

## Adsorption of Nickel Ions by Synthesized Chitosan

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### Abstract

Chitosan is an amino-polysaccharide with highly efficient properties for the binding of metal ions. Uptake may occur through chelation on free amino functions (at near-neutral pH) or by electrostatic attraction on protonated amino groups (in acidic solutions). Chitosan synthesis process from fish shells 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 nickel was studied using  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  solution as the heavy metal solution containing Ni (II) ions.

**Keywords:** Adsorption, chitosan, nickel chloride, chitin ,precipitate.

### 1. Introduction

Contamination of aquatic media by heavy metal ions is a serious environmental problem, mainly due to the discarding of industrial wastes [1]. Among the heavy metals chromium, cobalt, zinc, copper, nickel and iron ingestion beyond permissible quantities, causes various chronic disorders in human beings. It is well known that heavy metals can damage the nerves, liver and bones and they block functional groups of essential enzymes [2]. The increasing demand for new processes for wastewater treatment, more environmentally friendly and more competitive, has led to much research on the use of biopolymers such as alginate and chitin/chitosan for the recovery of metal ions [3,4] or organic compounds [5-8]. These biopolymers are characterized by high sorption capacities, easy degradation routes (at the end of life cycle) and relatively low costs [9]. These properties make them very promising for replacing conventional processes. Chitosan has a unique property among these biopolymers: its cationicity in acidic solutions. This property is due to the presence of a large number of amino groups, which are very reactive for (a) metal cations by chelation in near-neutral solutions, and for (b) metal anions that can be bound to protonated amino groups in acidic solutions [4].

Chitin is the second most abundant natural polymer on the earth after cellulose. Chitin exist widely the exoskeleton of insects and other marine crustaceans. It is of interest, not only as an underutilized resource, but also as a new functional material of high potential in various fields [10]. Chitosan is a biopolymer which is of interest to researchers concerning the adsorption of metal ions [11]. Chitosan is the N-deacetylated product of chitin (Fig.1). Although a sharp nomenclature border does not exist between chitin and chitosan, the term 'chitosan' usually represents copolymers of 2-amino-2-deoxy-D-glucopyranose and 2-acetamido-2- deoxy-D-glucopyranose.

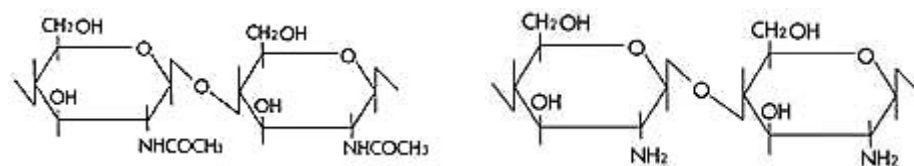


Figure 1. Structure of Chitin and Chitosan .

The objective of this study was the synthesis of the of chitosan and study of nickel recovery on chitosan by sorption (chitosan in solid state) The adsorption capability of chitosan was investigated using Ni(II) as the model metal contaminant because of its extensive environmental impacts.

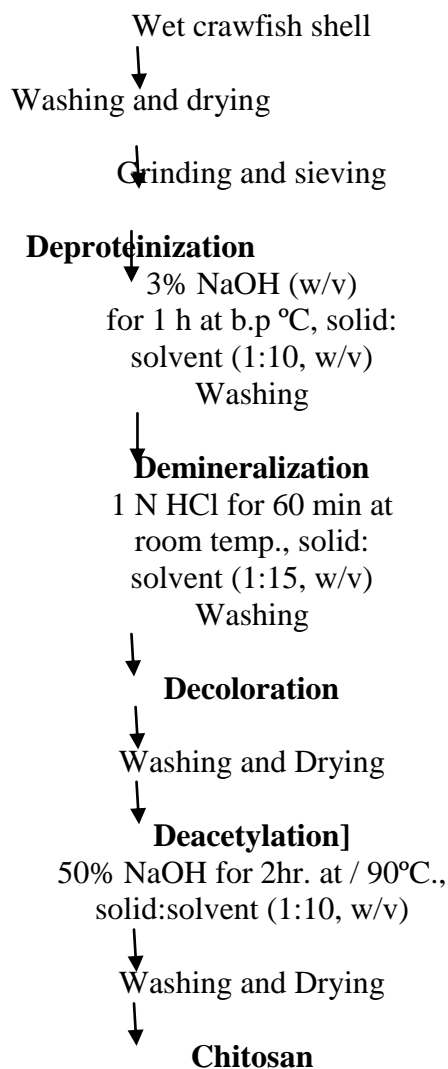
## 2. Materials and Methods

### **2.1 Raw Material**

Crawfish shells were obtained from a commercial crawfish shells that 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.

### **2.3 Isolation of Chitosan**

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).

## 2.4 Sorption of Nickel ions on Chitosan

20mg/L nickel solution was prepared by dissolving 0.01g analytical grade  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  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  $\text{NiCl}_2$  solution was taken and 50mg of chitosan was added. Then the mixture was continuously stirred using magnetic stirrer for 2 hours at ( $30^\circ\text{C}$  and  $\text{pH}=5-5.3$ ). After that solution was filtered, the filtrate and 3mg/L  $\text{NiCl}_2$  solution were analyzed using atomic adsorption spectroscopy to determine amount of nickel absorbed by chitosan. The same steps were repeated to the other dilute solutions.

Finally uptake of nickel by amine groups ( $-\text{NH}_2$ ) on chitosan was investigated using FTIR spectroscopy (Bruker Alpha-T) in the range of 400 to  $4000\text{ cm}^{-1}$ .

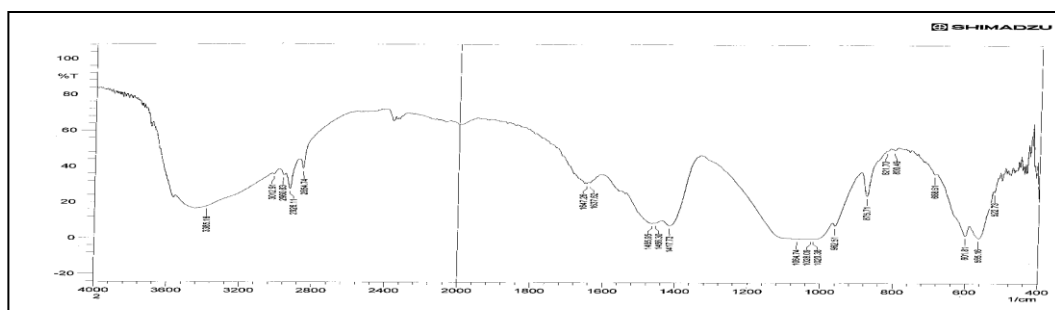
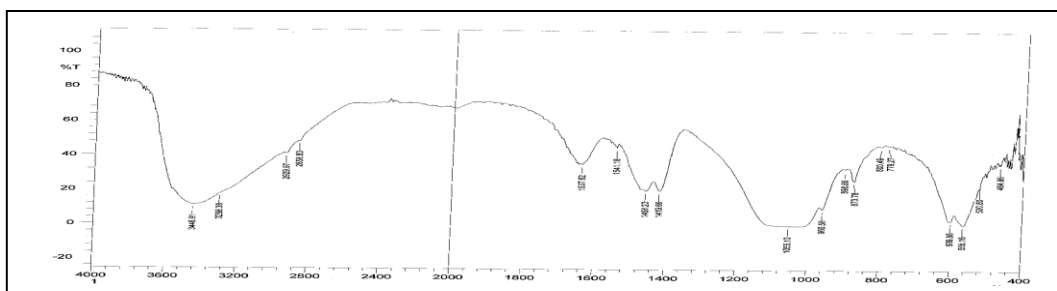
## Results and Discussion

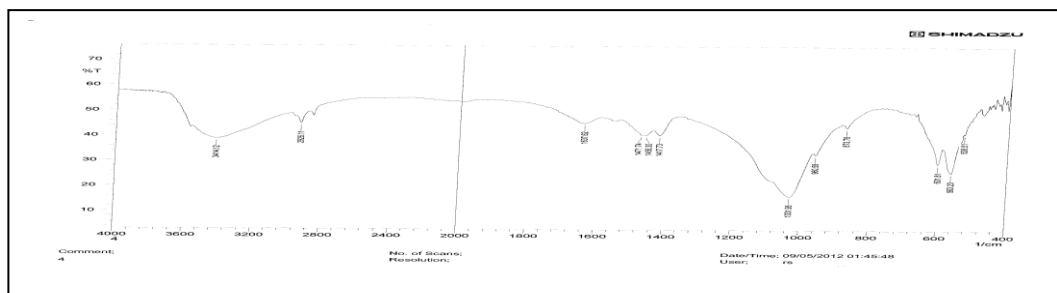
Table 1 amount of nickel adsorbed after adding 50mg of chitosan with  $30^\circ\text{C}$  and  $\text{pH}$  (5-5.3).

Total $\text{Ni}^{2+}$ in original solution (ppm)	Total $\text{Ni}^{2+}$ after addition of chitosan (ppm) (adsorb)
3	2.6299
5	4.5572
8	7.3018

### FT-IR analysis

The spectra of chitin, chitosan and chitosan-Ni polymeric complex is shown in Figure 3.





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

In the FTIR spectrum the strong and broad absorption band observed at  $3,400\text{--}3,500\text{ cm}^{-1}$  are attributed to the  $\text{--OH}$  and  $\text{--NH}_2$  groups overlay with each other. The peak located at  $1,585\text{ cm}^{-1}$  provides an evidence of the presence of primary amino groups. Absorption band at  $1,650\text{ cm}^{-1}$  could be related to the presence of  $\text{--CONH--}$ , i.e., a partly deacetylated form of chitin. The wide peak at  $3,400\text{--}3,500\text{ cm}^{-1}$  corresponding to the stretching vibration of  $\text{--NH}_2$  group and  $\text{--OH}$  group is split into two bands at  $3,363$  and  $3,456\text{ cm}^{-1}$  indicating that  $\text{--NH}_2$ , chemical group or  $\text{--OH}$  groups take part in complexation, 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  $1605\text{ cm}^{-1}$ . This observed red shift is due to interaction of chitosan with the metal ions. These changes in the FTIR spectra may be attributed to the interaction between the functional groups of chitosan and nickel ions during the adsorption process.

### Conclusions

This study showed that chitosan adsorbs heavy metals, in particular Ni (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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