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Research Article

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The adsorption of nickel ions in aqueous solution by chitosan gel beads

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ABSTRACT

In this study, chitosan beads were produced from chitosan flakes. The researches on adsorptive properties of chitosan beads were carried out. The effect of pH, contact time, temperature and initial concentration were investigated. The results obtained on the adsorption of nickel were analyzed by the well known models given by Langmuir and Freundlich. The maximum adsorption capacity for chitosan gel beads at a temperature of 293K, initial concentration of 40mg/L, contact time of 30min and pH 5.0 in solution was found to be 30.5mg/g. Thermodynamic parameters of the adsorption process such as the standard Gibb's free energy change, free energy change (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0) were calculated. The result showed that adsorption of nickel ions in aqueous solution by chitosan beads was spontaneous and endodermic in nature.

Key words: Adsorption; Nickel ions; Chitosan beads

INTRODUCTION

The ground and surface waters pollution by chemical contaminants is a worldwide problem. Heavy metal contamination of water sources is hazardous to plants, animals and microorganism and can be carcinogenic to mankind. On the other hand, metals are playing important roles in most industries [1]. Nickel is used to make metal alloys such as stainless steel. It can be used as compound fro coloring ceramics, nickel-plating, manufacturing batteries and as a catalyst [2]. Nickel ions can be removed from water or wastewater physically or chemically due to the fact that they are unbiodegradable. Several techniques have been proposed for the removal of nickel ions from water and wastewater including chemical precipitation, membrane filtration, ion exchange, electrolysis and adsorption. Most of these methods are inefficient when it comes to treating water with low metal concentration [3-5].

The use of chitosan as an adsorptive polymer in removing a wide range of contaminant has been a major development in the past years [6]. Chitosan is found abundantly on earth and is obtained by industrial alkaline deacetylation of chitin. It is worth noting that among many biopolymers, chitosan has the highest adsorption capacity for metals because the amino and hydroxyl groups on chitosan chains serve as coordination sites. Nitrogen and oxygen atoms have free electron doublets that can react with metal cations. Stronger attraction of the lone pair of electrons to the nucleus in an oxygen atom comparing to nitrogen atom causes the more tendency of nitrogen atoms to donate the lone pair of electrons for sharing with a metal ion to form a metal complex. So, amino groups are responsible for the uptake metal ion. Also, the high concentration of metal salt anions causes adsorption of these anions by polymer. Consequently, chitosan possesses a negatively charged characteristic and shows additional ability for metal cations by electrostatic mechanism [7-9].

In this study, chitosan gel beads were produced from chitosan flakes. The research on adsorptive properties of chitosan beads was carried out. The effect of pH, contact time, temperature and initial concentration was investigated.

EXPERIMENTAL SECTION

2.1 Preparation of the adsorbents

The 70% (w/w) chitosan solution was made by dissolving 75.3g of chitosan flakes in 1L of 3.0% (v/v) acetic acid solution. The dissolved chitosan solution was filtered through a polystyrene sieve with mush 100um to remove impurities, formation of chitosan gel beads is said to take place when the filtrate comes in contact with 1M of sodium hydroxide solution. The product of chitosan gel beads was thus obtained and then stored for later adsorption experiments.

2.2 Adsorption experiments

Adsorption experiments were conducted in a set of 250 mL Erlenmeyer flasks containing 0.50g of chitosan gel beads and 100 mL of nickel ion solutions with various initial concentrations (40mg/L, 60mg/L, 80mg/L, 100 mg/L and 120mg/L). The initial pH was adjusted to 5.0 with 1 mol/L HCl. The flasks were placed in a shaker at a constant temperature (293, 303 and 313K) and 200 rpm. The samples were filtered and the residual concentration of nickel ion was analyzed by atomic absorption spectrophotometry (AAS).

2.3 Analytical methods

The amount of adsorbed nickel ion q_t (mg/g) at different time, was calculated as follows:

$$q_t = \frac{(C_0 - C_t) \times V}{m} \qquad (1)$$

where C_0 and C_t (mg/L) are the initial and equilibrium liquid-phase concentrations of nickel ion respectively. V (L) is the solution volume and m (g) is the mass of adsorbent used.

2.4 Statistical analyses of data

All experiments were repeated in duplicate and the data of results were the mean and the standard deviation (SD). The value of the SD was calculated by Excel Software. All error estimates given in the text and error bars in figures are standard deviation of means (mean±SD). All statistical significance was noted at α=0.05 unless otherwise noted.

RESULTS AND DISCUSSION

3.1 Effect of pH in solution

The pH in solution is an important regulating factor in adsorption process. The adsorption of metal ions by surface functional group is highly dependent on pH in solution. To determine the optimum pH for the adsorption of Nickel(Ⅱ) ions onto chitosan gel beads, the percentage removal of Nickel(Ⅱ) ions as a function of hydrogen ion concentration was examined at an initial concentration of 40mg/L. Effect of pH was showed in Fig.1. As shown in Fig.1, it showed a decrease in the removal rate of Nickel(Ⅱ) ions at lower pH conditions. At lower pH, hydrogen ions occupy most of the adsorption sites on the surface of the adsorbent and the results to a very low adsorption of nickel ions due to electrostatic repulsion. However, increasing the pH of the solutions results to a decrease in the competition of hydrogen ions with nickel ions for adsorption sites and thus facilitating higher rate of removal of nickel ions. Moreover, increasing the pH above 6.0 resulted to the precipitation of insoluble nickel hydroxide, causing a decrease in the removal of nickel ions.

3.2 Effect of contact time

The effect of contact time is importance in adsorption experiment. Adsorption of nickel ions onto chitosan gel beads was investigated at various contact time from 30min to 210min. The results were shown as Fig.2. During the first 30min, the removal of nickel ions proceeds faster with time and then increases slightly. Finally, it reaches equilibrium.

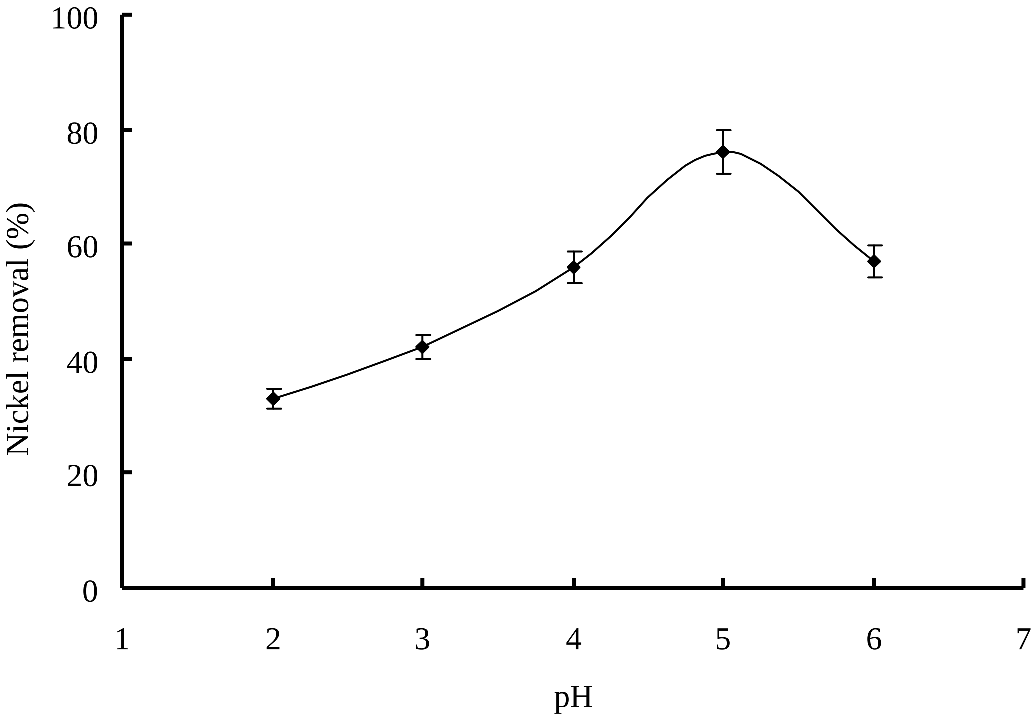

Fig.1 Effect of pH in solution on removal of nickel ions by chitosan gel beads at initial concentration of 40 mg/L, contact time of 30min, 293K and 200 rpm

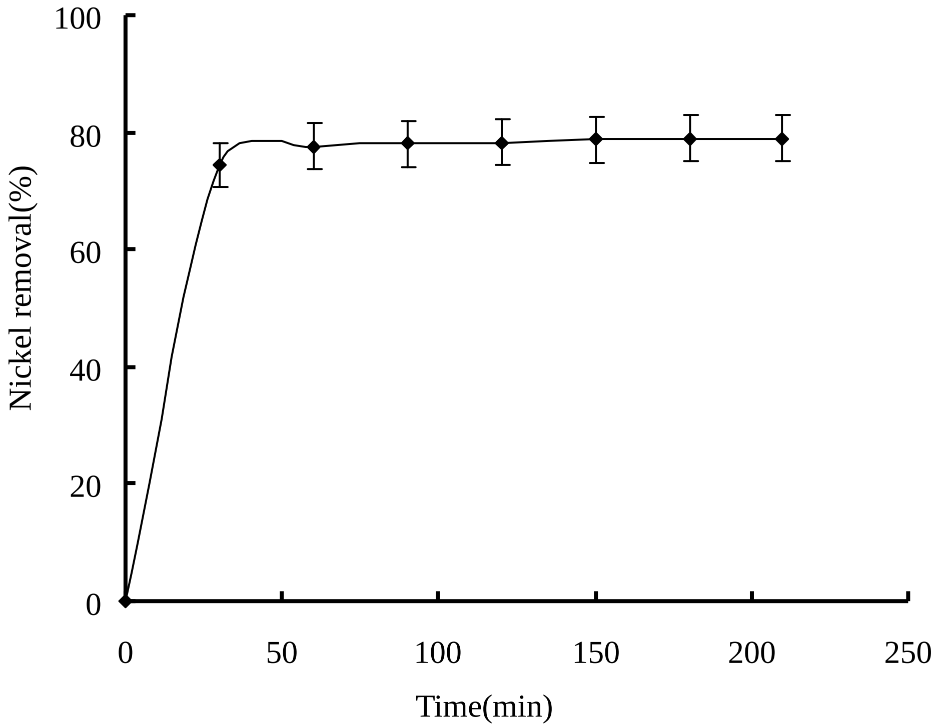

Fig.2 Effect of contact time on removal of nickel ions by chitosan gel beads at initial concentration of 40 mg/L, pH5.0, 293K and 200 rpm

3.3 Effect of initial concentration

The effect of initial concentration was carried out at various initial concentrations of 40-120mg/L. The adsorption results were shown as Fig.3. The equilibrium occurred faster with initial concentration. This observation is due to the fact that at lower initial nickel ions concentration, sufficient sites responsible for adsorption of nickel ions are available. As the concentration of nickel ions increases, the numbers of nickel ions become relatively higher compared to the availability of adsorption sites. Hence, the rate of removal of nickel ions is dependent on the initial concentration of nickel ions and also decreases with increase in concentration of nickel ions.

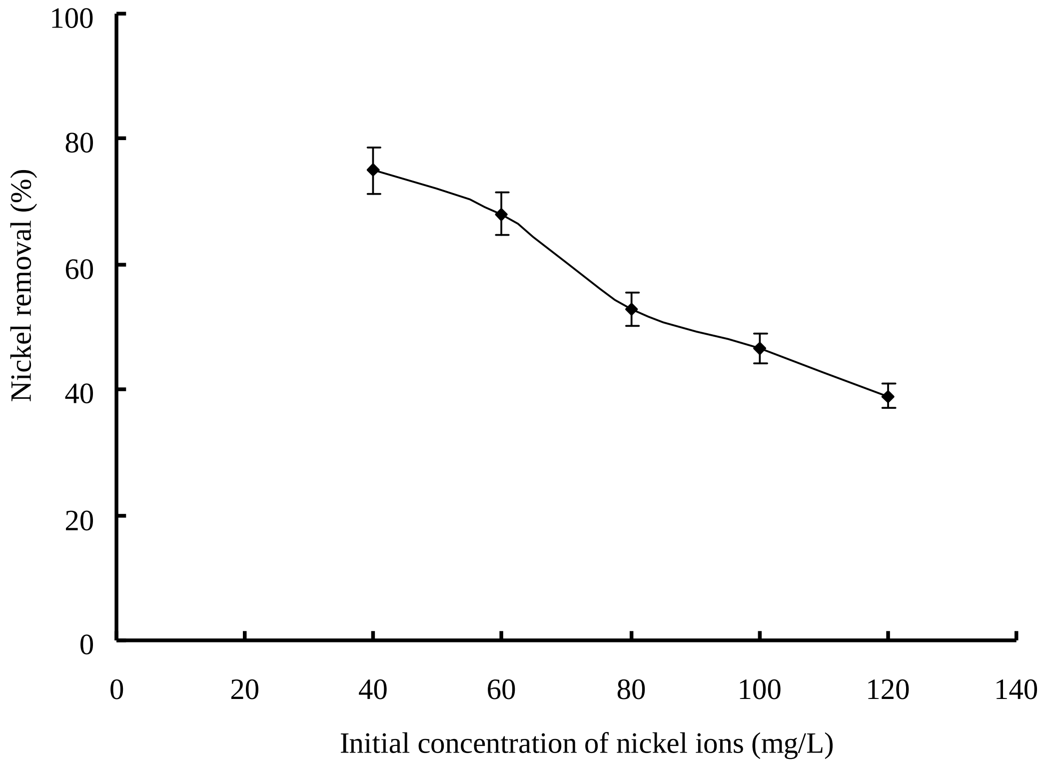

Fig.3 Effect of initial concentration of nickel ions on removal of nickel ions by chitosan gel beads at contact time of 30min, pH5.0, 293K and 200 rpm

3.4 Adsorption isotherm

The capacity of an adsorbent can be described by its equilibrium sorption isotherm. The Langmuir and Freundlich adsorption models are commonly adopted to investigate the adsorption behavior of materials and the correlation among adsorption parameters. Accordingly, equilibrium data were simulated by the Langmuir [10] and Freundlich models [11].

The Langmuir isotherm equation is represented by the following Eq. (2):

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \qquad (2)$$

Where C_e is the equilibrium concentration of nickel ions (mg/L), q_e is the amount of nickel ions adsorbed (mg/g), q_m is the maximum adsorption capacity of nickel ions (mg/g), and K_L is the Langmuir adsorption equilibrium constant (L/mg) related to the affinity of the binding sites.

The Freundlich isotherm equation is described by the following Eq. (3):

$$q_e = K_F C_e^{\frac{1}{n}} \qquad (3)$$

Where K_F and n are the Freundlich adsorption isotherm constants, which are indicators of adsorption capacity and adsorption intensity respectively.

The corresponding values of Langmuir and Freundlich isotherms for nickel ions adsorption on chitosan gel beads were listed in Table 1. The results indicate that the Langmuir isotherm fits better than the Freundlich isotherm, which may be due to homogeneous distribution of active sites onto chitosan gel beads. The value of K_L or K_f is between 0 and 1, which indicate heterogeneity of the adsorbents and favorable adsorption [12]. The maximum adsorption capacity obtained from the Langmuir isotherm is 30.5 mg/g.

Table 1 Equilibrium model parameters for the adsorption of nickel ions onto chitosan gel beads. Experimental conditions: 0.50g of chitosan gel beads, contact time of 30 min, 293 K, 200 rpm and pH 5.0 in solution

Langmuir model			Freundlich model		
q_m (mg/g)	K_L (L/mg)	R^2	K_f (mg/g)	n	R^2
30.5	0.024	0.9713	0.431	0.4892	0.945

3.5 Thermodynamic studies

The thermodynamic parameters of free energy change (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0) were used to describe thermodynamic behavior of the adsorption of nickel ions onto the chitosan gel beads. These parameters were calculated from the following equations [13].

$$\Delta G^0 = -RT \ln K_a \qquad (4)$$

$$\ln K_a = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \qquad (5)$$

$$K_a = \frac{q_e}{C_e} \qquad (6)$$

where T is the solution temperature (K), K_a is the adsorption equilibrium constant, R is the gas constant (8.314 $J \cdot mol^{-1} \cdot K^{-1}$), q_e is the amount of adsorbate adsorbed per unit mass of adsorbate at equilibrium (mg/g) and C_e is the equilibrium concentration of the adsorbate (mg/L).

Thermodynamic parameters ($\Delta H^0, \Delta S^0$ and ΔG^0) for nickel ions adsorption were evaluated using Eqs. (4)-(6). The values of ΔH^0 and ΔS^0 were determined from the slope and intercept of the plot of $\ln K_a$ versus 1/T. The values of $\Delta H^0, \Delta S^0$ and ΔG^0 are listed in Table 2.

Table 2 Thermodynamic parameters for the adsorption of nickel ion onto chitosan gel beads

Temperature (K)	ΔG^0 (KJ/mol)	ΔH^0 (KJ/mol)	ΔS^0 (KJ/mol)
293	-1.46	34.29	0.21
303	-4.32	34.29	0.21
313	-5.26	34.29	0.21

As the temperature increases, and the value of ΔG^0 decreases. It indicated that less driving force and hence resulting in lesser adsorption capacity at higher temperatures. The negative values of ΔG^0 indicates the adsorption of nickel ion onto chitosan gel beads is spontaneous and thermodynamically favorable. The positive value of ΔH^0 indicated that the sorption process was endothermic in nature. The positive value of ΔS^0 showed the increasing randomness at solid/solution interfaced with some structural changes in the adsorbate and the adsorbent and an affinity of the adsorbent.

CONCLUSION

In this experiment, chitosan beads were produced from chitosan flakes. The chitosan gel beads were used in the removal of nickel ions in solution. The results indicate that the Langmuir isotherm fits better than the Freundlich isotherm. The values of the thermodynamic parameters revealed that the adsorption of nickel ion onto chitosan gel beads is spontaneous and thermodynamically favorable. The increasing randomness at solid/solution interfaced with some structural changes in the adsorbate and the adsorbent and an affinity of the adsorbent.

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REFERENCES

[1] S Hasan; TK Ghosha; DS Viswanath; VM Boddub, *J. Hazard. Mater.*, **2008**, 152, 826-837.
[2] AE Ofomaja; EB Naidoo; SJ Modise, *J. Ind. Eng. Water. Res.*, **2010**, 49, 2562-2572.
[3] WSW Ngah; S Fatinathan, *Chem. Eng. J.*, **2008**, 143, 62-72.
[4] S Eleonora; K Jan, *J. Environ. Chem. Eng.*, **2013**, 1, 581-588.
[5] RK Zanaty; MS Ali; EMH Said; EAE Mohamed, *Chemosphere*, **2014**, 99, 117-124.
[6] Y Kun; H Jackie; M Elizabeth; B Brian; P Rajesh; ZB Li, NC Shapley, *Colloid. Surf. A: Physico. Eng. Aspects*, **2013**, 425, 31-41.
[7] A Ghaee; MS Niassar, J Barzin; A Zarghan, *Appl. Surf. Sci.*, **2012**, 258, 7732-7743.
[8] N Li; R Bai, *J. Appl. Polym. Sci.*, **2005**, 237-245.
[9] WSW Ngah; S Fatinathan, *J. Environ. Manage*, **2010**, 91, 958-969.
[10] I Langmuir, *J. Am. Chem. Soc.*, **1916**, 38, 2221-2295.
[11] HMF Freundlich, *Z. Phys. Chem.*, **1906**, 57, 384-470.
[12] FS Zhang; JO Nriagu; H. Itoh, *Water Res.*, **2005**, 39, 389-395.
[13] F Bouhamed; Z Elouear; J Bouzid, *J. Taiwan Inst. Chem. Eng.*, **2012**, 43, 741-749.