

Study of heavy metal Mn^{2+} Adsorption by Synthesized Chitosan

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Abstract

In this research work natural bio polymer "chitosan" was synthesized using fish shells and adsorption of manganese by chitosan was studied. Synthesize 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 manganese was studied using $MnCl_2 \cdot 4H_2O$ solution as the heavy metal solution containing Mn (II) ions.

The ability of chitosan as an adsorbent for Mn (II) ions in aqueous solution was studied. The capacity of chitosan to trap manganese 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 manganese concentrations of 3, 5 and 8 mg/L, the adsorbed manganese ion concentrations are 2.6136, 4.3954, and 7.3638 mg/L, respectively.

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, manganese, 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 [1]. 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 [2]. 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. The main sources of manganese pollution are mining, the iron and steel industry, fuel oil, incineration, coal and dry cell batteries. Continued exposure may lead to chronic manganese poisoning and manganese pneumonia." Chronic manganese poisoning is clearly characterized as resulting from the inhalation of fumes or dusts of manganese [3]. The central nervous system is the chief site of damage. When well established, the disease results in permanent disability [4,5].

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 fish shells available in Babylon-Hilla.

2. Materials And Methods

2.1 Samples Preparation

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.

2.2 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) [6]. 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) [6], 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 [6]). 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 [6]. The N-acetyl groups cannot be removed by acidic reagents without hydrolysis of the polysaccharide, thus, alkaline methods must be employed for N-deacetylation [7].

2.3 Sorption of manganese ions on chitosan

20mg/L manganese solution was prepared by dissolving 8.99 mg analytical grade $MnCl_2 \cdot 4H_2O$ 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 $MnCl_2$ 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 $MnCl_2$ solution were analyzed using atomic adsorption spectroscopy to determine amount of manganese absorbed by chitosan. The same steps were repeated to the other dilute solutions. Finally uptake of manganese by amine groups (-NH₂) on chitosan was investigated using FTIR spectroscopy (Bruker Alpha-T) in the range of 400 to 4000 cm⁻¹.

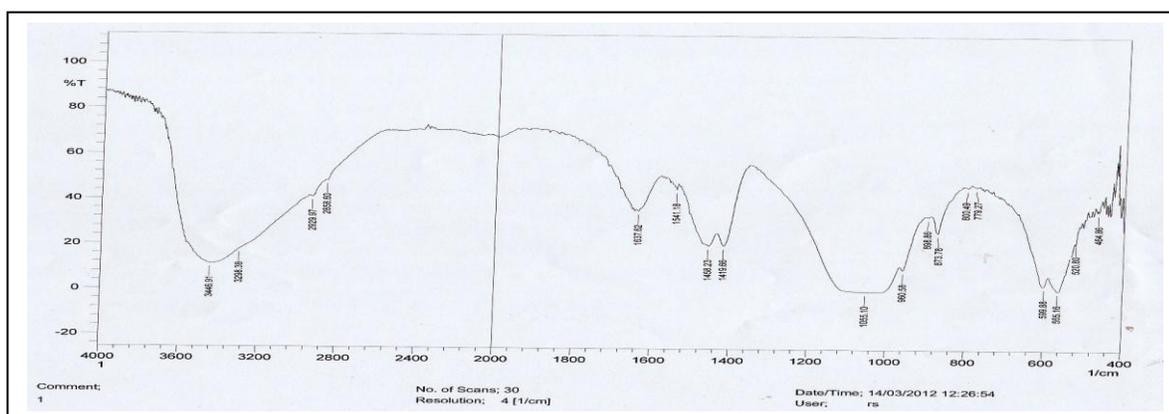
Results and Discussion

Table 1 amount of manganese adsorbed after adding 50mg of chitosan with 30° C and pH=5.4 (atomic absorption method).

Total Mn ²⁺ in original solution (ppm)	Total Mn ²⁺ after addition of chitosan (ppm) (adsorb)
3	2.6136
5	4.3954
8	7.3638

FT-IR analysis

The spectra of chitin, chitosan and chitosan-Mn polymeric complexes are shown in Figure 1. 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 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 Mn 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.



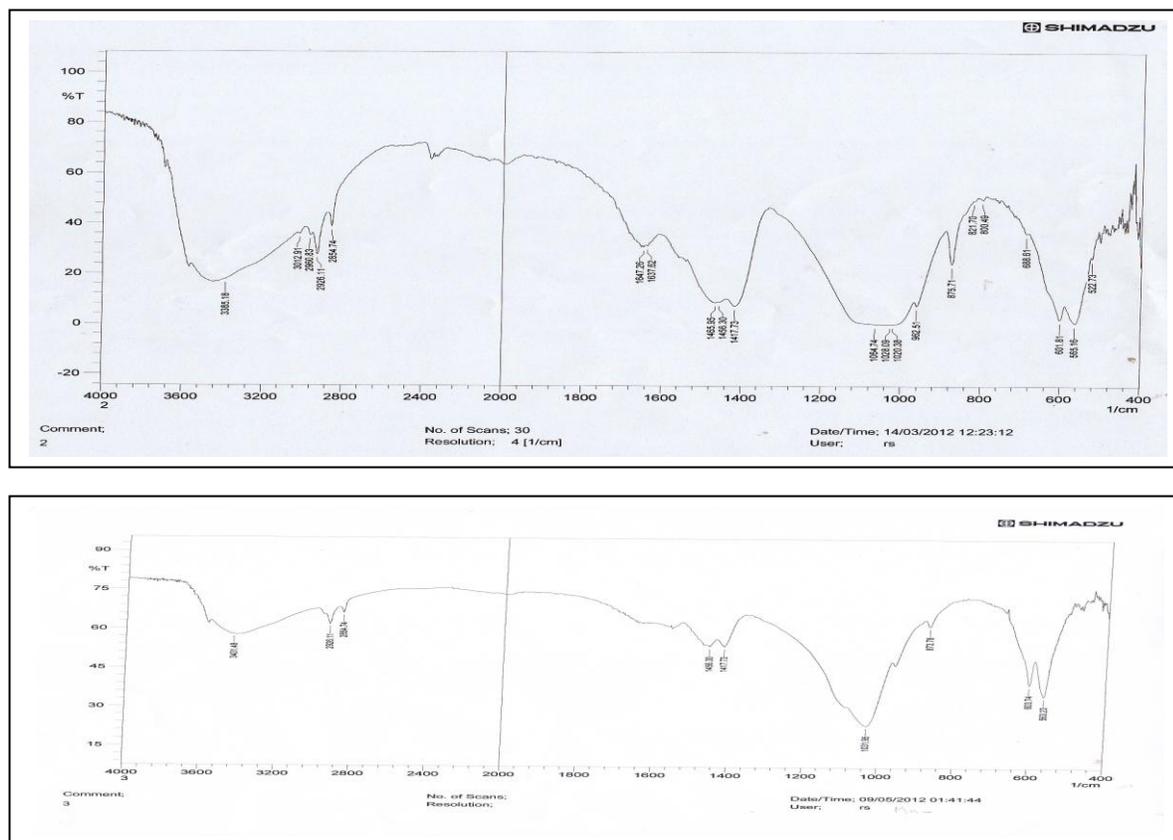


Figure 1. FT-IR Spectra of a: Chitin, b: Chitosan and c: Chitosan-Mn complex.

Conclusions

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

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