

Batch Equilibrium and Kinetics Studies of Cd (II) Ion Removal from Aqueous Solution Using Porous Chitosan Hydrogel Beads

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ABSTRACT: *In this study chitosan hydrogel beads with porosity ~ 0.86 and diameter ~ 2 ± 0.07 mm were prepared from 85 % deacetylated chitosan for removal of Cd^{2+} ions from aqueous solutions. Chitosan powder was dissolved into dilute acetic acid as solvent and formed into spherical beads using a phase inversion technique. The effect of temperature, initial concentration of Cd^{2+} ions, and the period of agitation were perused to achieve the best isotherm model. Freundlich model was better fitted than Langmuir model ($R^2 > 0.99$ and $R^2 > 0.93$ respectively, at pH of 6.3, and shaker speed of 200 rpm), the constants of Langmuir and Freundlich models were calculated, which R_L value and q_{max} (mg/g wet weight) at 30 °C, 40 °C, 50 °C showed maximum uptake capacity of 61.35 (mg/g wet weight) obtained at 30 °C. The calculated heat of adsorption was -8.69, -7.051, -5.513 kJ mol⁻¹ at 30, 40, 50 °C respectively which verified an exothermic process. Kinetic studies of the adsorption phenomena were conducted in a batch system by initial concentrations from 100 to 500 mgL⁻¹ until the equilibrium concentration C_e (mgL⁻¹) was reached. First-order, and second-order kinetic models were used; the experimental data were in reliable compliance with second-order kinetic model with R^2 value greater than 0.97. The rate constants of the kinetic models were also calculated and tabulated. To investigate the surface morphology of the chitosan beads before and after adsorption process, they were observed by the use of Scanning Electron Microscopy (SEM). The surface characterization of the beads in both cases showed metal ions binding toward the surface of porous chitosan beads. All of the experiments carried out at pH of 6.3 and agitation rate of 200 rpm, which were opted according to optimum status of previous researcher's reports*

KEY WORDS: *Chitosan, Hydrogel beads, Adsorption, Cd^{2+} , Kinetic.*

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1021-9986/09/3/81

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INTRODUCTION

Cadmium is one of the toxic heavy metal which is extremely used in industry, including electroplating and battery industries. The chronic toxicity of cadmium to human and its environmental concerns have been well documented. In the U.S., the safety level of cadmium in drinking water has been set at 0.01 mgL^{-1} [1]. So far, different methods have been used for the removal of trace heavy metals from aqueous solutions, such as ion exchange, reverse osmosis, adsorption, complexation and chemical precipitation [2]. Adsorption has been shown to be an economically feasible alternative method to remove pollutants from wastewater [3].

Chitosan is a partially deacetylated form of Chitin by thermo-chemical deacetylation in concentrated sodium hydroxide or enzymatic deacetylation. Chitin is a substance found naturally in the exoskeletons of insects, shells of crustaceans such as crab, shrimp, crawfish and fungal cell walls. Chitin and Chitosan, as biopolymers, are used in a wide range of fields such as biotechnology (enzyme immobilization), food and nutrition (emulsifying, thickening and stabilizing agent, packaging membrane, antioxidant and dietary supplement), water engineering (flocculent, metals chelating agents), and medical applications (artificial skins, drug-delivery systems, blood anticoagulant and recently in gene therapy too) [4].

Metal cations can be adsorbed by chelation on amine groups of chitosan in near neutral solutions [5]. The increasing demand for new and economic processes for the recovery of metal ions from industrial effluents has encouraged many research groups to investigate the possibility of using biomaterials like chitosan for metal uptake [6]. One of the key properties of chitosan is its ability to complex strongly with heavy metal ions, particularly with Hg, Cu, Cd, Zn, Pb, Ni, Cr, and so on, several proposed applications are in water purification for removing toxic metals by complexation [7]. Chitosan is just one of the most representative biopolymers, receiving considerable interest in recent years for heavy metals removal due to its excellent metal-binding capacities and its low cost. It has been reported that heavy metal ions could be effectively removed by chitosan hydrogel beads or flakes [3]. The maximum uptake capacity that is; q_{max} (mg/g dry), of Cd^{2+} by raw chitosan as adsorbent (flakes/beads) at pH 7 has been reported in range of 67.44 to 146.12 mg/g dry (Eric Guibal) [6].

The objective of this research was to focus on removal of cadmium ions from aqueous solutions using biomaterials like chitosan which has not been surveyed yet regarding to its kinetics and equilibrium. In this research, chitosan hydrogel beads were prepared using phase inversion technique. After analyzing the diameter, porosity and morphology of hydrogel beads; it was examined for adsorptive removal of Cd^{2+} in batch experiments. The effects of some effective parameters such as initial concentration of metal, temperature, and contact time on cadmium removal were also studied by isotherm curves and the best kinetic model and equilibrium system were chosen for the adsorption experiments.

MATERIALS AND METHOD

Materials

The powder of chitosan (CS) was purchased from Sigma Co.; Minimum 85 % deacetylated Chitosan from Crab Shells. Acetic acid (HAC), Sodium Hydroxide (NaOH), and Cadmium Sulphate Octahydrate ($3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$), (min. 99 %), were supplied from MERK. All other reagents used in the experiments were of analytical grade.

Chitosan Hydrogel Beads Preparation

According to former investigations by Zhao *et al.*, 2007 [8]; it was concluded that weight percentage of HAC solution, weight percentage of chitosan in CS-HAC solution, and NaOH concentration would affect the porosity of beads. Therefore HAC and NaOH solution concentration (3 % wt HAC, NaOH 1 N) were adapted similar to that study to obtain the hydrogel with high adsorptive characteristics. Weight percentage of chitosan in CS-HAC solution was also set at 3 % wt [8].

In order to prepare the hydrogel beads by the phase inversion technique, 1.5 g of chitosan powder was dissolved into 50 mL acetic acid solution (3 % wt); the chitosan-acetic acid solution was continuously stirred in 50°C for about 4 h to ensure that the suitable dissolution has occurred. Then, it was left for nearly 4 h, to approach ambient temperature. Viscous solution (CS-HAC) was dripped into a precipitation bath containing 200 mL of aqueous NaOH 1N, by a syringe, and stirred using a magnetic stirrer, which neutralized the acetic acid within the chitosan gel and therefore coagulated the chitosan to

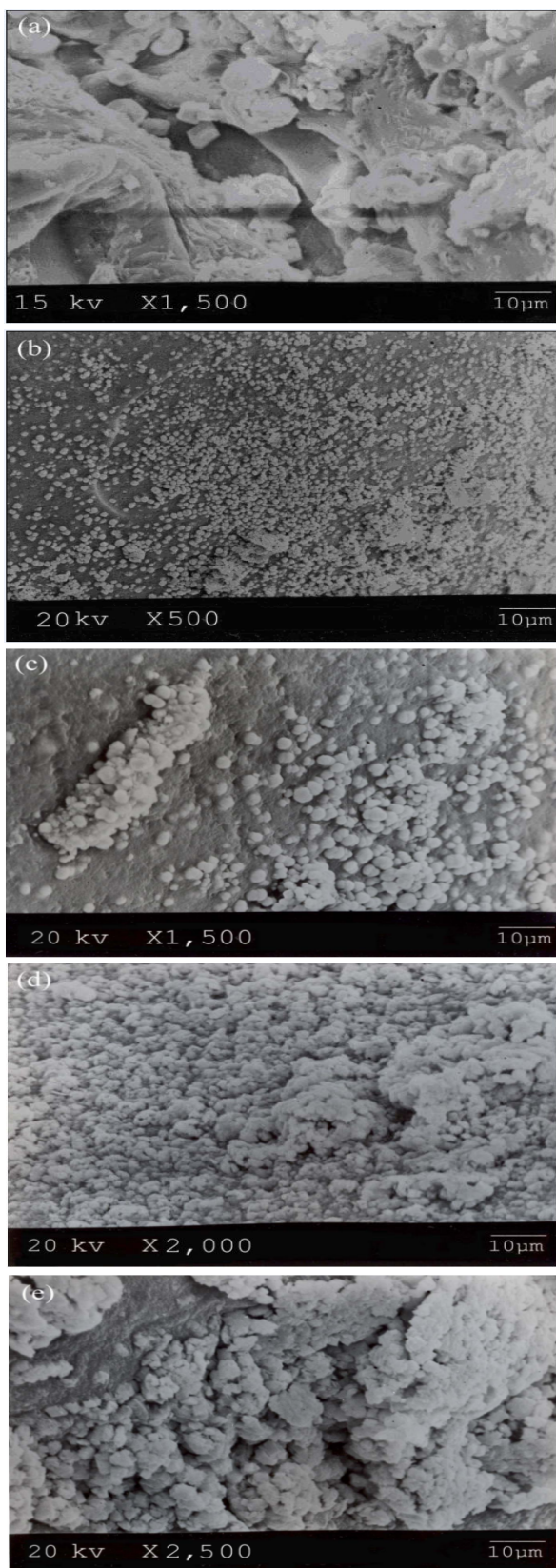


Fig. 1: SEM micrographs of Chitosan hydrogel beads $\times 2500$, after adsorption.

slope of the correlated straight line with R^2 value 0.97 by drawing $\ln(C_e)$ versus $1/T$, as shown in Fig. 3. The calculated heat of adsorption per one mol of Cd^{2+} was -8.69, -7.051, -5.513 kJ mol^{-1} at 30, 40, 50 $^\circ\text{C}$ respectively. In previous studies by Trimukhe, it was recognized that presence of metal ions on the surface of chitosan can be detected with decrease in metal ion binding, in the following sequence [7]:

$\text{Hg} > \text{Cu} > \text{Cd} > \text{Zn} > \text{Pb} > \text{Mn}$

With respect to the reported heat of adsorption -12.3 kJ/mol per one mol of mercury ion [11], and different metal ions binding sequence (as shown above) [7], it was seen that calculated heat of adsorption per one mol of Cd^{2+} ion (-7.051 kJ/mol) is a proper result.

Effect of Cd (II) Concentration on the amount of binding

Adsorption batch experiments were performed with different initial concentrations of metal ions (200, 300, 400, and 500 mg/L at pH of 6.3), and sufficient time was given to achieve equilibrium concentrations. It is well known that by increasing the concentration of metal ions, the adsorbed amount increases (Fig. 4).

Adsorption Isotherms

The equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms, usually the ratio between the quantity adsorbed and that remaining in solution at a fixed temperature at equilibrium. There are basically two well established types of adsorption isotherms: Langmuir adsorption isotherm and Freundlich adsorption isotherm. The simplest theoretical model that can be used to describe monolayer adsorption is the Langmuir equation. The Langmuir isotherm model assumes a monolayer adsorption on a surface with a finite number of identical sites, which all sites are energetically equivalent and there is no interaction between adsorbed molecules [12]. This model is useful when there is a strong specific interaction between the surface and the adsorbate so that a single adsorbed layer is formed and no multi-layer adsorption occurs [13]. The Langmuir model is described by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{\max}} + \frac{C_e}{q_{\max}} \quad (3)$$

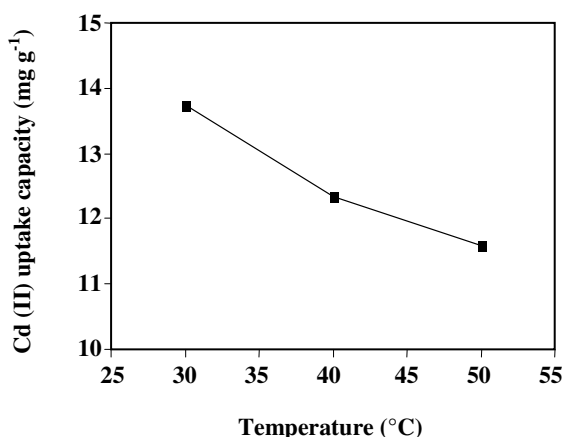


Fig. 2: Cd (II) adsorption capacity (q_e) vs. Temperature ($^{\circ}\text{C}$), $C_0=500$ mg/l, pH 6.3, agitation rate=200 rpm, wet basis: one gram chitosan hydrogel bead.

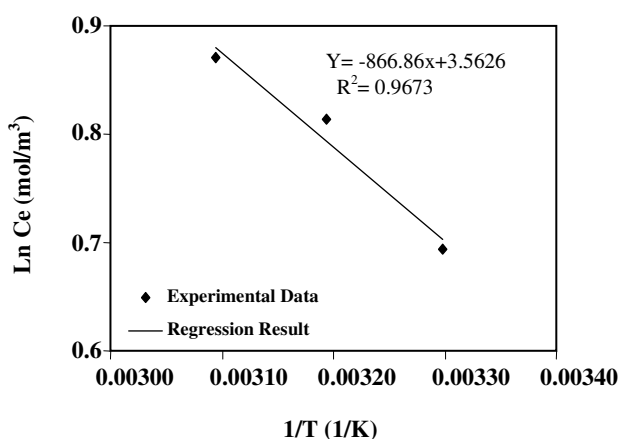


Fig. 3: $\text{Ln}(C_e)$ versus $1/T$ for Cd (II) adsorption on chitosan hydrogel bead in calculation of adsorption heat.

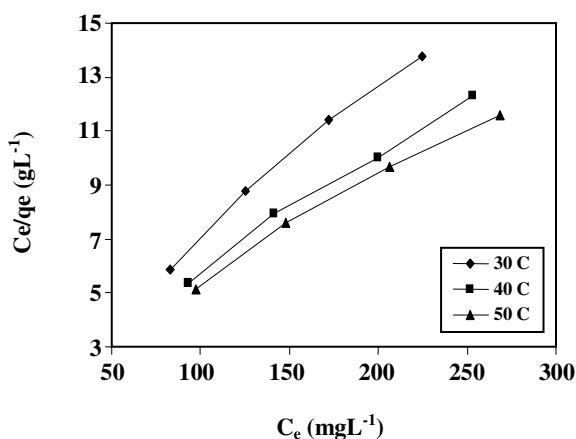


Fig. 4: Cd (II) adsorption capacity q_e (mg/g) vs. C_e (ppm).

Where C_e (mg/l) and q_e (mg/g) are the equilibrium concentrations in solution, and in adsorbed phase, respectively, q_{\max} (mg/g) is the maximum adsorption capacity, and K_L (l/mg) is the Langmuir binding constant which is related to the energy of adsorption [11].

The maximum adsorption capacity is determined by Plotting C_e/q_e versus C_e that yields a straight line with slope and intercept equal to $1/q_{\max}$ and $1/K_L q_{\max}$, respectively (Fig. 6). The values of K_L and q_{\max} at several temperatures for adsorption of Cd^{2+} are presented in table 1. The Freundlich model is an empirical equation based on the distribution of solute between the solid phase and the aqueous phase at equilibrium. The Freundlich expression is an empirical equation based on adsorption on a heterogeneous surface [13]. The Freundlich model is expressed of the following form:

$$q_e = K_F C_e^{1/n} \quad (4)$$

where K_F is the equilibrium constant indicative of adsorption capacity (mg/g), and the larger the value of K_F the greater the adsorption capacity. 'n' is the adsorption equilibrium constant whose reciprocal ($1/n$) is indicative of adsorption intensity. The reciprocal of 'n' is called heterogeneity factor and its value ranges from 0 to 1; the more the surface is heterogeneous, the value of $1/n$ is closer to zero (see table 2).

The monitored R^2 value at 30°C indicates that adsorption of Cd^{2+} is properly correlated with the Freundlich model (Fig. 5). It is also seen that as the temperature increases, the correspondence of adsorption of Cd^{2+} with Langmuir model increases (see R^2 values in table 2). This may be attributed to the thermal rearrangement of active sites and Cd^{2+} ions to give a monolayer adsorption. R_L which is known as separation factor constant gives indication for the possibility of the adsorption process to proceed. $R_L > 1.0$ unsuitable; $R_L = 1$ linear; $0 < R_L < 1$ suitable; $R_L = 0$ irreversible. The value of R_L can be calculated from the following relation:

$$R_L = \frac{1}{1 + K_L C_0} \quad (5)$$

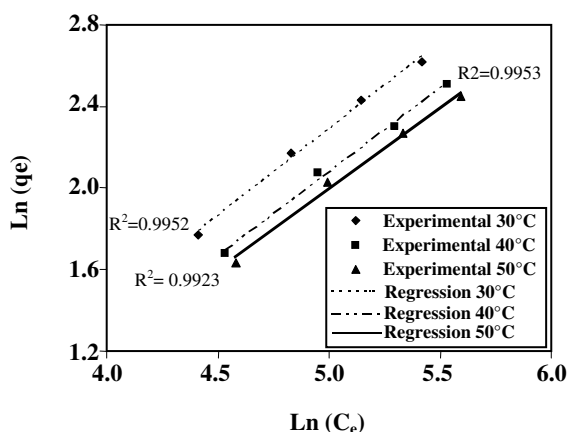
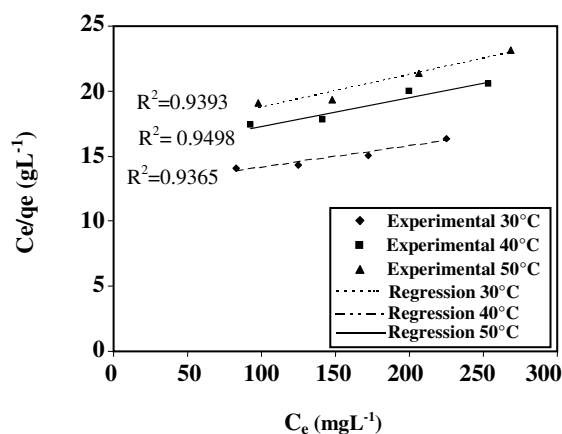
Where K_L (L/ mg) is the Langmuir equilibrium constant and C_0 (mg/l) is the initial concentration of metal ion. The values of R_L lie between 0.56 and 0.79 indicating the suitability of the prepared chitosan hydrogel beads as adsorbent for cadmium ions from their

Table 1: Langmuir Constants.

T (°C)	q _{max} (mg/g wet weight)	K _L (L mg ⁻¹)	R ²
30	61.35	0.00131	0.936
40	45.45	0.00138	0.950
50	39.84	0.00155	0.939

Table 2: Freundlich Constants.

T (°C)	K _F (mg/g)	n	R ²
30	0.138	1.171	0.995
40	0.135	1.225	0.995
50	0.131	1.242	0.992

Fig. 5: Relationship of Ln (q_e) and Ln (C_e) in Freundlich isotherm in three different temperatures.Fig. 6: Relationship of C_e/q_e and C_e in Langmuir isotherm in three different temperatures.

aqueous solutions (table 3). The observed decrease in values of q_{max} and at elevated temperatures indicates the exothermic nature of the adsorption process. The values of K_L at different temperatures were used to calculate thermodynamic properties according to van't Hoff equation [14]:

$$\ln K_L = \frac{-\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (6)$$

Where ΔH^0 (J mol⁻¹) and ΔS^0 (J/mol K⁻¹) are the enthalpy and entropy changes, respectively, R is the universal gas constant and T is the absolute temperature (K). Plotting Ln (K_L) against 1/T gives a straight line with slope and intercept equal to $\Delta H^0/R$ and $\Delta S^0/R$, respectively. The values of ΔH^0 and ΔS^0 were calculated from Fig. 7, and presented in table 4, the negative values of ΔH^0 show the exothermic nature of adsorption process. Gibbs free energy of adsorption (ΔG^0) was calculated from the following relation:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (7)$$

The values of ΔG^0 at different temperatures were calculated and presented in table 4. The negative value

of ΔG^0 indicates that the adsorption reaction is spontaneous. The observed decrease in negative values of ΔG^0 with increasing temperature implies that the adsorption becomes less favourable at higher temperatures [14]. A minor change in the value of $T\Delta S^0$ at all temperatures and $\Delta H^0 > T\Delta S^0$ indicate that the adsorption process is dominated by enthalpic rather than entropic changes.

Kinetics Studies

The change in Cd²⁺ concentrations in metal solutions via adsorption onto chitosan hydrogel beads in five different initial concentrations are depicted in Fig. 8. In order to examine the controlling mechanism of adsorption processes such as mass transfer and chemical reaction, the pseudo-first-order and pseudo-second-order kinetic models were used to check the experimental data. The pseudo-first-order kinetic model is given by equation (8):

$$\ln (q_e - q_t) = \ln (q_e) - k_1 t \quad (8)$$

Where q_e and q_t are the amounts of Cd ion adsorbed on adsorbent (mg/g) at equilibrium and at definite time t,

Table 3: R_L Value at different temperature.

T (°C)	R_L	Initial concentration C_0 (mg/l)
30	0.61	500
	0.66	400
	0.72	300
	0.79	200
40	0.59	500
	0.64	400
	0.71	300
	0.78	200
50	0.56	500
	0.62	400

Table 4: Thermodynamic Properties.

T (K)	ΔG° (KJ/mol)	ΔH° (kJ/mol)	ΔS° (J/ molK ⁻¹)
303.15	-8.893	-6.878	6.646
313.15	-8.959		
323.15	-9.025		

Table 5: Second-order kinetic model parameters for Cd (II) adsorption on chitosan beads.

Initial concentration(ppm)	$k_2 \times 10^{-4}$ (g mg ⁻¹ min ⁻¹)	R^2
100	7.69	0.998
200	5.19	0.997
300	1.46	0.990
400	0.50	0.973
500	2.94	0.998

Table 6: First-order kinetic model parameters for Cd (II) adsorption on chitosan beads.

Initial concentration(ppm)	$k_1 \times 10^{-4}$ (min ⁻¹)	R^2
100	2.13	0.795
200	1.33	0.610
300	3.17	0.904
400	3.62	0.932
500	1.35	0.539

respectively, and k_1 is the rate constant of pseudo-first-order adsorption (h^{-1}). The change in q_e at different contact times is also depicted in Fig. 9. With the increase of time, the amount of adsorbed Cd ion increased, and reached an equilibrium value after nearly 48 h (Fig. 9).

The straight-line plots of $\ln(q_e - q_t)$ versus t were used to determine the rate constant, k_1 (h^{-1}) and regression coefficient value (R^2) of the Cd^{2+} ion over different concentrations were calculated using these plots. The following pseudo-second-order equation was used as equation (9):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (9)$$

Where k_2 is the rate constant of pseudo-second-order adsorption ($g/mg \ h^{-1}$). The straight-line plots of t/q_t against t have been tested to obtain rate parameters and it suggests the applicability of this kinetic model to fit the experimental data. The validity of second order kinetic model was checked (Fig. 10) which showed a reliable agreement with second-order kinetic model. On the contrary, the first-order kinetic model poorly correlates the experimental data. The results of the kinetic parameters for Cd^{2+} ion adsorption are shown in table 5 and Table. 6. The pseudo- first-order kinetic model has been used for reversible reaction with an equilibrium being established between liquid and solid phases. Whereas, the second-order kinetic model assumes that the rate-limiting step may be chemical adsorption [3]. In many cases, the second-order equation correlates well to the adsorption studies [3, 9].

CONCLUSIONS

The ability of biopolymers like chitosan for heavy metals adsorption is concluded via SEM analysis. The surface of dried chitosan bead, before adsorption, has large porous structures which are obviously seen by SEM. SEM studies indicated that Cd metal ion has a good complexation and binding to chitosan surfaces. The exothermic nature of adsorption process of heavy metal cations discloses that the optimum temperature occurs at 30 °C. The calculated maximum uptake capacity reach to 61.35 (mg/g wet weight) at 30 °C. The maximum uptake capacity has appropriate agreement with previous studies. Subsequent studies were focused on kinetic study and

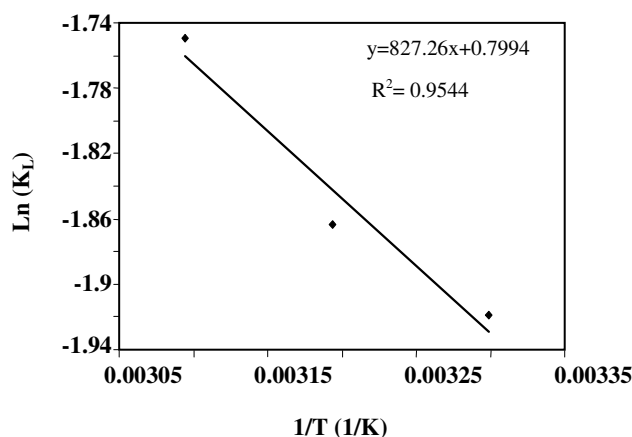
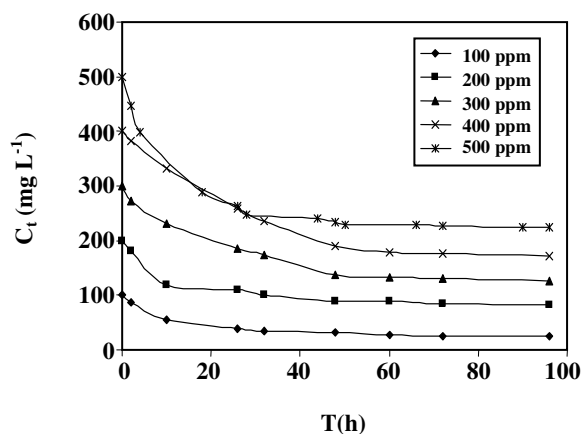
Fig. 7: $\ln(K_L)$ vs. $1/T$.

Fig. 8: Cd (II) concentration vs. time.

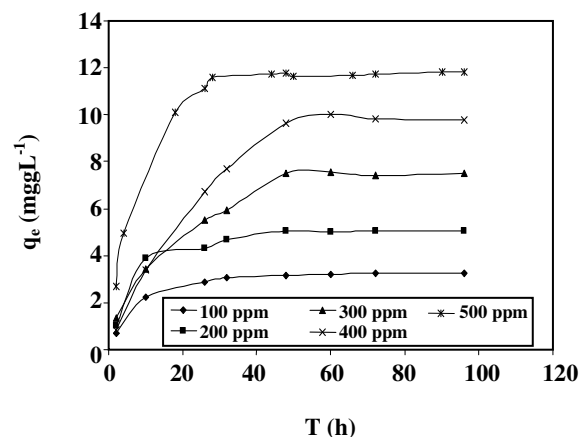
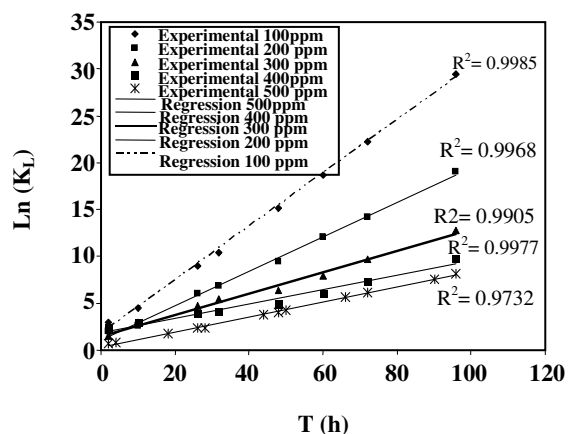
Fig. 9: Cd (II) adsorption capacity q_e vs. time.

Fig. 10: The validity of second order kinetic model.

isotherm considerations of the Cd (II) ion uptake. The best kinetic model was pseudo-second-order model and Freundlich isotherm model was correlated with R^2 value greater than 0.99.

Acknowledgements

The authors wish to acknowledge the technical support and assistance of BBRC staff, and Technology Development Institute, Materials Research Centre Division, Sharif University of Technology, Tehran, Iran.

Nomenclatures

T	Time(h)
W	Weight of chitosan hydrogel beads (g)
C	Concentration of Cd (II) solution (mg/L)
C_0	Initial concentration of Cu(II) solution (mg/L)
V	Volume of the Cd (II) solution (L)

R	Universal gas constant ($J/mol K^{-1}$)
R^2	Correlation coefficient (regression coefficient)
T	Temperature (K)
ΔH_{ads}	Heat of adsorption per one mol of metal ion ($kJ mol^{-1}$)
q	The amount of metal adsorbed on the beads (mg/g wet weight)
K_L	Langmuir binding constant (l/mg)
q_{max}	Maximum adsorption capacity (mg/g)
K_F	Freundlich coefficient (mg/g)
ΔH°	Enthalpy change (J/mol)
ΔS°	Entropy change ($J/mol K^{-1}$)
ΔG°	Gibbs free energy of adsorption (KJ/mol)
k_1	Rate constant of pseudo-first-order kinetic model (h^{-1}) or (min^{-1})
k_2	Rate constant of pseudo-second-order kinetic model ($g/mg h^{-1}$) or ($g/mg min^{-1}$)

R_L	Dimensionless constant separation factor or equilibrium parameter
rpm	Round per minute
A	Angstrom
n	Freundlich adsorption Equilibrium constant

Subscripts

e	Equilibrium
c	Chitosan gel bead
ads	Adsorption
F	Freundlich
L	Langmuir
t	Time

Received : 11th May 2008 ; Accepted : 10th March 2009

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