



# The removal of nitrate from aqueous solutions by chitosan hydrogel beads

Sudipta Chatterjee, Seung Han Woo\*

Department of Chemical Engineering, Hanbat National University, San 16-1, Deokmyeong-Dong, Yuseong-Gu, Daejeon 305-719, Republic of Korea

## ARTICLE INFO

### Article history:

Received 8 April 2008

Received in revised form 30 August 2008

Accepted 1 September 2008

Available online 5 September 2008

### Keywords:

Adsorption

Chitosan

Hydrogel beads

Nitrate

## ABSTRACT

A physico-chemical investigation of the adsorption of nitrate by chitosan hydrobeads was conducted. The adsorption of nitrate by chitosan hydrobeads was increased with a decrease in the pH of the solution. The adsorption process was found to be temperature dependant with an optimum activity at 30 °C. Adsorption capacity was found to decrease with increases in temperature after 30 °C, indicating the exothermic nature of this process. Theoretical correlation of the experimental equilibrium adsorption data for the nitrate–chitosan hydrobeads system was properly explained by the Langmuir isotherm model. This was supported by the fact that homogeneity index was close to unity (0.98–1.08) from Langmuir–Freundlich isotherm model. The maximum adsorption capacity was 92.1 mg/g at 30 °C. The kinetic results corresponded well with the pseudo-second-order rate equation. Intra-particle diffusion also played a significant role at the initial stage of the adsorption process. Thermodynamic parameters such as the Gibbs free energy ( $\Delta G^0$ ), enthalpy ( $\Delta H^0$ ), and entropy ( $\Delta S^0$ ) for the nitrate adsorption were estimated. Results suggest that the adsorption process is a spontaneous, exothermic process that has positive entropy. Desorption of nitrate from the loaded beads was accomplished by increasing the pH of the solution to the alkaline range, and a desorption ratio of 87% was achieved around pH 12.0.

© 2008 Published by Elsevier B.V.

## 1. Introduction

Water resources are heavily polluted by several nitrogen containing compounds, such as nitrate, nitrite, and ammonium, which may cause severe environmental problems including eutrophication [1]. Nitrate, in particular, causes outbreaks of infectious diseases such as cancer of the alimentary canal and cyanosis among children [2]. Excess nitrate in drinking water may cause blue-baby syndrome, which results from the conversion of haemoglobin into methaemoglobin, which cannot carry oxygen [3].

Therefore, numerous techniques for the removal of nitrate from water samples have been reported. These include biological de-nitrification [4], chemical reduction [5], reverse osmosis, electrodialysis [6], and ion exchange [7]. Biological de-nitrification is not effective at temperatures below 7 °C, and therefore, it may not be useful for treating groundwater. A chemical reduction process requires the addition of chemicals and may release toxic compounds into the environment, especially when H<sub>2</sub> is used as a reductant. Reverse osmosis is too expensive to treat a large amount of wastewater. Compared with these methods, ion exchange is a

simple and effective method. But the main problem is that the ion exchange resin is still quite expensive and retains some sulphate and hydrogen carbonate, which induce significant changes in the water composition. It also causes an increase in the chloride concentration of water because the ion exchange resin replaces nitrate with chloride [8].

Adsorption is the process that is used to collect soluble substances in solution on a suitable interface. Adsorption onto activated carbon is a very traditional way to treat wastewater. However, activated carbon is quite expensive and also can be used for nonionic pollutants in most cases. Recently, different low cost adsorbents including some industrial and agricultural wastes such as activated waste sepiolite [1] and modified wheat residue [9] have been used to remove nitrate from water. The biopolymer chitosan has gained importance in environmental biotechnology due to its very high adsorption capacity of dyes and metal ions [10,11]. Moreover, chitosan can be obtained on an industrial scale by chemical deacetylation of crustacean chitin. Chitosan hydrobeads have become a very effective biosorbent for the removal of heavy metals in the field of industrial wastewater treatment [12–14].

The aim of this study is to determine the efficacy of chitosan in the form of hydrobeads to remove nitrate from its aqueous solution and to investigate the interaction between nitrate and chitosan during adsorption.

\* Corresponding author. Tel.: +82 42 821 1537; fax: +82 42 821 1593.  
E-mail addresses: [shwoo@hanbat.ac.kr](mailto:shwoo@hanbat.ac.kr), [shwoo@postech.ac.kr](mailto:shwoo@postech.ac.kr) (S.H. Woo).

## 2. Materials and methods

### 2.1. Preparation of chitosan beads

Chitosan and all other chemicals used in this study were purchased from Sigma Chemical Co., USA. Ten grams of chitosan was dissolved in 300 ml of 5% acetic acid (v/v) solution and it was diluted to 1 l by stirring overnight. Then it was allowed to stand for another 6 h. Chitosan hydrobeads were prepared by drop-wise addition of this chitosan solution to an alkaline coagulating mixture (H<sub>2</sub>O:MeOH:NaOH: 4:5:1, w/w) as described by Mitani et al. [15]. The beads were spherical in shape with an average diameter of 2.5 mm. Prior to use, chitosan beads were kept in water for 30 min with the pH adjusted to that required for different experimental conditions.

### 2.2. Analysis and data calculation

A stock solution (1.000 g/l) of nitrate was prepared in deionized water and diluted to obtain the desired concentrations of nitrate. The concentration of the nitrate ion in the experimental solution was determined from the calibration curve prepared by measuring the area ( $\mu\text{S}/\text{cm}/\text{sec}$ ) of the nitrate ion by 790 Personal Ion Chromatography (Metrohm Ion Analysis, Switzerland) using Suppressed CD detector. The analytical column was METROSEP A Supp 5 column (100 mm l  $\times$  4.0 mm ID). The sample was eluted (eluent: 3.2 mM Na<sub>2</sub>CO<sub>3</sub> + 1.0 mM NaHCO<sub>3</sub>) at a flow rate of 0.7 ml/min with a retention time of 7.0 min for nitrate detection. The adsorption capacity of chitosan in the form of hydrobeads is calculated using equilibrium studies. The mass balance equation for this process at equilibrium condition is given by

$$q = \frac{(C_0 - C_{\text{eq}}) \times V}{W} \quad (1)$$

where  $q$  (mg/g) is the adsorbent capacity,  $C_0$  (mg/l) is the initial concentration of nitrate,  $C_{\text{eq}}$  (mg/l) is the final or equilibrium concentration of nitrate,  $V$  is the experimental solution volume (l), and  $W$  is the weight of chitosan in the form of hydrobeads (g).

### 2.3. Effect of pH

The effect of pH on nitrate adsorption process was studied over the pH range 3.0–8.0; and the initial nitrate concentration was fixed at 50, 100, 250, 500, and 1000 mg/l. Then 50 ml of a pH-adjusted nitrate solution with a predetermined initial concentration and 1 g of chitosan hydrobeads with a water content of 96.4% were placed in separate 125 ml Erlenmeyer flasks. The flasks were agitated (120 rpm) at 30 °C for 24 h. At the end of incubation, beads were separated from the solution by filtration and the concentration of the nitrate in the solution was determined.

### 2.4. Equilibrium adsorption isotherm

The equilibrium adsorption isotherm was used to describe the effect of pH when the initial nitrate concentration was varied from 1 to 1000 mg/l. The pH and temperature of incubation were 5.0 and 30 °C, respectively. The same experiment was also repeated at three different temperatures (viz., 20, 40, and 50 °C).

### 2.5. Kinetic study

The rate of adsorption of nitrate was studied at different time intervals that were as long as 1440 min using different initial concentrations (100, 250, 500, and 1000 mg/l) at pH 5 and 30 °C. Other experimental conditions were the same as described earlier.

### 2.6. Desorption study

After performing the equilibrium study with an initial nitrate concentration of 500 mg/l, nitrate-adsorbed chitosan hydrobeads were collected by filtration by thoroughly washing with deionized water. Loaded beads were transferred to different 125 ml Erlenmeyer flasks; each flask contained 50 ml water and the pH was adjusted to 9.0, 10.0, 11.0, and 12.0. The flasks were agitated at 100 rpm for 24 h at 30 °C. The concentration of the eluted nitrate was measured. Desorption of the nitrate from the chitosan beads was evaluated by the following equation.

$$\text{Desorption ratio (\%)} = \frac{\text{Amount of desorbed nitrate}}{\text{Amount of adsorbed nitrate}} \times 100 \quad (2)$$

## 3. Results and discussion

### 3.1. Effect of pH

The effect of pH on the adsorption of nitrate by chitosan hydrobeads is shown in Fig. 1. Nitrate adsorption was found to increase with a decrease in the pH of the solution because a decrease in the pH of the solution resulted in more protons being available to protonate the chitosan amine group. This resulted in an enhancement of nitrate adsorption by chitosan beads due to increased electrostatic interactions between chitosan's negatively charged nitrate group and positively charged amine group.

The surface charge of chitosan is positive in acidic pH, gradually decreases with increasing in pH and has zero potential at pH 6.4. However, the adsorption at pH 6.4, where the surface charge of chitosan beads is neutral may be due to physical forces. At pH above 6.4, an appreciable amount of nitrate adsorption by chitosan beads indicates the involvement of physical forces.

### 3.2. Equilibrium adsorption isotherm

The adsorption of nitrate from its aqueous solution by chitosan hydrobeads at different temperatures is presented in Fig. 2. The adsorption of the nitrate was at its maximum at 30 °C. The equilibrium adsorption capacity decreased when the temperature was increased from 30 to 50 °C. This result indicates the exothermic nature of nitrate adsorption onto chitosan beads. A decrease in the nitrate uptake value with the rise in temperature may be due to

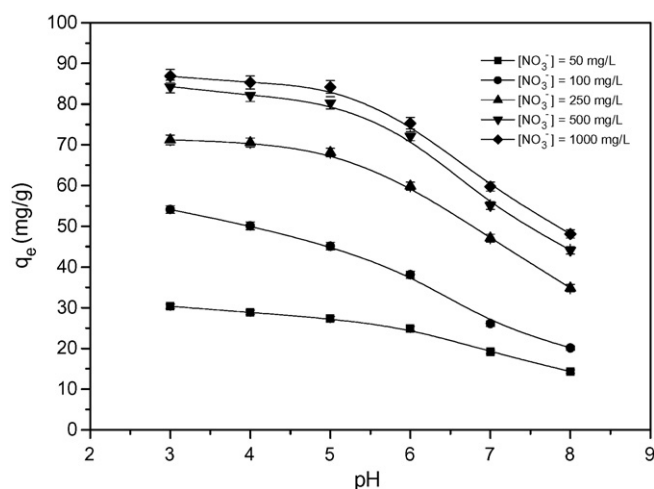


Fig. 1. Effect of pH on nitrate adsorption by chitosan hydrobeads at different initial nitrate concentrations.

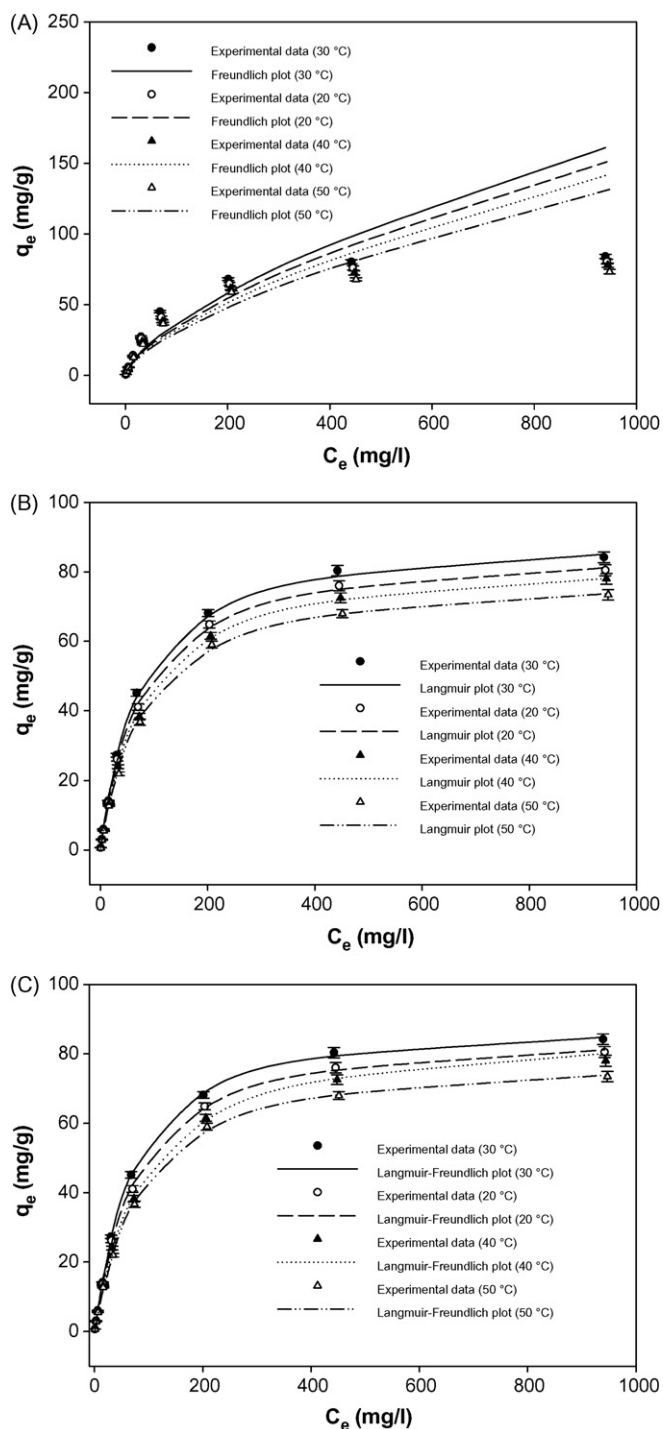


Fig. 2. Isotherm plots for the adsorption of nitrate onto chitosan beads at different temperatures (A) Freundlich isotherm; (B) Langmuir isotherm; and (C) Langmuir–Freundlich isotherm.

either the damage of active binding sites of the adsorbent [16] or increasing tendency to desorb nitrate ions from the interface to the solution [17]. However, increase in temperature from 20 to 30 °C reduced the nitrate adsorption, which might be due to an increase of the mobility of the nitrate ions and a swelling effect within the internal structure of chitosan beads [18,19]. At this temperature range, these effects might be more significant than the exothermic effect. The equilibrium adsorption data of nitrate by chitosan hydrobeads show that the adsorption capacity increases

with an increase in equilibrium concentration and finally achieves a saturated value.

The adsorption isotherm model helps the comprehensive understanding of the nature of interaction between adsorbate and adsorbent. In the present investigation, the equilibrium adsorption data are analyzed according to the linear form of the Freundlich (Eq. (3)) and Langmuir (Eq. (4)) isotherm models and non-linear form of the Langmuir–Freundlich (Eq. (5)) isotherm model.

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (3)$$

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} C_e \quad (4)$$

$$q_e = \frac{q_{\max} K_{\text{eq}} C_e^N}{1 + K_{\text{eq}} C_e^N} \quad (5)$$

where  $C_e$  (mg/l) is the equilibrium nitrate concentration in solution,  $q_e$  (mg/g) is the nitrate concentration in the adsorbent,  $K_F$  (l/g) is the Freundlich constant, and  $1/n$  is the heterogeneity factor.  $a_L$  (l/mg) and  $K_L$  (l/g) are the Langmuir constants, and  $a_L$  is related to the adsorption energy. The Langmuir–Freundlich isotherm model is also known as Sips isotherm model.  $N$  is the heterogeneity index, which varies from 0 to 1.  $K_{\text{eq}}$  (l/mg) represents the equilibrium constant of Langmuir–Freundlich isotherm equation and  $q_{\max}$  (mg/g) is the maximum adsorption capacity.

The Freundlich isotherm model describes adsorption on a heterogeneous surface and is not restricted to monolayer formation. Fig. 2A shows that predicted equilibrium adsorption values using Freundlich isotherm model do not show good fit to experimental equilibrium adsorption data. The values of  $K_F$  and  $1/n$  calculated from the intercept and slope of the plot of  $\log q_e$  vs.  $\log C_e$  at different temperatures are listed in Table 1. In general, as the  $K_F$  value increases, the adsorption capacity of the adsorbent increases. The maximum value of  $K_F$  at 30 °C indicates that the nitrate adsorption process is most effective at 30 °C. For these adsorption processes,  $n$  values have been found to vary between 1.52 and 1.54; and, therefore, nitrate adsorption onto chitosan beads at different temperature represents beneficial adsorption [20]. The relatively low values of the correlation coefficients ( $R^2$ ) obtained from the Freundlich isotherm equation (0.94–0.95) indicate that the adsorption process is not much heterogeneous. This indicates that the adsorption process occurs mainly by the ionic interactions between nitrate anions and amine cations even though the adsorbent surface contains some different groups such as hydroxyl and acetyl in the chitosan molecule [21].

In the Langmuir isotherm model, it is assumed that intermolecular forces decrease rapidly with distance, and this leads to monolayer coverage of the adsorbate at specific homogeneous sites on the outer surface of the adsorbent. Fig. 2B indicates that predicted equilibrium adsorption values using Langmuir isotherm fit well to experimental equilibrium adsorption data at all the temperatures tested in this study. The values of the correlation coefficients ( $R^2 = 0.970$ – $0.980$ ) indicate that the adsorption of nitrate on chitosan beads fit well to the Langmuir model. The general shape of the curve and the sharp curvature near saturation possess characteristics of the Langmuir equilibrium and show a high degree of irreversibility. Therefore, it is suggested that this sorption process takes place at the functional groups/binding sites on the surface of the chitosan beads, which is considered as monolayer adsorption. From the slope of the line, the theoretical monolayer saturation capacity  $Q_0 [=k_L/a_L]$  of the adsorbate has been calculated. The Langmuir monolayer saturation capacity  $Q_0$  and the Langmuir constants are listed in Table 1. The maximum value of  $a_L$  at 30 °C for this adsorption process indicates strong binding, and a decrease in the value of  $a_L$  with increasing temperature indicates that the binding

**Table 1**  
Constants for equilibrium isotherm models

Temperature (°C)	$K_F$ (l/g)	$1/n$	$R^2$		
Freundlich isotherm model					
20	1.679	0.657	0.943		
30	1.782	0.658	0.941		
40	1.605	0.654	0.949		
50	1.549	0.648	0.952		
Temperature (°C)	$a_L$ (l/mg)	$k_L$ (l/g)	$k_L/a_L [=Q_0]$ (mg/g)	$R^2$	$R_L^a$
Langmuir isotherm model					
20	0.0132	1.156	87.576	0.972	0.0704
30	0.0136	1.252	92.059	0.980	0.0685
40	0.0127	1.055	85.081	0.975	0.0730
50	0.0125	0.996	79.680	0.970	0.0741
Temperature (°C)	$q_{max}$ (mg/g)	$K_{eq}$ (l/mg)	$N$	$R^2$	
Langmuir–Freundlich isotherm (Sips isotherm) model					
20	86.926 ± 1.245	0.0115 ± 0.00125	1.038 ± 0.0320	0.999	
30	89.656 ± 0.897	0.0109 ± 0.00093	1.077 ± 0.0252	0.999	
40	88.156 ± 1.964	0.0120 ± 0.00101	0.981 ± 0.0289	0.999	
50	79.566 ± 1.588	0.0098 ± 0.00147	1.050 ± 0.0428	0.999	

<sup>a</sup>  $C_0$  is 1000 mg/l.

force is weaker at higher temperatures. The experimental findings also corroborated the saturation capacities predicted by the Langmuir equation at different temperatures.

The essential features of the Langmuir isotherm can be expressed in terms of the dimensionless equilibrium parameter,  $R_L$ , which is defined as

$$R_L = \frac{1}{1 + a_L C_0} \quad (6)$$

where  $a_L$  is the Langmuir constant as described above and  $C_0$  (mg/l) is the initial nitrate concentration.  $R_L$  values within the range  $0 < R_L < 1$  indicate favorable adsorption.  $R_L$  values calculated using  $C_0 = 1000$  mg/l are well within the defined range (Table 1) and indicate the acceptability of the process.

Langmuir isotherm model is one of the simplest adsorption models and therefore Langmuir–Freundlich isotherm (Sips isotherm) model was used to more accurately analyze the homogeneity of the adsorption process. Langmuir–Freundlich isotherm is found to provide an accurate prediction of experimental results (Fig. 2C) with the higher determination coefficients ( $R^2$ ) of 0.999. Table 1 represents the parameters of Langmuir–Freundlich isotherm model where heterogeneity index ( $N$ ) for adsorption of nitrate at each temperature is demonstrated to be quite close to unity. When  $N = 1$ , indicating the adsorption process is homogeneous, the Langmuir–Freundlich isotherm (Eq. (5)) reduces to the Langmuir isotherm. This implies monolayer coverage of nitrate ion on the surface of chitosan beads. This would be reasonable that the  $-NH_2$  groups are the major functional groups in the adsorption process and there is no interaction between sorbed nitrate ions due to small size of nitrate ions compared to the distance between the amine groups of chitosan. Therefore, in this adsorption process the use of Langmuir isotherm model could be regarded as appropriate.

### 3.3. Kinetic study

Adsorption kinetics is an important characteristic for evaluating the efficiency of adsorption. The kinetic behavior of this process was studied at pH 5 and 30 °C using four different initial nitrate concentrations (Fig. 3). It appears from Fig. 3 that the kinetics of nitrate adsorption consists of two phases, an initial rapid phase when the process is very fast and a second slower phase when it reaches equilibrium. The initial high rate of nitrate uptake is probably due to the

greater availability of binding sites near the surface of the chitosan hydrobeads [22]. Adsorption capacity increases with an increase in the initial nitrate concentration, but the time required to reach equilibrium is independent of the initial nitrate concentration [23].

In order to study the controlling mechanisms of the adsorption process, pseudo-first-order (Eq. (7)) [24] and pseudo-second-order kinetic (Eq. (8)) [25] rate models and an intra-particle diffusion model (Eq. (9)) are used to test the experimental kinetic data.

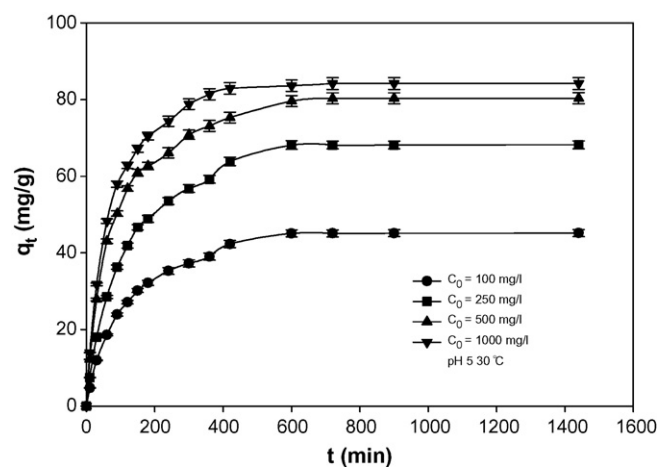
$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (7)$$

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \quad \text{where, } h = k_2 q_e^2 \quad (8)$$

$q_e$  (mg/g) and  $q_t$  (mg/g) are the amounts of nitrate adsorbed by chitosan beads at equilibrium and at different time intervals, respectively.  $k_1$  (1/min) and  $k_2$  (g/mg min) are the pseudo-first-order and pseudo-second-order rate constants, and 'h' represents the initial adsorption rate (mg/g min).

$$q_t = k_p t^{0.5} \quad (9)$$

$k_p$  is the intra-particle diffusion rate constant (mg/g min<sup>0.5</sup>).



**Fig. 3.** Effect of contact time on nitrate adsorption by chitosan hydrobeads at different initial nitrate concentrations.

**Table 2**  
Constants of different rate models

$C_0$ (mg/l)	$q_{e(\text{exp})}$ (mg/g)	Pseudo-first-order		Pseudo-second-order			Intra-particle diffusion
		$q_{e(\text{cal})}$ (mg/g)	$k_1$ (1/min)	$q_{e(\text{cal})}$ (mg/g)	$k_2$ (g/mg min)	$h$ (mg/g min)	$k_p$ (mg/g min <sup>0.5</sup> )
100	45.12	42.76	$7.370 \times 10^{-3}$	49.02	$2.300 \times 10^{-4}$	0.553	2.818
250	68.15	64.92	$7.600 \times 10^{-3}$	73.86	$1.582 \times 10^{-4}$	0.863	4.354
500	80.35	74.70	$1.010 \times 10^{-2}$	84.75	$2.051 \times 10^{-4}$	1.473	5.396
1000	84.20	77.80	$1.152 \times 10^{-2}$	87.87	$2.680 \times 10^{-4}$	2.070	5.916

Upon correlation of the kinetic data with the above two rate models, it was found that both linear-form plots using different initial nitrate concentrations give straight lines (Fig. 4). The lines for pseudo-second-order rate model have higher correlation coefficients ( $R^2 \approx 0.999$ ) compared to the correlation coefficient ( $R^2 \approx 0.988$ ) obtained from the linear plot of the pseudo-first-order rate model. In this study, all of the kinetic data up to 1440 min are used for modeling with pseudo-second-order rate model but for modeling with pseudo-first-order rate model, only initial kinetic data (up to 150 min) have been used because the calculated values of  $q_{e(\text{cal})}$  (mg/g) for all four initial concentrations of nitrate from pseudo-first-order rate model using whole range of contact time are physically unacceptable (e.g., lower  $q_{e(\text{cal})}$  (mg/g) values were obtained from higher initial concentration of nitrate ions). In many cases the pseudo-first-order rate model does not fit well to the whole range of contact time and is generally applicable over the initial stage of the adsorption processes [26]. Table 2 shows that the calculated and experimental equilibrium uptake value fit well to pseudo-second-order rate model which indicates that the pseudo-second-order reaction is better than pseudo-first-order reaction.

The plot of  $q_t$  vs.  $t^{0.5}$  (Fig. 4C) using initial kinetic data up to 150 min has straight lines with correlation coefficients ( $R^2$ ) ranging from 0.972 to 0.984. The linearity of the plots indicates that intra-particle diffusion might play a significant role in the initial stage of adsorption of nitrate on chitosan hydrobeads [27] because Eq. (9) is valid only for initial kinetic data. If the intra-particle diffusion is involved in the initial stage of adsorption process, then plot of  $q_t$  vs.  $t^{0.5}$  would result in a linear relationship and intra-particle diffusion would be the rate controlling step if these lines have zero intercept [28]. In the present study, plot of  $q_t$  vs.  $t^{0.5}$  (Fig. 4C) for the initial kinetic data do not pass through the origin. Based on present data at initial times of adsorption, intra-particle diffusion is not the only rate controlling step for this adsorption process and the mechanism is simultaneous adsorption and intra-particle diffusion.

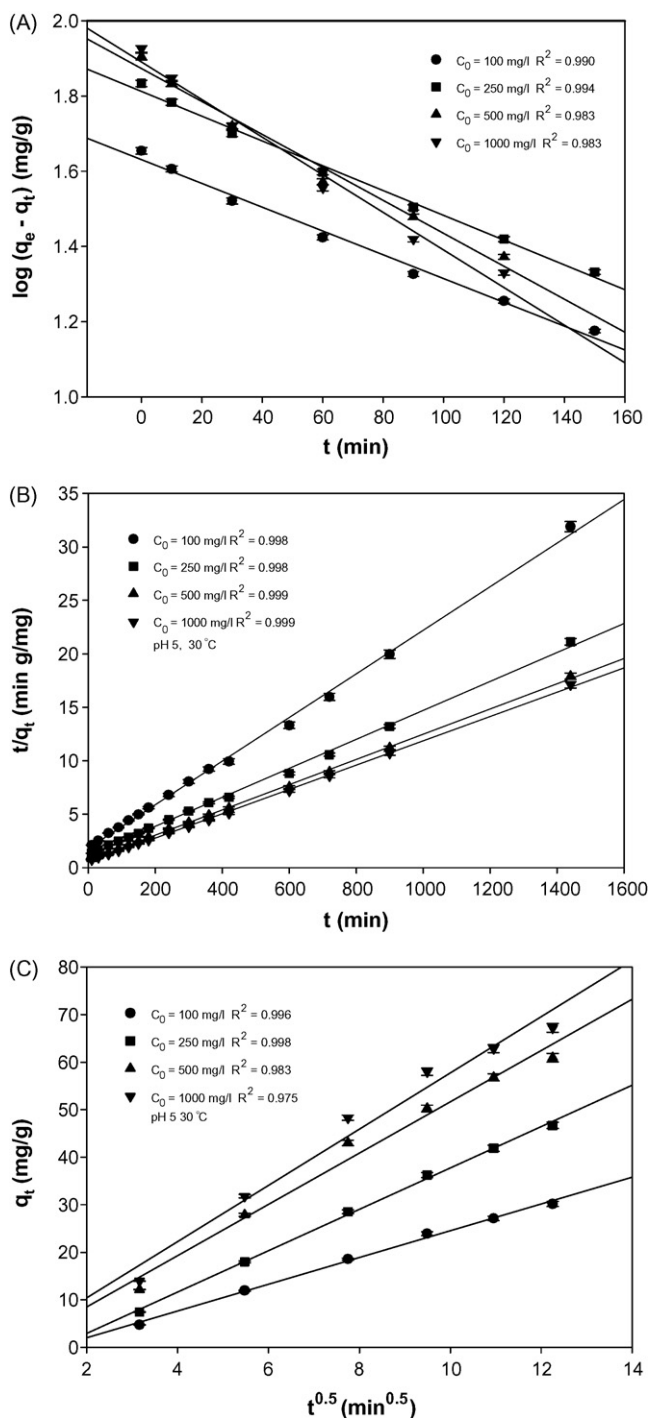
Table 2 shows that the intra-particle diffusion rate constant ( $k_p$ ) increases as the initial nitrate concentration increases because  $k_p$  is directly related to  $q_e$  and intra-particle diffusivity ( $D$ ).

### 3.4. Thermodynamic study

The Langmuir isotherm is used to predict the adsorption capacity of adsorbent, and the linearized form of the Langmuir isotherm can be given by the Eq. (10)

$$\frac{C_e}{q_e} = \frac{1}{Q_0 K} + \frac{C_e}{Q_0} \quad (10)$$

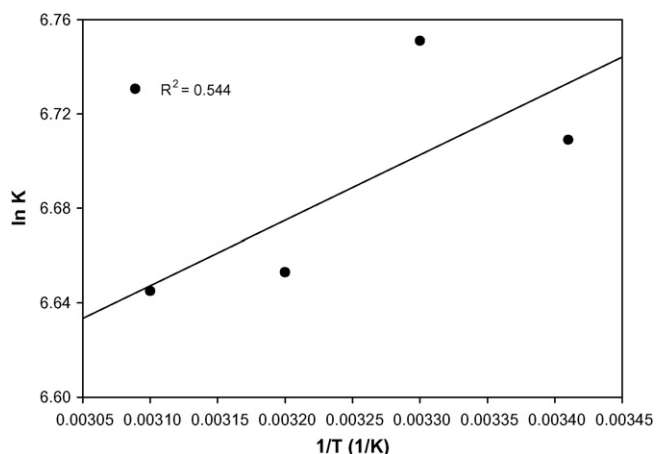
where  $Q_0$  (mg/g) is the maximum adsorption capacity of nitrate and  $K$  (l/mol) is the adsorption equilibrium constant. When the equilibrium concentration is referred to as the standard concentration,  $K$  is found to be nondimensional. It is clear from Table 3 that  $K$  decreases with increasing temperature above 30 °C. This suggests this adsorption process is exothermic. Adsorption equilibrium constants  $K$  for varying temperatures have been used to evaluate the thermodynamic parameters of this adsorption process, and all the thermodynamic parameters of the adsorption process are shown in



**Fig. 4.** Curve fit with different kinetic models at different initial nitrate concentrations. (A) A pseudo-first-order model; (B) a pseudo-second-order model; and (C) intra-particle diffusion rate model kinetic model.

**Table 3**  
Thermodynamic parameters

Temperature (°C)	K	Thermodynamic parameters		
		$\Delta G^0$ (kJ/mol)	$\Delta H^0$ (kJ/mol)	$\Delta S^0$ (J/mol K)
20	819.67	-16.343		47.92
30	854.70	-17.006	-2.302	48.53
40	775.19	-17.313		47.96
50	769.23	-17.846		48.12

**Fig. 5.** van't Hoff plot of  $\ln K$  vs.  $1/T$  for nitrate adsorption by chitosan hydrobeads.

**Table 3.** The values of the standard Gibbs free energy were estimated using the following equation.

$$\Delta G^0 = -RT \ln K \quad (11)$$

The negative values of free energy change ( $\Delta G^0$ ) indicate that this adsorption process is spontaneous in nature whereby no energy input from outside of the system is required. The higher negative value reflects a more energetically favorable adsorption [29]. The Gibbs free energy value at 50 °C is the highest negative value than the values of other temperatures. For that reason more energetically favorable adsorption occurs at 50 °C.

The enthalpy change upon adsorption can be calculated from the van't Hoff equation.

$$\frac{d \ln K}{dT} = \frac{\Delta H^0}{RT^2} \quad (12)$$

If  $\Delta H^0$  is assumed to be independent of temperature, the above differential equation can be easily integrated.

$$\ln K = \frac{-\Delta H^0}{RT} + \text{constant} \quad (13)$$

Therefore, if  $\Delta H^0$  is constant, the plot of  $\ln K$  vs.  $1/T$  gives a straight line whose slope is equal to  $-\Delta H^0/R$  (Fig. 5). The negative value of  $\Delta H^0$  (-2.302 kJ/mol) as shown in Table 3 suggests that the reaction is exothermic and the adsorption process is enthalpically favored. Generally, the enthalpy change due to chemisorption takes value between 40 and 120 kJ/mol, which is larger than due to physisorption [30]. Therefore, the low value of heat of adsorption ( $\Delta H^0$ )

**Table 4**  
Desorption ratio of nitrate from loaded chitosan beads at different pH

pH	Desorption ratio (%)
9	77.72
10	81.76
11	86.89
12	87.12

obtained in this study indicates that adsorption is likely due to physisorption and the interaction between chitosan beads and nitrate ions is mainly electrostatic (Coulombic interactions). The heat of physical adsorption involves only relatively weak intermolecular forces such as van der Waals and mainly electrostatic interactions.

The standard change in entropy can be calculated from the following equation.

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T} \quad (14)$$

The positive values of  $\Delta S^0$  indicate the increased randomness at the solid/solution interface during the adsorption of nitrate onto chitosan hydrobeads and significant changes occur in the internal structure of the adsorbent during adsorption [31]. The  $R^2$  value in the plot of  $\ln K$  vs.  $1/T$  in Fig. 5 was not high for the experiments including low temperature such as 20 °C, which altered the trend of temperature effect. With excluding this temperature, the plot was closer to a straight line with 0.806 of  $R^2$  value. Nevertheless, the values of  $\Delta H^0$  (-4.407 kJ/mol) and  $\Delta S^0$  (41.58, 41.23, and 41.61 J/mol K for 30 °C, 40 °C, and 50 °C) do not produce any remarkable difference from the values calculated considering all the temperatures. Therefore, it would be acceptable that the process is exothermic and the randomness is increased at the solid/solution interface during the adsorption of nitrate onto chitosan hydrobeads.

### 3.5. Desorption study

Desorption studies help scientists to understand the nature of adsorption process and to regenerate the chitosan beads so that they can be reused. Table 4 shows that amount of nitrate desorbed from the loaded chitosan beads increased when the pH of the eluent was increased to the alkaline range. A desorption ratio of around 87% at pH 11 and pH 12 indicates that electrostatic interaction between nitrate and chitosan beads plays a predominant role in the removal of nitrate by the chitosan hydrobeads.

## 4. Conclusion

Chitosan hydrobeads have been found to be an effective biosorbent for the removal of nitrate from an aqueous solution. The adsorption process is dependent on pH, and the adsorption capacity increases with decreasing pH. This process is exothermic, and the maximum uptake was found at 30 °C. The Langmuir adsorption isotherm fit well to the equilibrium adsorption data. Langmuir-Freundlich model fit also demonstrates that the Langmuir isotherm is acceptable and the adsorption process is homogeneous. This adsorption process follows a pseudo-second-order kinetics rate model. Intra-particle diffusion also plays a significant role at the initial stage of adsorption process. This adsorption is a spontaneous and exothermic process that has positive entropy. The beads are recyclable when an alkaline solution is used.

## Acknowledgement

This work was supported by grants from the Korea Science and Engineering Foundation (KOSEF) through the Advanced Environmental Biotechnology Research Center (AEBRC, R11-2003-006).

## References

- [1] N. Ozturk, T.E. Bektas, Nitrate removal from aqueous solution by adsorption onto various materials, J. Hazard. Mater. B112 (2004) 155–162.

- [2] A. Afkhami, Adsorption and electrosorption of nitrate and nitrite on high-area carbon cloth: an approach to purification of water and waste-water samples, *Carbon* 41 (2003) 1320–1322.
- [3] P.J. Golden, R. Weinstein, Treatment of high-risk refractory acquired with automated red blood cell exchange, *J. Clin. Apheresis* 13 (1998) 28–31.
- [4] L.A. Schipper, M. Vojvodic-Vukovic, Five years of nitrate removal, denitrification and carbon dynamics in a denitrification wall, *Water Res.* 35 (2001) 3473–3477.
- [5] H.-Y. Hu, N. Goto, K. Fujie, Effect of pH on the reduction of nitrite in water by metallic iron, *Water Res.* 35 (2001) 2789–2793.
- [6] A. Pinter, J. Batista, Improvement of an integrated ion-exchange/catalytic process for nitrate removal by introducing a two-stage denitrification step, *Appl. Catal., B: Environ.* 63 (2006) 150–159.
- [7] B.U. Baes, Y.H. Jung, W.W. Han, H.S. Shin, Improved brine recycling during nitrate removal using ion exchange, *Water Res.* 36 (2002) 3330–3340.
- [8] A. Deguin, Incidence des resines échangeuses d'anions sur la qualite de l'eau traitee selon le procede nitracycle, *L'Eau* 4 (1988) 213–234.
- [9] Y. Wang, B.Y. Gao, W.W. Yue, Q.Y. Yue, Adsorption kinetics of nitrate from aqueous solutions onto modified wheat residue, *Colloids Surf., A* 308 (2007) 1–5.
- [10] H. Yoshida, T. Takemori, Adsorption of direct dye on cross-linked chitosan fiber: breakthrough curve, *Water Sci. Technol.* 35 (1997) 29–37.
- [11] L. Jin, R. Bai, Mechanisms of lead adsorption on chitosan/PVA hydrogel beads, *Langmuir* 18 (2002) 9765–9770.
- [12] W.S. Wan Ngah, C.S. Endud, R. Mayanar, Removal of copper(II) ions from aqueous solution onto chitosan and cross-linked chitosan beads, *React. Funct. Polym.* 50 (2002) 181–190.
- [13] S. Chatterjee, S. Chatterjee, B.P. Chatterjee, A.R. Das, A.K. Guha, Removal of Eosin Y from aqueous solution by chitosan hydro beads, *J. Colloid Interface Sci.* 288 (2005) 30–35.
- [14] S. Chatterjee, S. Chatterjee, B.P. Chatterjee, A.K. Guha, Adsorptive removal of congo red, a carcinogenic textile dye by chitosan hydrobeads: binding mechanism, equilibrium and kinetics, *Colloids Surf., A* 299 (2007) 146–152.
- [15] T. Mitani, N. Fukomuro, C. Yoshimoto, H. Ishii, Effect of counter ions on the adsorption of copper and nickel by swollen chitosan beads, *Agric. Biol. Chem.* 55 (1991) 2419.
- [16] A. Ozer, D. Ozer, Comparative study of the biosorption of Pb(II), Ni(II) and Cr(VI) ions onto *S. Cerevisiae*: determination of biosorption heats, *J. Hazard. Mater.* 100 (2003) 219–229.
- [17] K. Saltali, A. Sari, M. Aydin, Removal of ammonium ion from aqueous solution by natural Turkish (Yildizeli) zeolite for environmental quality, *J. Hazard. Mater.* 141 (2007) 258–263.
- [18] H. Yoshida, A. Okamoto, T. Kataoka, Adsorption of acid dye on cross-linked chitosan fibers—equilibria, *Chem. Eng. Sci.* 48 (1993) 2267–2272.
- [19] S.M. Venkat, D.M. Indra, C.S. Vimal, Use of bagasse fly ash as an adsorbent for the removal of brilliant green dye from aqueous solution, *Dyes Pigments* 73 (2007) 269–278.
- [20] K. Mohanty, M. Jha, B.C. Meikap, M.N. Biswas, Biosorption of Cr(VI) from aqueous solutions by *Eichhornia crassipes*, *Chem. Eng. J.* 117 (2006) 71–77.
- [21] W. Fritz, E.U. Schlunder, Competitive adsorption of two dissolved organics onto activated carbon-1: adsorption equilibria, *Chem. Eng. Sci.* 36 (1981) 731–741.
- [22] K.G. Bhattacharya, S.S. Gupta, Pb(II) uptake by kaolinite and montmorillonite in aqueous medium: influence of acid activation of the clays, *Colloids Surf., A* 277 (2006) 191–200.
- [23] M.S. Chiou, H.Y. Li, Adsorption behavior of reactive dye in aqueous solution on chemical cross-linked chitosan beads, *Chemosphere* 50 (2003) 1095–1105.
- [24] Y.S. Ho, G. McKay, Sorption of dye from aqueous solution by peat, *Chem. Eng. J.* 70 (1998) 115–124.
- [25] S. Azizian, Kinetic models of sorption: a theoretical analysis, *J. Colloid Interface Sci.* 276 (2004) 47–52.
- [26] G. McKay, Y.S. Ho, The sorption of lead (II) on peat, *Water Res.* 33 (1999) 578–584.
- [27] G. Annadurai, R.-L. Juang, D.-J. Lee, Use of cellulose-based wastes for adsorption of dyes from aqueous solutions, *J. Hazard. Mater.* B92 (2002) 263–274.
- [28] Y.S. Ho, G. McKay, Sorption of dyes and copper ions onto biosorbents, *Process Biochem.* 38 (2003) 1047–1061.
- [29] Z. Aksu, E. Kabasakal, Batch adsorption of 2,4-dichlorophenoxy-acetic acid (2-4-D) from aqueous solution by granular activated carbon, *Sep. Purif. Technol.* 35 (2004) 223–240.
- [30] M. Alkan, Ö. Demirbaş, S. Çelikçapa, M. Doğan, Sorption of acid red 57 from aqueous solution onto sepiolite, *J. Hazard. Mater.* B116 (2004) 135–145.
- [31] M. Mahramanlioğlu, S.I. Kirbasalar, I. Kizilcikil, Mass transfer and adsorption kinetics during the adsorption of fluoride onto activated clays in agitated systems, *Fresenius Environ. Bull.* 12 (2003) 1483–1491.