

## Removal of nickel from aqueous solutions using crab shells

Swapna Pradhan, Shyam S. Shukla, Kenneth L. Dorris\*

*Department of Chemistry, Lamar University, Beaumont, P.O. Box 10022, TX 77710, USA*

Received 31 December 2004; received in revised form 17 May 2005; accepted 24 May 2005

Available online 5 July 2005

### Abstract

Partially converted crab shell waste, which contains chitosan, was used to remove nickel from water. The chelating ability of chitosan makes it an excellent adsorbent for removing pollutants. Advantages of chitosan in crab shells include availability, low cost, and high biocompatibility. The metal uptake by partially converted crab shell waste was successful and rapid. The sorption occurred primarily within 5 min. The sorption mechanism appears to be quite complicated and cannot be adequately described by either the Langmuir or Freundlich theories. Various anions, including chloride, bromide, fluoride, acetate, sulfate, nitrate, and phosphate, were found to have a very small effect on the capacity of the crab shells for uptake of nickel. The effect of pH was also found not to be prominent.

© 2005 Elsevier B.V. All rights reserved.

*Keywords:* Chitosan; Crab shell; Nickel; Adsorption; Heavy metal

### 1. Introduction

Water pollution, due to disposal of heavy metals, continues to be of great concern worldwide. One of the metals released to the environment from a number of sources is nickel. Nickel is an essential element but the levels required by both plants and animals are very low. At higher concentrations, it is known to be toxic to both plants and animals, whereas at very high levels of exposure, nickel salts are known to be carcinogenic [1]. California's South San Francisco Bay has been designated an impaired water body under the U.S. Clean Water Act due to the presence of seven metals including nickel.

Various technologies have been developed over the years to remove toxic metal ions from water. The most important of these technologies include filtration, chemical precipitation, ion exchange adsorption, electro-deposition, and membrane systems. All these technologies have advantages and limitations [2–5]. A technique that has been studied in the laboratory but not widely applied industrially is the use of chelation ion exchange [6–10]. As opposed to sim-

ple ion exchange, chelation ion exchange takes advantage of the three-dimensional structure of molecules to chelate and remove ions of a specific size in the presence of large quantities of other ions. This approach is inherently attractive since only the offending metal ions may be selectively removed at certain conditions. Some of the best chelation materials are biopolymers. Biopolymers [11] are industrially attractive because they are capable of lowering transition metal ion concentrations to sub-part per billion concentrations, widely available and environmentally safe. Another attractive feature of biopolymers is that they possess a number of different functional groups, such as hydroxyls and amines, which increase the efficiency of metal ion uptake and the maximum chemical loading possibility. Chitosan, which can be formed by deacetylation of chitin [12], is the most important derivative of chitin. Chitin, poly- $\beta$ -(1,4)-*N*-acetyl-D-glucosamine is a cellulose-like biopolymer. Chitosan in partially converted crab shell waste has the advantages of low cost and high biocompatibility. Chitosan, a polyglucosamine, is a powerful chelating agent and interacts very efficiently with transition metal ions [13–16]. The nitrogen in the amino group of the chitosan molecule acts as an electron donor and is presumably responsible for selective chelation with metal ions.

\* Corresponding author. Tel.: +1 409 880 8274; fax: +1 409 880 8270.  
E-mail address: dorriskl@hal.lamar.edu (K.L. Dorris).

## 2. Experimental procedure

A Varian 220 Atomic Absorption Spectrometer was used to analyze the nickel metal concentrations. Standard solutions in the linear range of the instrument were used to construct a calibration curve. Sample readings beyond the linear range of the references were diluted to appropriate concentrations. A Fisher Scientific pH-meter using glass electrode was employed and standardized using buffer solutions of pH 4.0, 7.00, and 10.00. American Optical Corporation (Buffalo, New York) and Precision scientific Corporation, Chicago (Dubnoff metabolic shaking incubator) water bath shakers were used for all the adsorption experiments. They were set to 80 cycles/min. Analytical grade standards of nickel, potassium chloride, potassium bromide, potassium fluoride, sodium acetate, sodium sulfate, sodium nitrate, and sodium phosphate were obtained from Fisher Scientific. A.C.S. reagent grade concentrated nitric acid, and sodium hydroxide were obtained from Aldrich Chemical Company, and used to adjust pH values of samples. pH buffer solutions were obtained from Fisher Scientific Company and Chemlab Supply Co. All experimental work used deionized water. Gulf Coast blue crab waste was obtained from Fisherman's Reef Shrimp Co. of Beaumont, TX. Partially converted crab shell waste was prepared from air-dried waste that had first been crushed using a mortar and pestle. The shells then soaked in a 5% HCl solution for one hour at room temperature to remove calcium salt (demineralization). After being washed in water to remove HCl, the shells were soaked in 50% NaOH solution at 90 °C for one hour to cause deacetylation [13]. Protein was also removed by the foregoing NaOH treatment, after which the shells were rinsed in water, HCl adjusted the pH to neutral, and then the shells were air-dried. For the pH-effect experiment, the time was uniformly established as 360 min to reach equilibrium. In each experiment, 100 mL of metal ion solution of known initial concentration (2.5, 5, 7.5, and 10 mg/L,) were placed together with a fixed mass of adsorbent crab shell (10, 25, and 50 g/L). Experiments done without adsorbent indicate that no precipitation of metal ions occurred under the conditions selected. Samples were obtained after 5, 20, 60, 180, and 360 min. To determine the effect of anions on crab shells, 100 mL of metal ion solution whose initial concentration was 2.5 mg/L was placed together with 10 g/L of crab shell and anion solution (1000 and 50 ppm). The experiments were carried out at room temperature (about 23 °C).

## 3. Results and discussion

The adsorption kinetics [17,18] is influenced by various factors, which include initial metal ion concentration, amount of adsorbent, pH, and temperature. The initial metal ion concentration is one of the most important factors that determines the equilibrium concentration, but also determines the uptake rate of metal ion and the kinetic character.

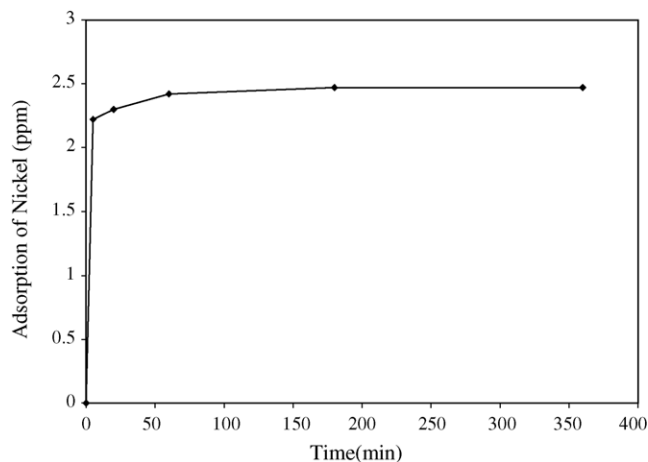


Fig. 1. Effect of crab shell loading (10 g/L) on sorption of Ni (2.5 mg/L).

### 3.1. Effect of time and nickel concentration

Fig. 1 shows the uptake tendency of nickel on crab shell, which was performed in the region of pH 4.5–7. The amount of crab shell is an important factor that directly influences the uptake of the metal ion. When the quantity of crab shells and concentration of metal ion is increased, the uptake rose sharply. This is attributed to greater adsorbent surface (or number of adsorbent sites). The adsorption occurs primarily within 5 min.

### 3.2. Effect of anions on crab shell adsorption

The effect of chloride, bromide, fluoride, acetate, sulfate, nitrate, and phosphate interference was investigated. These various anions were studied since they could be present in the wastewater at relatively high concentrations. If these ions could bind the metals more strongly than the crab shells, then the adsorption on the crab shells would be greatly inhibited. It is obvious from Figs. 2–4 that these ions have a very small effect on the capacity of the crab shells for uptake of nickel. Initially, for most of the anions, the metal ion concentration

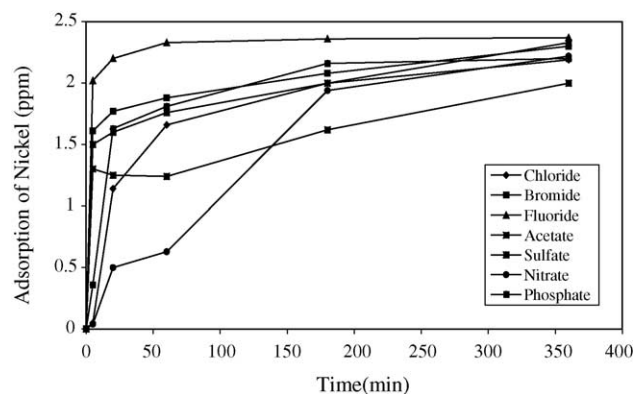


Fig. 2. Effect of crab shell loading (10 g/L) on sorption of Ni (2.5 mg/L) and anion solution (1000 ppm).

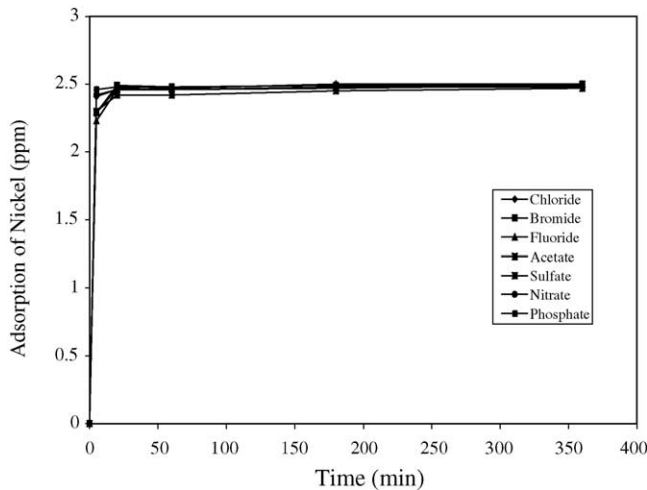


Fig. 3. Effect of crab shell loading (25 g/L) on sorption of Ni (2.5 mg/L) and anion solution (1000 ppm).

decreases somewhat. However, after a few hours the metal concentration returns to its original value. The results for phosphate at 360 min seem to be an outlier. The results indicate that crab shell binds nickel more strongly than the ions whose effect was studied. The experiments were carried out in pH range of 7–8. The pH of the solutions was adjusted by addition of  $\text{HNO}_3$  and  $\text{NaOH}$ . The pH of the solution rose during the experiment on adding crab shells. Since the demineralization as a pretreatment only took place at the outside of the crab shell particles, the proton in the acidic solution would react with calcium salts on the inside of crab shell during the sorption process, so the pH was readjusted at regular intervals.

### 3.3. The effect of pH

As can be seen from Fig. 5, the sorption of nickel did not change significantly with an increase in pH which may be due to opposing forces. When pH was approaching a neutral region and above the concentration of hydrogen ion in solution decreased and the extent of protonation of amino groups became smaller, but at the same time, metal ions may be hydrated with multiple hydroxyl groups and the solubility may be lower.

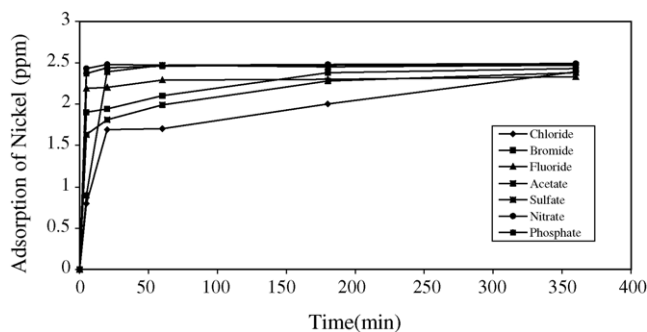


Fig. 4. Effect of crab shell loading (50 g/L) on sorption of Ni (2.5 mg/L) and anion solution (1000 ppm).

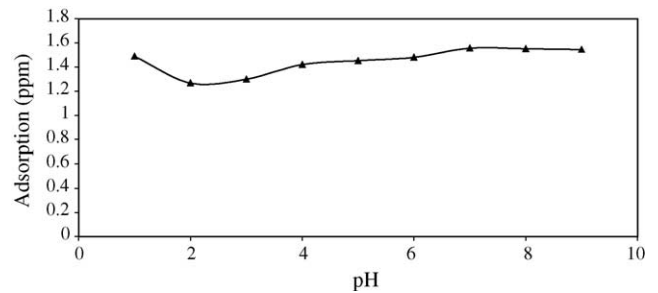


Fig. 5. Effect of pH on nickel removal.

### 3.4. Adsorption isotherms

The simplest isotherm is based on the assumptions that every adsorption site is equivalent and that ability of a particle to bind there is independent of whether or not adjacent sites are occupied. The Langmuir isotherm can be represented by the equation

$$\frac{C_{\text{eq}}}{x/m} = \frac{1}{K_1 K_2} + \frac{C_{\text{eq}}}{K_2} \quad (1)$$

where  $x$  is the amount of metal ion adsorbed by a mass of adsorbent,  $m$ ,  $C_{\text{eq}}$  the equilibrium concentration of metal ion in solution,  $K_1$  the adsorption coefficient,  $K_2$  the limiting adsorptive capacity, and  $K_1 K_2$  is used as a measure of the relative affinity of metal ion to the adsorbed. The limitation of Langmuir's theory is an assumption of unimolecular adsorption, and equivalence and independence sites. The experiments indicate the Langmuir's isotherm was not able to describe adequately the adsorption behavior of uptake of nickel ions, by chitosan in crab shell. The linear least squares analysis of the data using Eq. (1) produces a poor fit as measured by the correlation coefficient ( $R^2 = 0.3937$ ).

The Freundlich isotherm equation is also used to describe adsorption from a solution and is given by

$$\frac{x}{m} = K_c C_{\text{eq}}^{1/N} \quad (2)$$

where  $x$ ,  $m$ , and  $C_{\text{eq}}$  are the same as in the Langmuir isotherm and  $K_c$  is a constant for relative adsorptive capacity, and  $N$  is an affinity constant. The equation can be written as

$$\log \frac{x}{m} = \log K_c + \frac{1}{N} \log C_{\text{eq}} \quad (3)$$

Based on the least squares fit of the points, the correlation coefficient was found to be  $R^2 = 0.7418$ . The judgment as to which mechanism is operative is normally based upon the correlation coefficient, which sometimes is better for Langmuir and other times for Freundlich. Based on the correlation coefficients, the adsorption mechanism appears to be more complicated than either of these adsorption isotherms predict. The interactions of metals with chitosan are complex, probably simultaneously dominated by adsorption, ion exchange and chelation. It can be reasonably concluded that an  $n$ -valent metal ion is adsorbed according to the cation-exchange

mechanism, releasing a total of  $n$  hydrogen ions. Here, the adsorption reaction consists of two consecutive reactions:

1. Protonation of the primary amino groups.
2. Adsorption of the metal ions to form stable five-membered chelate rings coordinated by free nitrogen atoms of primary amino groups and oxygen atoms of alcoholic hydroxyl groups of chitosan.

When pH value approaches 7, hydroxylated metal ion may appear. Under basic conditions, all the metals combine with multiple hydroxyl groups. The dominant complex of nickel is proposed to have two OH groups and one NH<sub>2</sub> group as ligands and the fourth site either occupied by a water molecule or by the OH group on the C3 carbon atom of chitosan ring. If a neighboring amino group is close enough, Ni(OH)<sub>2</sub> may cross link two amino groups.

The above-mentioned adsorption behavior of chitosan for metal ions with high adsorption capacity can be attributable to the following factors:

1. the high hydrophilicity of chitosan with a large number of hydroxyl groups;
2. the large number of primary amino groups with high activity;
3. the flexible structure of the polymer chains of chitosan, which enables a suitable configuration for complexation with metal ions.

#### 4. Conclusions

The present work shows that partially converted crab shell waste can be used to achieve nickel ion adsorption successfully. Chitosan in the crab shell not only has a rather high adsorption capacity, but also it is capable of lowering transition metal ion concentration to sub-part per billion levels. The metal ion concentration gradient is a fundamental force that transfers metal ion from solution to adsorbent surface and diffuses metal ion into the inside of adsorbent. When the crab shell concentration is changed, the adsorbent surface or adsorbent sites will be changed sequentially, which determines the uptake rate, and the equilibrium metal ion concentration. Normally the pH greatly influences adsorption, but we observed that pH effect was not prominent. The adsorption isotherms do not match Langmuir isotherms very well, and can be better described by Freundlich isotherms, but not substantially better. Other simple isotherm models such as the Redlich–Peterson or Combined Langmuir and Freundlich could be used however; non-linear methods would probably produce better results. The crab shell surface is not homogeneous, and the adsorption process should be complicated. The sorption of nickel by chitosan in crab shell waste is accomplished by ion exchange and chelating mechanisms. The excellent adsorption behavior of chitosan in the crab shells may be attributed to stable five-membered chelate rings

coordinated by amino groups. Results indicate that there is little or no effect of anions on crab shells, which suggest that binding of metal ion, dominates the binding of anions. Hence the metals bind to the crab shells and can be easily removed from the wastewater. Chitosan produced by deacetylation of chitin is responsible for the sorption. The extent of deacetylation is also a very important factor for the sorption.

#### Acknowledgement

Funding for this study came from the Robert A. Welch Foundation Departmental Grant V-0004.

#### References

- [1] T. Smith-Sivertsen, E. Lund, Y. Thomassen, T. Norseth, Human nickel exposure in an area polluted by nickel refining. The Sør-Varanger study, *Arch. Environ. Health* 52 (1997) 464–471.
- [2] A. Wood, Trace metal removal from effluents, *Water Waste Treat.* 35 (May) (1992) 32–36.
- [3] C. Raji, T.S. Anirudhan, Removal of Hg (II) from aqueous solution by sorption on polymerised sawdust, *Indian J. Chem. Technol.* 3 (1996) 49–54.
- [4] Y. Bin Yu, A. Zhang, S.S. Shukla, K. Shukla, L. Dorris, Use of maple sawdust for removal of copper from wastewater, *J. Hazard. Mater. B* 80 (2000) 33–42.
- [5] Y. Bin Yu, A. Zhang, S.S. Shukla, K. Shukla, L. Dorris, The removal of lead from aqueous solutions by sawdust adsorption, *J. Hazard. Mater. B* 84 (2001) 83–94.
- [6] J.L. Yu, Y. Zhang, A. Shukla, S.S. Shukla, K.L. Dorris, J.L. Margave, Adsorption of chromium from aqueous solutions by maple sawdust, *J. Hazard. Mater. B* 100 (2003) 53–63.
- [7] E. Onsoy, O. Skaugrud, Metal recovery using chitosan, *J. Chem. Technol. Biotechnol.* 90 (1990) 395–405.
- [8] R. Coughlin, M. Deshaies, Chitosan in crab shell wastes purifies electroplating wastewater, *Environ. Prog.* 9 (1990) 35–39.
- [9] P. Tong, Y. Baba, Adsorption of metal ions on a new chelating ion-exchange resin chemically derived from chitosan, *Chem. Lett.* (1991) 1529–1532.
- [10] Q. Li, T. Dunn, Applications and properties of chitosan, *J. Bioact. Compat. Polym.* 7 (1992) 370–397.
- [11] J. Deans, B. Dixon, Uptake of Pb<sup>2+</sup> and Cu<sup>2+</sup> by novel biopolymers, *Water Res.* 26 (1992) 469–472.
- [12] A. Muzzarelli, *Natural Chelating Polymers*, Pergamon Press, New York, 1973, pp. 188–195.
- [13] R. Coughlin, M. Deshaies, Chitosan in crab shell wastes purifies electroplating wastewater, *Environ. Prog.* 9 (1990) 35–39.
- [14] K. Draget, M. Varum, Chitosan cross-linked with Mo(VI)polyoxyanions. A new gelling system, *Biomaterials* 13 (1992) 635–638.
- [15] D. Rout, K. Pulapura, Liquid crystalline characteristics of site-selectively-modified chitosan, *Macromolecules* 26 (1993) 5999–6006.
- [16] M.S. Masri, F.W. Reuter, M. Friedman, Binding of metal cations by natural substances, *J. Appl. Polym. Sci.* 18 (1974) 675–681.
- [17] E. Guibal, S. Roussy, Uranium sorption by glutamate glucan: a modified chitosan Part II. Kinetic studies, *Environ. Ind. Lab.* 19 (1993) 119–126.
- [18] P. Carlos, A. Waldo, Kinetic study of the thermal degradation of chitosan and a mercaptan derivative of chitosan, *Polym. Degrad. Stab.* 39 (1993) 21–28.