REMOVAL OF HEAVY METALS FROM WASTEWATER USING CHITOSAN

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***ABSTRACT*:** In this research work natural bio polymer "chitosan" was synthesized using locally available shrimp shells and adsorption of chromium by chitosan was studied. Synthesize of chitosan involved four main stages as preconditioning, demineralization, deprotenisation and deacetylation. Chitosan was characterized using Fourier Transform Infrared Spectroscopy (FTIR) and X-ray diffraction (XRD). Both characterization techniques confirm the existence of chitosan. The affinity of chitosan for chromium was studied using $K_2Cr_2O_7$ solution as the heavy metal solution containing Cr (VI) ions. Adsorption of chromium ions by chitosan was investigated under different conditions. The effect of reaction temperature, particle size of chitosan and pH of solution were studied. Amount of chromium absorbed under different conditions was evaluated using atomic adsorption spectroscopy.

KEYWORDS: chitosan, heavy metal, bio-adsorption

1. INTRODUCTION

In the past century there has been a rapid expansion in industries. This has lead to an increase in the complexity of toxic effluents. Several industrial processes generate metal containing wastes. Heavy metal contamination has been a critical problem mainly because metals tend to persist and accumulate in the environment. Copper, Nickel, Mercury, lead, Zinc, Arsenic etc. are such toxic metals which are being widely used. They are generated by dental operation, electroplating, tanning, textile, paper and pulp industry and are potentially toxic to humans (Palanisamy, 2005). These heavy metals are used in many industries for different purposes and released to the environment with industrial wastage. Therefore the effluents being generated by these industries are rich in heavy metals should be treated before discharge in to the common waste water.

On the other hand aquatic systems are particularly sensitive to pollution possibly due to the structure of their food chain. In many cases harmful substances enter the food chain and are concentrated in fish and other edible organisms. As they move from one ecological tropic level to another, metallic species start damaging the ecosystem. They also become difficult to track as they move up in tropic levels. They accumulate in living tissues throughout the food chain. Due to biomagnifications, human receive the maximum impact, since they are at the top of the food chain. Hence heavy metal contamination has been a critical problem (Volesky, 2001).

The efficient removal of toxic metals from wastewater is an important matter and it is being studied. A number of technologies have been developed over the years to remove toxic metal from wastewater. Physical treatment can also be used to remove small concentrations of hazardous substances dissolved in water that never settle out. The current physico-chemical processes for heavy metal removal like precipitation, reduction, ion-exchange etc. are expensive and inefficient in treating large quantities. They also cause metal bearing sludges which are difficult to dispose off (Volesky, 2001). Some of these traditional methods are also extremely expensive, thereby proving uneconomical, especially for developing countries like Sri Lanka, where large volumes of these wastes are generated. Therefore there is a requirement for newer and effective methods which are also cost-effective and environmentally friendly. And also more stringent rules by the government and media and public pressure regarding effluent discharges have necessitated the search for newer methods of treatment.

One of the most commonly used techniques involves the process of adsorption, which is the physical adhesion of chemicals onto the surface of solid. Bio-adsorption is a good alternative to traditional processes. Widely available biopolymers are also being used for adsorption mainly because they are a cheap resource or a freely available resource (Niu and Volesky, 2003).

Chitosan is a biopolymer, which is extracted from crustacean shells or from fungal biomass. The structure of chitosan is presented schematically in Figure 1.

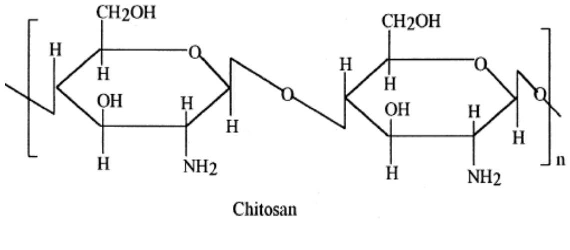

Figure 1 Structure of chitosan

The high porosity of this natural polymer results in novel binding properties for metal ion such as cadmium, copper, lead, uranyl, mercury and chromium. Chitosan has been used for about three decades in water purification processes. When chitosan is spread over oil spills it holds the oil mass together making it easier to clean up the spill. Water purification plants throughout the world use chitosan to remove oil, grease, heavy metals, and the fine particulate matter that cause turbidity in wastewater streams (Varma *et al.*, 2004). Chitosan have the potential to reduce and solve some environmental pollution problems for creating `Greener ` environment and chitosan is a renewable polymer in this application. Some of the properties which are commercially attractive are polymeric, including natural decomposition, non-toxic to both the environment and human, with no side effects or allergic effects if implanted in the body. Chitosan occur naturally in the environment in large quantities and run second in abundance to cellulose. It has an amine functional group which is strongly reactive with metal ions. Considerable research has been done on the uptake of metal cations by chitosan.

Chitosan has been used successfully in Asia, Europe and North America to remove sediment from water.

The amine groups on chitosan bind metal cations at pH close to neutral. At low pH, chitosan is more protonated and therefore it is able to bind anions by electrostatic attraction. (Guibal, 2004).

The aim of this study was to demonstrate the use of chitosan as a bio-adsorbent for uptake of heavy metal ion.

The chitosan used in this work was derived from shrimps shells available in Sri Lanka. Most of them are exported by shrimp processing industries without head and shell.The shrimp processing industry turns out tons of head and shell waste per annum. These shell decay process makes awful smell.

Therefore shrimp processing industries have the problem with disposing shell waste. Chitosan can be produce from the shrimp head and shell which are thrown out as waste. In this work chitosan is chosen as the bioadsorption material for waste water treatment.

1.1 Objectives

The overall objective of this study is to investigate the heavy metals removal from wastewater by adsorption using chitosan. The specific objectives included;

1. To synthesize chitosan from Sri Lankan shrimp shells.
2. To evaluate factors affecting on the removal of heavy metals (chromium) using as a bio-adsorption material.

2. METHODOLOGY

2.1 Preparation of chitosan

The shrimp shells which were used for chitosan isolation was purchased from local seafood processing industry. A preconditioning process was introduced as the first step to the common procedure of chitosan extraction. At the preconditioning stage, shrimp shells were allowed to soak in 0.05 M acetic acid solution for 24 hours. Then shells were washed thoroughly with water and dried to remove excess water. Then dried shells were demineralized using 0.68 M HCL (1:10 w/v) at ambient temperature (approximately 30 ^{0}C) for 6 hours. The residue was washed with distilled water until PH in the range of 6.5 -7.5 was obtained and then the residue was dried. After that the demineralized shrimp shells were deproteinized using 0.62 M NaOH solution (1:10 w/v) at ambient temperature (approximately 30 ^{0}C) for 16 hours. Then residue was washed thoroughly with water followed with distilled water until PH in the range of 6.5 -7.5 was obtained. The chitin was dried and ground and screened with 150μm sieve. The chitin obtain from the above process was deacetylated in 25 M and NaOH (1:10 w/v) for 20 hours at 65 ^{0}C. After deacetylation, the chitosan was washed thoroughly with water followed with distilled water until PH in the range of 6.5 -7.5 was obtained.

The synthesized chitosan was characterized by Fourier transformed infrared (FT-IR) spectroscopy (Bruker Alpha-T) in the range of 400 to 4000 cm^{-1}.

The crystallinity of chitosan in powder form was studied by X-ray diffraction method (Bruker D8) using Cu Kα radiation generated at 40 kV and 40 mA at scanning speed of 0.3 2θ/ min within a range of 5^0 to 35^0.

2.2 Study of heavy metal adsorption by synthesized 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 3mg/l solution was prepared by diluting stock solution.

50ml of 3mg/l $K_2Cr_2O_7$ solution was taken and 50mg of 150 μm particle size chitosan was added. Then the mixture was continuously stirred using magnetic stirrer for 6 hours at room temperature (30 ^{0}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.

Similar effect of temperature was studied by changing only reaction temperature to 50 ^{0}C and keeping other parameters as constant.

Effect of particle size of chitosan powder on amount of metal uptake was studied by increasing the particle size of powder to 355μm and repeated the above mentioned procedure.

pH of $K_2Cr_2O_7$ solution was set to 5.7 by using 1M NaOH solution.

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}.

3. RESULTS AND DISCUSSION

Figure 2 shows FTIR spectra of chitosan derived from the above mentioned process. It represents all the relevance peaks of chitosan compared to standard FTIR spectrum of chitosan. (Zouhour *et al*., 2010)

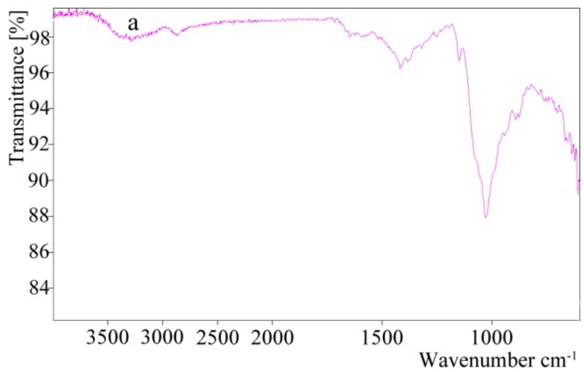

Figure 2 FTIR spectrum of synthesized chitosan

Figure 3 shows the X-ray diffractrogams of synthesized chitosan powder. The strong reflections at 2θ around 9-10^0 and 19-20^0 corresponds to (020) and (110) planes of chitosan (Jolanta *et al*., 2010).

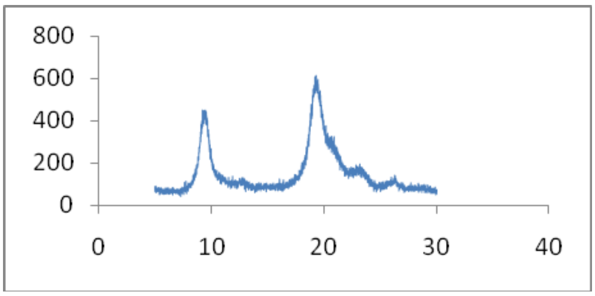

Figure 3 X-ray diffraction spectra of synthesized chitosan powder

Table 1 amount of chromium adsorbed after adding 50mg of chitosan with a agitation speed of 250 rpm

Total Cr $^{6+}$ in original solution (ppm)	Total Cr $^{6+}$ after addition of chitosan (ppm)	Chitosan particle size (μm)	Temp. ^{0}C)	pH
25.7	18.6	150	30	5.7
25.7	20.5	355	30	5.7
25.7	15.7	150	50	5.7
25.7	24.4	150	30	4.6

Amount of Chromium content in the original solution of $K_2Cr_2O_7$ was found as 25.7 ppm. Table 2 represents the amount of Chromium available in different in solution at by different conditions.

According to the table 1 chromium adsorption was considerably increased with increasing temperature. Minimum adsorption was observed with low pH.

In general adsorption is the process of collecting soluble substances that are in a solution, on a suitable interface. The interface can be between the liquid and a gas, a solid, or another liquid (Metcalf and Eddy, 1991). Adsorption at the liquid solid interface is used in this study.

Adsorption can be classified as physical adsorption and chemical adsorption. Physical adsorption is primarily due to van der waals forces and is a reversible occurrence. When the molecular forces of attraction between the substance and interface are greater than the forces of attraction between substance and the solvent, the substance will be adsorbed onto the adsorbent surface. In chemical adsorption a chemical reaction occurs between the solids and the absorbed solute and the reaction is usually irreversible.

Chitosan react with metal ion with following equilibrium.

$$M^{2+} + RNH_2 \longleftrightarrow M(RNH_2)^{2+} \quad (1)$$

The amine groups of chitosan react with H^+ as follows,

$$H^+ + RNH_2 \longleftrightarrow RNH_3^+ \quad (2)$$

According to the equation 2 at low pH the amine group get protonated. That means chitosan get positively charged. Chromium ion also positively charged. As a result repulsive forces occur between metal ion and chitosan instead of attraction. Therefore at low pH chromium uptake will be reduced. As per the Table 1, at lower pH value of 4.6 negligible adsorption was taken place. Therefore pH of the media should be properly control according to the type of metal to be absorbed.

According to the Table 1, when particle size of chitosan powder was increased the amount of heavy metal up take was reduced. Because, large particle size reduce the accessible surface to metal ions and small particles gives high surface area to metal ion adsorption.

Figure 4 shows the mechanism of adsorption of Cr(VI) ions by chitosan using $-NH_2$ group and –OH group

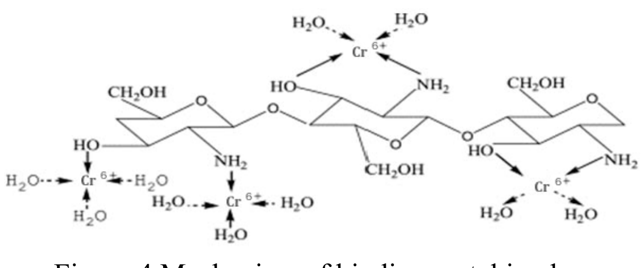

Figure 4 Mechanism of binding metal ion by chitosan

The amine group initiates a coordinate bond with the metallic ions. The bond is formed between the free electron pairs of the nitrogen in the amine group and the void orbitals of the metal.

There are several factors effect on metal ion adsorption by chitosan (Guibal, 2004).

1. The fraction of acetylated units. This determines the number of free amine groups available for binding. To be good sorbent, the polymer needs to have a high degree of deacetylation.
2. Number of amine groups accessible to the metal ion. Some of the amine sites are sometimes involved in some kind of inter- and intra-molecular bonds. The crystallinity of the polymer may make some groups inaccessible to the metal ions.
3. Chain length or the degree of polymerization.
4. Degree of mixing of the metal-chitosan complex.
5. Physical state of the chitosan affected the capacity of chitosan

Uptake of chromium metals was mainly affected via coordination with the amine groups ($-NH_2$) on chitosan. This is illustrated by the FT-IR spectra presented in Figure 5. Chitosan charged with metal ion forms a new energy band at 1632 cm^{-1} . This band corresponds to the bending of plane of N-H.

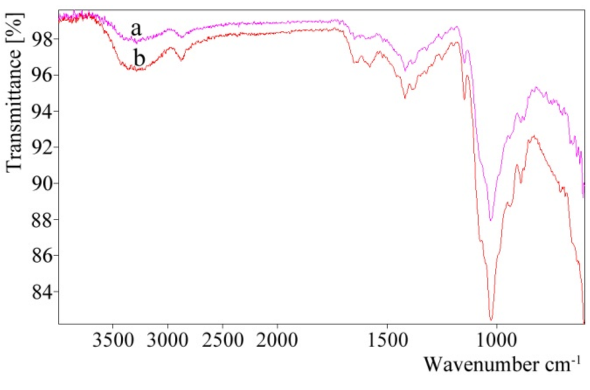

Figure 5 FTTR spectra of a) Chitosan, b) Chitosan-Cr

4. CONCLUSION

Chitosan was successfully synthesized from shrimp shells available in Sri Lanka. FTIR spectrum of chitosan showed all the characteristics bond energies of standard chitosan sample. According to the results optimum Cr^{6+} adsorption was observed in the solution with 150 μm chitosan powder at 50^0C temperature. Particle size of chitosan, reaction temperature and pH of the solution highly affect on chromium adsorption. According to the study chitosan can be a good candidate to remove heavy metals from wastewater. Chitosan may offer an alternative to traditional coagulants in wastewater treatment. The unique properties of chitosan together with availability make chitosan an exciting and promising agent for the heavy metal adsorption from wastewater.

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