

Metal Anion Removal Cr(Vi) from Wastewater Using Chitosan Extracted from Fish Shells

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Abstract

In this research work natural bio polymer "chitosan" was synthesized using fish shells and adsorption of chromium by chitosan was studied. Synthesis of chitosan involved four main stages as preconditioning, demineralization, deproteinization, decolorization and deacetylation. Chitosan was characterized using Fourier Transform Infrared Spectroscopy (FTIR) and solubility in 1% acetic acid. The affinity of chitosan for chromium was studied using $K_2Cr_2O_7$ solution as the heavy metal solution containing Cr (VI) ions.

The ability of chitosan as an adsorbent for Cr (VI) ions in aqueous solution was studied. The capacity of chitosan to trap chromium ions in aqueous solution was carried out at 30°C using concentration as parameters. Our results show that the adsorption process is concentration-driven with high capacity of chitosan for the adsorption of these metal 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 chromium concentrations of 1, 3, 5 and 8 mg/L, the adsorbed chromium ion concentrations are 0.74, 2.36, 4.34, and 7.38 mg/L, respectively.

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

الخلاصة:

في هذا البحث تم تخليق مادة الكيتوزان من قشور السمك و امتزاز الكروم بمادة الكيتوزان قيد الدراسة. تخليق الكيتوزان تضمن أربع مراحل رئيسية هي: إزالة المعادن، إزالة البروتين، إزالة اللون، إزالة الاستايل. تم تشخيص الكيتوزان بطيف الأشعة تحت الحمراء والإذابة بحامض ألكليك المخفف 1%. ألفة الكيتوزان للكروم درست باستخدام محلول داي كرومات البوتاسيوم كمحلول يحوي ايونات الكروم السداسية. قابلية الكيتوزان كمتزاز للكروم في المحلول المائي تم دراستها كذلك عند درجة 30 درجة مئوية مع تغير التركيز. أظهرت النتائج قابلية عالية للكيتوزان لامتزاز الكروم من خلال طيف الأشعة تحت الحمراء للكيتوزان والمعدن الناتج وكذلك طريقة الامتصاص الذري. التراكيز الابتدائية لايون الكروم كانت 1,3,5,8 ملغم/لتر وتراكيز ايون الكروم الممتزة كانت 0.74، 2.36، 4.34، 7.38 على التوالي.

مفتاح الكلمات:- كيتين، كيتوزان، امتزاز.

Introduction

Industrial and mining waste waters are important sources of pollution of heavy metals (Quek et al., 1998). The use of chromate and dichromate in metal plating and as corrosion control agents in cooling waters is quite extensive. It is well-known that Cr (VI) is toxic to living systems and must be removed from wastewater before it can be discharged. Current treatment for the removal of Cr (VI) involves acid catalyzed chemical reduction to Cr^{3+} . The Cr^{3+} is then precipitated as hydroxide at alkaline conditions using either caustic or lime (Udaybhaskar et al., 1990). Owing to their wide use, the efficient removal of toxic metal ions from wastewater is an important and widely studied research area where a number of technologies have been developed over the years (Deans and Dixon, 1992). The most important of these methods include filtration, chemical precipitation, ion exchange, adsorption, electro deposition and membrane systems. All these approaches have their inherent advantages and limitations. Although filtration and chemical precipitation are low-cost and effective in removing large quantities of metal ions quickly, neither is capable of removing trace levels of metal ions. Adsorption is also ineffective at very low concentrations of metal ions. Ion exchange can be used to reduce metal concentrations to the region of parts per million. In recent years studies on polymers, which bind metal ions, have increased significantly. Studies on the polymer-metal complexes are

of great practical importance. Complexing abilities of polymers are used in nuclear chemistry, electrochemistry, hydrometallurgy and environmental protection of particular significance among many methods of metal-ion separation is the one which combines two processes: Complexing of a polymer with metal ions and ultra filtration of the complexes through membranes of appropriate selectivity (Kamiński and Modrzejewska, 1997). A technique, which has been widely studied in the laboratory, but not widely applied industrially, is the use of chelation ion exchange. Chelation ion exchange takes advantage of the three dimensional structure of the molecules to chelate and remove ions of a specific size in the presence of large quantities of other ions (Deans and Dixon, 1992). This approach is inherently attractive since only the toxic metal ions are removed while the harmless ions can be released into the environment. Some of the best chelation ion-exchange materials are biopolymers.

Biopolymers are industrially attractive for a number of reasons; their capability of lowering transition metal-ion concentration to parts per billion concentrations, they are widely available and are environmentally safe. Such materials include cellulose, alginates, carrageenan, lignins, proteins, chitin and chitin derivatives [figure 1]. Another attractive feature of biopolymers is that they possess a number of different functional groups, such as hydroxyls and amines, to which metal ions can bind either by chemical or by physical adsorption (Deans and Dixon, 1992). Metal removal can be more effective by using chelation ion exchange as a polishing step after the majority of the metal ions have been removed. Since the metals used for chelation ion exchange will tend to have higher associated production costs, it is impractical to use them for removing massive quantities of heavy metals from water.

This study focuses on chitin derivatives for the removal of heavy metals such as Cr. Low pH would favour protonation of the amino sites, resulting in a reversal of charge, and would greatly diminish the metal chelating ability of chitin and chitosan. This suggests that at a neutral pH more of the metal ions should be adsorbed by the chitosan.

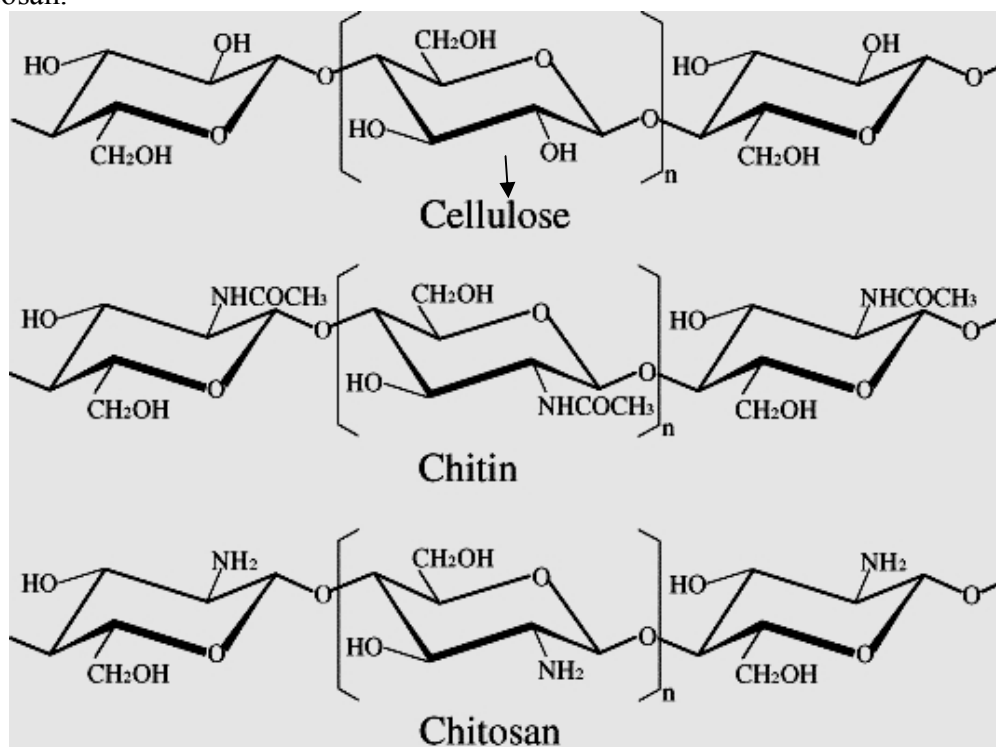


Figure 1. Chemical structures of chitin, chitosan and cellulose [WEB_4 2007] .

Traditional isolation of chitin consists of four traditional steps (Figure 2): demineralization (DM), deproteinization (DP), decolorization (DC), and deacetylation (DA).

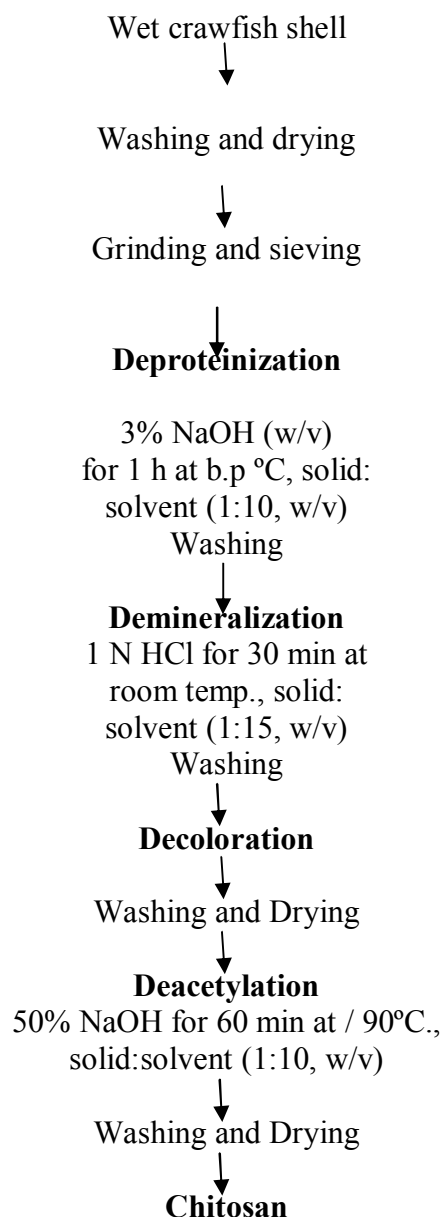


Figure 2. Traditional Chitosan Production (Modified from No and Meyers, 1995).

The overall objective of this study is to investigate the heavy metals removal from wastewater by adsorption using chitosan. The specific objectives included; synthesize chitosan from fish shells and removal of heavy metals (chromium) using as a bio-adsorption material.

Apparatus; FTIR-8400S Shimadzu, Japan.

Atomic absorption spectroscopy, AA-6300 Shimadzu, Japan.

In Babylon University/college of science/chemistry department.

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). The poiled sample was removed from hot plate and placed in hood then allowed to cooled at room temperature for 30minutes. 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 50% at 90°C or higher for 2hours 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 chromium ions on chitosan

20mg/L chromium solution was prepared by dissolving 556mg analytical grade $K_2Cr_2O_7$ 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 $K_2Cr_2O_7$ 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 $K_2Cr_2O_7$ solution were analyzed using atomic adsorption spectroscopy to determine amount of chromium absorbed by chitosan. The same steps were repeated to the other dilute solutions. Finally uptake of chromium by amine groups ($-NH_2$) 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 chromium adsorbed after adding 50mg of chitosan at 30°C and pH6.

Total Cr^{6+} in original solution(ppm)	Total Cr^{6+} after chitosan addition(adsorb)ppm
1	0.74
3	2.63
5	4.43
8	7.38

From the above table its appeared that the adsorption process was increased by increasing the cobalt ion concentration(Angham G. Hadi,2012).

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 (Duarte et al., 2001, Ravindra et al., 1998). However, in chitosan-metal complexes, a new band around $1625\text{--}1635\text{ cm}^{-1}$ 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 $3000\text{--}3600\text{ cm}^{-1}$ 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 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.

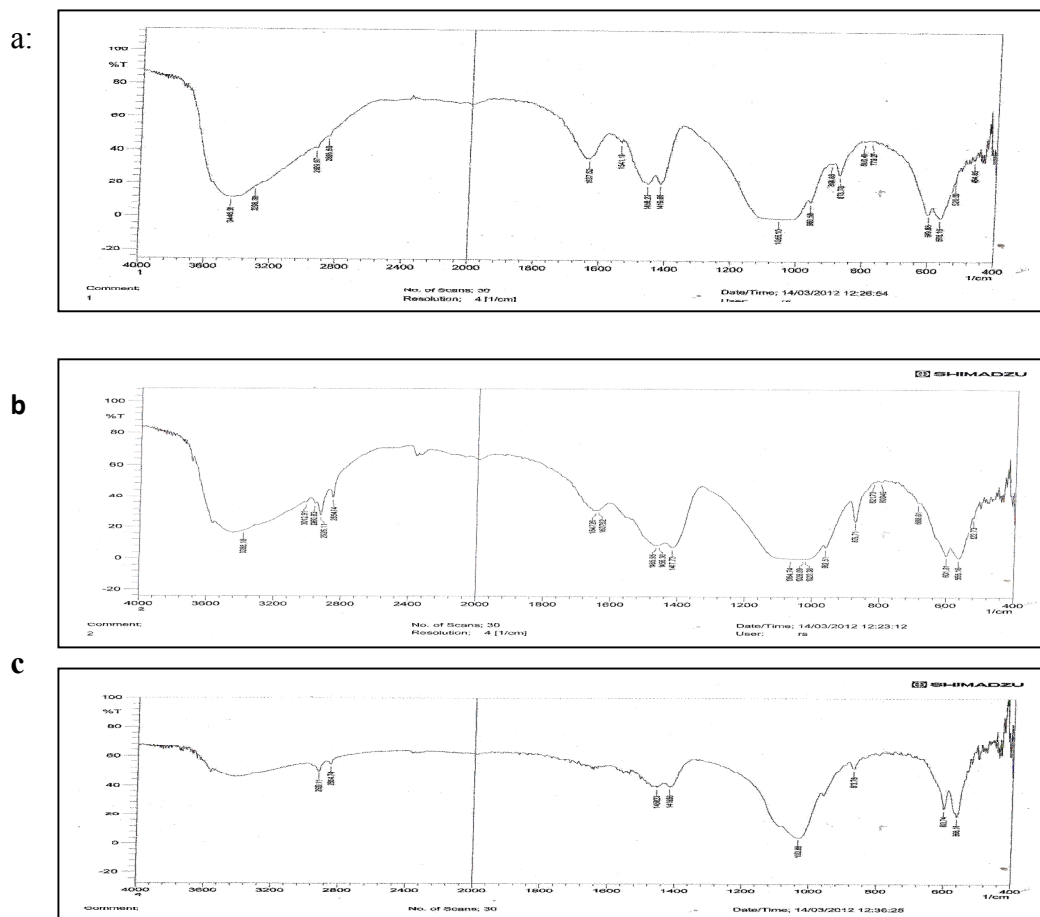


Figure 3. FT-IR Spectra of a: Chitin, b: Chitosan and c: Chitosan-Cr complex.

Conclusions

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

Recommendation

1. Affection study for the application of chitosan on other heavy metals.
2. Optimization max dose of heavy metal, with high removal efficiency.

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