprotonated form, the free electron doublets on nitrogen atoms may be used to form

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ductive bonds with some transition metal ions (Gamage *et al.*, 2007). Chitosan attains positive charge in acidic condition through the protonation on its amino groups and can attract suitable anionic species electrostatically (Guibal, 2004; Juang *et al.*, 2000).

Due to industrial revolution in the developing countries like Bangladesh, both the ground and surface water systems has largely been polluted, mostly with heavy metals. The textile, tannery and pharmaceutical industries produce large amounts of wastewater with a range of pollutants (Sabur *et al.*, 2012, 2013; Safiullah *et al.*, 2011). The leather industries are very rising in Bangladesh and these industries are primarily based on chrome tanning process. As most of the tanning industries are running without any effluent treatment plant, the effluent with high chromium content are polluting the surrounding soil, water, and finally entering the food chain. So, the removal of chromium from tannery effluent has been a matter concern and a number of papers have been published (Rajendran *et al.*, 2011; Fadali *et al.*, 2004; Rao *et al.*, 2007). In most of the cases, the authors have described efficiency of their methods in a quantitative basis. But the detailed mechanism for the adsorption of chromium on chitosan has not been reported elsewhere to the best of our knowledge. The present study aims for the removal of chromium from tannery effluent by using environment friendly biopolymer chitosan with the mechanistic details.

Materials and Methods

In this paper, we are presenting our experimental works in two different parts; (a) the method for the extraction of chitosan from crab shell; and (b) the description how the extracted chitosan has been used for the removal of chromium.

(a) Extraction of chitosan from crab shell

Crabs were collected from Savar Bazar, Dhaka, Bangladesh and then the shell and operculums were removed from the animals. They were washed, dried and pulverized with pestle and mortar into fine powder. For digestion, 200.0 g of the powder with 400.0 mL of 30% KOH solution was taken in a round bottle flask (1000 ml). The mixture was then refluxed on a sand bath for about 50 hours maintaining the bath temperature within 115-120°C. The whole system was then allowed to stand for few hours and the digested portion from top was taken out carefully leaving the suspended materials on the bottom. The pH of the highly alkaline decanted portion was made slightly basic (pH >7.0 to <8.0) using 50% acetic acid (≈ 8 M). In this pH range, a brown colored solid material was observed to get precipitated on the bottom which was then separated with the help of a Buckner funnel. The sample was dried first in sunlight and then in an oven at 120°C. Total 33.0 g of chitosan material was obtained from the process. As the sample is hygroscopic in nature, it was kept in airtight wide mouth bottle under desiccation.

For thermo gravimetric analysis (TGA), 5.0 g of oven dried sample (at 80°C) was taken and investigated up to 250°C. The percentage of weight loss and the IR spectra recorded in each subsequent step of analysis indicate that the extracted chitosan becomes suitable for metal binding at or over 180°C. The IR spectra collected herein for the extracted chitosan seems to be comparable with other previously reported chitosan spectra (Brugnerottoa *et al.*, 2001).

(b) Removal of aqueous chromium by crab shell chitosan

In this study we carried out trials for the removal of chromium from tannery effluent as well as from the aqueous solution of chromium prepared in laboratory. The effluent was collected from the Chowdhouri tannery located at Hazaribagh, Dhaka. Detailed sample collection procedure and the analytical methods for the determination of some physicochemical characteristics of the effluent have been discussed in our earlier publication (Sabur *et al.*, 2013). The effluent was characterized with high COD (3175.32 mg O₂/l), TSS (22915 mg/l), TDS (13360 mg/l) along with high dissolved chromium content (987 mg/l). In the present study, we used simple column based adsorption filtration technique for the removal of aqueous chromium. Two columns of approximately 18.0 cm length and 1.1 cm diameter were prepared using 5.0 g extracted chitosan in each column. Raw effluent (987 mg/l total chromium) and 1000 mg/l chromium solution (prepared by dissolving hexavalent chromium nitrate in distilled water) were passed through the columns separately. Elutes were collected in each 100.0 ml portions for both the systems and the flow rates were controlled apparently same (2 ml/min) for each column. During this adsorption process, when the solutions were moving down the columns, the brown colored chitosan material was gradually turning blue in both the columns. Initially, the eluates coming out from each column were colorless (water color) which gradually received the color of original solutions with longer adsorption time. Flame atomic absorption spectrophotometric method was used to quantify chromium before and after adsorption. Adsorption capacity of each column containing the same chitosan material differs for both the tannery effluent and chromium solution. Blue colored chitosan materials were then taken out of the columns and dried at 180°C for IR spectroscopic investigations.

Results and Discussion

Characterization of the extracted material

From the TGA analysis, it was seen that sample was almost dried at or over 140°C (figure not shown here) as interpreted by weight loss. The characteristic IR band ($-NH_2$) for chitosan cannot be defined clearly at 120°C which starts appearing on heating the material at or above 140°C and finally began disappearing the spectral feature when heated at or above 200°C. Fig. 1 shows the IR spectra of the extracted chitosan dried at 120, 180 and 200°C.

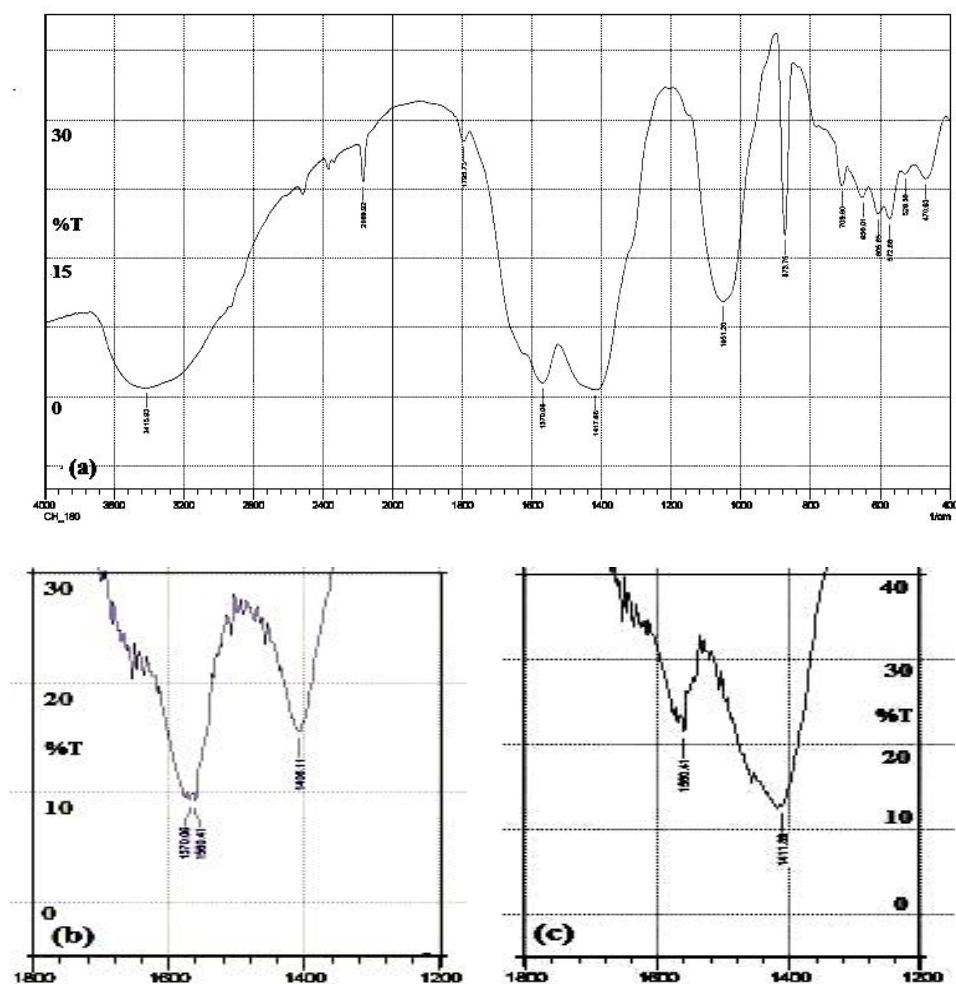


Fig. 1. IR spectra of the extracted crab shell chitosan heated at (a) 180°C, (b) 120°C and (c) 200°C.

The IR spectrum collected for chitosan heated at 180°C is in agreement with that reported by Brugnerotto *et al.* (2001). In all the spectra (full scale shown only for Fig. 1a), the broad peak between 3200 and 3600 cm^{-1} can be assigned to the combined contribution of amino ($-\text{NH}_2$) and hydroxyl ($-\text{OH}$) groups present in the sample. The peak at around 1417 and 1570 cm^{-1} are arising due to symmetric and anti symmetric bending vibration from $-\text{NH}_2$ group and the peak at 1053 cm^{-1} corresponds to C-N bond. No characteristic spectral feature for amide group within the range 1640-1680 cm^{-1} is observed which indicating the complete conversion of amide groups of chitin to amine. All these characteristics IR absorptions are the supportive enough for defining the extracted sample as chitosan. The IR spectra of the hydrolyzed product recorded at various stages of TGA analysis show similar peaks of the functional groups. This indicates that hydrolysis has generally given rise to the conversion of chitin to chitosan.

Removal of chromium by adsorption filtration

Both the raw effluent and the prepared chromium solution were passed through the columns containing 5.0 g of chitosan separately. The results demonstrate that chitosan columns used for original effluent got saturated after flowing around 500 ml of the effluent (figure not shown here). The raw effluent contained some undesirable material such as dissolved and suspended organic matters (Sabur *et al.*, 2012; Safiullah *et al.*, 2012) and reasonably disturbs the porous architecture of chitosan material. For this reason, the flow of solutions through the chitosan column had to be stopped after passing 500 ml and chromium concentration in the fifth 100 ml portion of the eluate was as low as 2.6 mg/l.

As both the raw effluent contained some other organic matter along with some unknown substances, so to observe the efficiency of the prepared adsorbent freshly prepared chromium solution (1000 mg/l) was passed through the column. The break through point appeared just after passing 800 ml of the solution as shown by the sharp change in the graph (Fig. 2) and also by the rapid color change of elute. Up to 800 ml, elute seems to be colorless but in the ninth portion, blue color started appearing and finally looked like the original solution from the 10th 100 ml portion. The sharp breakthrough point indicates that the adsorbent chitosan was completely saturated by incoming chromium species from aqueous solution. From this study, it can also be inferred that a substantial amount of chitin was converted to chitosan which exhibits stronger binding affinity towards the hexavalent chromium.

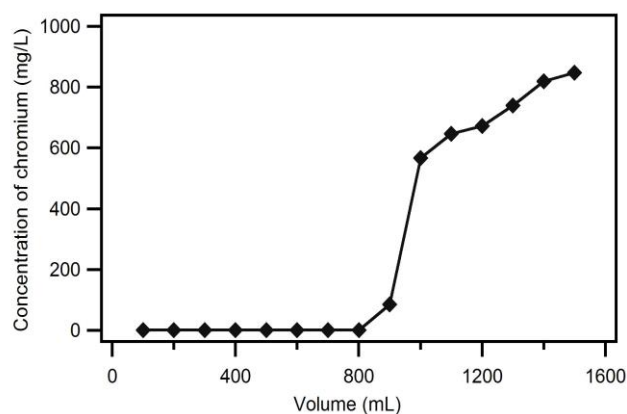


Fig. 2. Concentration of chromium in various portions after passing through the same chitosan (5.0 g) material.

Characteristic adsorption of Cr^{6+} on chitosan

IR spectra of the chitosan materials after passing chromium rich tannery effluent as well as aqueous chromium (both heated at 180°C) were compared to that of pure chitosan (heated at 180°C) before adsorption (Fig. 3).

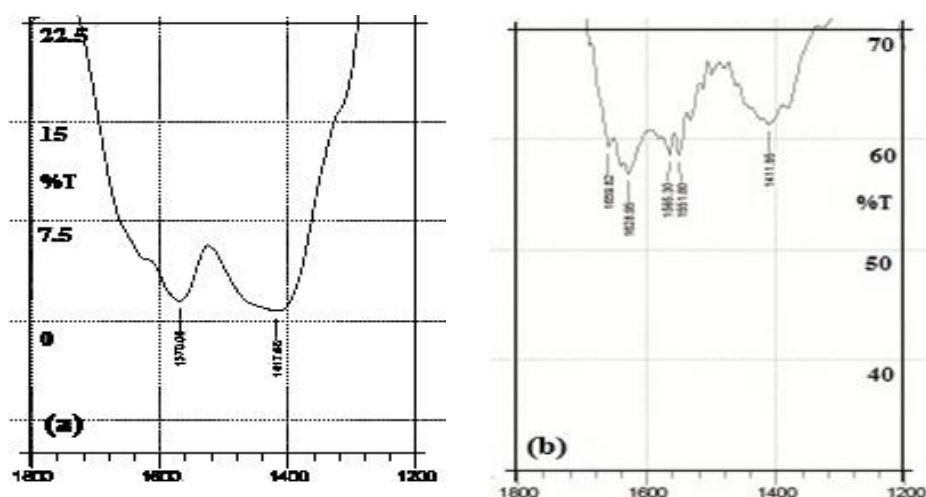


Fig. 3. IR spectra of (a) pure chitosan; and (b) chromium adsorbed chitosan.

The comparative spectroscopic study suggests a scheme how the chromium ions are trapped in contact with chitosan. From all the spectra mentioned here, it seems that spectral components arising for N-H vibration within the range 1400 to 1600 cm^{-1} are losing their intensity due to chromium adsorption on chitosan surface. This suggests that chemisorptions of chromium take place through nitrogen atoms of the chitosan amino groups.

Conclusion

The discharge of significant amount of chromium with tanning waste could be a serious threat to nearby environmental ecosystem including the possibility of ground water pollution. In this study, a cheap and convenient process for the removal of aqueous chromium has been approached which could be used in tertiary wastewater treatment stage in conjunction with other conventional technique. The chitosan can be extracted in a cost effective way from crab shells with a very simple laboratory facilities which can remove chromium effectively from aqueous medium. However, it should be a matter of study how the biosorbent chitosan material could be used in industrial scale.

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