Removal of Ni² Ions from Aqueous Solution by Sorption into Poly(Acrylamide-co-Sodium Acrylate) Hydrogels

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In this study, removal of Ni (II) ions from aqueous solution by sorption into poly(acrylamide−co−sodium acrylate) hydrogels has been examined by a batch equilibration technique at 30°C. The sorption process follows a Langmuir−type behavior, with the extent of sorption of Ni (II) ions depending upon composition of the co−polymeric gels, presence of other ions in the solution, and temperature of the system. Low temperature favors the sorption process. The various kinetic and absorption parameters, such as rate constant for sorption, intraparticle diffusion rate constant, Langmuir constant, and absorption capacity have been evaluated. The activation energy was found to $-3.556 \, kJ \, mol^{-1}$. Finally, various thermodynamic parameters have also been calculated to elucidate the mechanism involved in the sorption process. The negative values of enthalpy change and the free energy change indicate the exothermic and spontaneous nature of the sorption process, respectively. Similarly, negative entropy change suggests faster interaction with the active sites of sorbent.

Keywords: sorption; Langmuir isotherm; ion−exchange; activation energy

1 Introduction

The tremendous increase in the use of heavy metals over the past few decades has inevitably resulted in an increased flux of metallic substances in the aquatic environment. Industrial waste constitutes the major source of various kinds of metal pollution in natural water (1). The heavy toxic metals enter into the water bodies through waste water from metal plating, Cd−Ni batteries, phosphate fertilizer, mining, pigments and stabilizers alloys industries (2).

Some of the important technologies, employed to remove toxic metal ions, include chemical precipitations, electroflotation, ion−exchange, and reverse osmosis. However, these processes result in incomplete removal, exhibit high energy and reagent requirements, and finally, they generate toxic sludge that requires careful disposal (3).

The need for cost−effective and safe methods to remove toxins from industrial effluents and domestic water has resulted in the development of new technologies such as polymer-assisted ultra filtration (4, 5), sorption into polysaccharides (11−15), biomass (9, 10) and polymeric hydrogels (11−15). Out of these, synthetic polymers have been the focus of research for environmental scientists and polymer chemists due to their characteristic properties, such as renewable origin, environment friendly behavior, cost−effectiveness and ability to carry out almost complete removal. These materials normally function through adsorption, ion−exchange, and chelation mechanisms.

Most recently, we synthesized poly (acrylamide−co−sodium acrylate) hydrogels and reported a detailed investigation of their water uptake behavior (16). The gels demonstrated drastic volume phase transition when swollen gels were put in solutions of divalent ions. In this connection, here we report the sorption of Ni²⁺ ions by the equilibration method onto these hydrogels.

2 Experimental

2.1 Materials

Acrylamide (AAm) and acrylic acid (AAc) monomers were obtained from Hi Media, Mumbai, India. The crosslinker N,N′− methylene bisacrylamide (MB), initiator potassium persulfate (KPS) and sodium hydroxide flakes (NaOH) were obtained from Research Lab, Pune, India. The sodium acrylate (SA) monomer was obtained from the neutralization

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of AAc according to the procedure of Liu et al. (15). The monomer AAm was also recrystallized in methanol to remove the inhibitor. Double distilled water was used throughout the investigations.

2.2 Synthesis of Polymeric Hydrogels

Free radical, aqueous copolymerization of AAm and SA, in the presence of MB crosslinker, yielded copolymeric gels as described previously (16). In brief, to synthesize the control set, 11.970 mM of AAm, 9.036 mM of SA and 0.290 mM of crosslinker MB were dissolved in water to give a clear solution, with a final volume of 5.0 ml. Finally, 0.072 mM of KPS initiator was added and the reaction mixture was poured into a petri dish, which was kept in an electric oven (Tempstar, India) at 60°C for a period of 2 h. The gel was crushed and washed with distilled water to remove the unreacted salts, and allowed to be dried at 40°C in a dust free chamber. The dried hydrogel powder was passed through a standard sieve of a mesh size 100, having a geometrical mean particle diameter of 150 μm. The entire sorption studies were carried out with these sieved gel powders. The sample was designated as HG (44), where the number in parenthesis denotes the percent mole fraction of sodium acrylate in the feed mixture.

2.3 Sorption Studies

Batch mode sorption studies were carried out by agitating a 20 ml of Ni^{2+} solution of desired concentration with 0.10 g of ground sorbent powder in a temperature–controlled shaking water bath. Continuous mixing was provided during the experimental period with a constant agitation speed of 120 rpm. At the end of predetermined time intervals, the sorbent was separated by filtration and the supernatant was analyzed spectrophotometrically for the remaining concentration of Ni^{2+} ions using the dimethyl–glyoxime method (17).

3 Results and Discussion

3.1 Effect of Contact Time and Temperature

Figure 1 depicts the dynamic sorption of Ni (II) into the copolymeric absorbent as a function of time at three different temperatures, namely 30, 40, and 50°C, with a initial Ni^{2+} concentration of 20 mg l^{-1}. It is clear that the amount of Ni (II) sorbed increases with contact time and finally attains maximum value. Moreover, the sorption increases with a decrease in temperature, thus indicating an exothermic sorption process and, the equilibrium time is observed to be independent of temperature. It is also worth mentioning that the removal of Ni (II) ions decreases from 84.00% to 62.00% with the increase in temperature from 30 to 50°C. This clearly indicates that the proposed hydrogel system is highly effective in removing Ni (II) from solutions and with
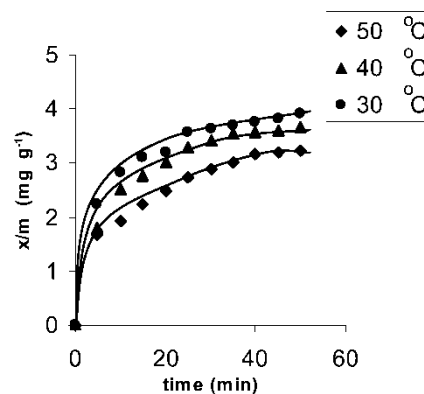

Fig. 1. Effect of contact time and temperature on the Ni (II) uptake by copolymeric sorbent.

the temperature having a marked effect on the sorption process.

3.2 Sorption Kinetics

The sorption of a metal ion from the liquid phase to the solid phase (i.e., sorbent) may be considered as a reversible reaction (18) of an equilibrium type:

$$Sol \underset{k_2}{\overset{k_1}{\rightleftarrows}} Sorb \qquad (1)$$

where both the reactions are of first order. The resultant rate equation for the overall sorption process may be given as:

$$\ln\left(1 - \frac{q}{q_e}\right) = K't \qquad (2)$$

where K' is overall rate constant for sorption and,

$$K' = k_1\left(1 + \frac{1}{K_c}\right) = k_1 + k_2 \qquad (3)$$

where:

$$K_c = \frac{[C_0 - C_e]}{[C_e]} = \frac{k_1}{k_2} \qquad (4)$$

In the above equations, k_1 and k_2 are rate constants for forward and backward reactions, respectively; and K_c is the equilibrium constant which may be given as a ratio of equilibrium concentration of metal ion in the sorbent to that in the solution phase.

The overall rate constants of sorption (i.e., K') at different temperature (see Figure 2) were determined from the slopes of the linear plots of ln $(1-q/q_e)$ vs. t and are given in Table 1. The values obtained clearly indicate that low temperature favors the sorption of Ni (II) into a polymeric sorbent. By determining K_c and using Equations (3) and (4), we also evaluated rate constants k_1 and k_2 for forward and backward reaction, respectively. All these constants are shown in Table 1.

Due to the sorbent porous nature, pore diffusion is also expected in addition to surface adsorption. The rate
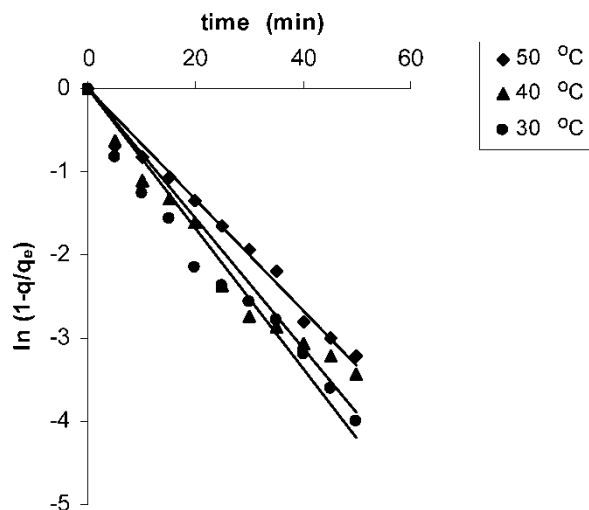
Fig. 2. First order reversible kinetic fit of Ni (II) uptake by poly (AAm−co−SA) gels at different temperatures.

constant of intraparticle diffusion (K_{id}) may be calculated according to the following equation given by Weber and Morris (19),

$$\frac{C_t}{C_0} = K_{id}t^{0.5} \quad (5)$$

where C_t and C_0 are the concentrations (mg l^{-1}) of Ni (II) at time t and at the beginning, respectively. The values of K_{id} were calculated from the slope of the linear plots, obtained between C_t/C_0 and $t^{0.5}$, as shown in Figure 3. We also calculated activation energy of sorption E_s, using the logarithmic Arrhenius plot.

$$\ln K_{id} = \ln A - \frac{E_s}{RT} \quad (6)$$

For this, $\ln K_{id}$ values where plotted against $1/T$ and E_s were calculated from the slope of the linear plot as shown in Figure 4. The value of E_s was found to be -3.556 kJ mol^{-1}.

The pore diffusion coefficient $\bar{D}$ for the intraparticle transport of Ni (II) was calculated assuming spherical geometry of the sorbent (20), using the following equation:
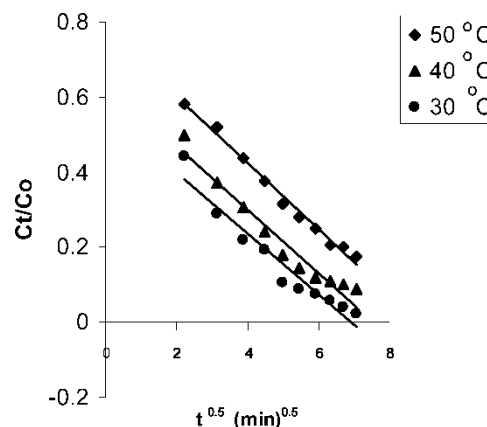
$$\bar{D} = \frac{0.03r_0^2}{t_{1/2}} \quad (7)$$

Fig. 3. Variation of fractional uptake of Ni (II) with under root of time at 30°C.

where r_0 is the radius of the sorbent, $\bar{D}$ is the pore diffusion coefficient (cm^{2}s^{-1}) and $t_{1/2}$ is the time for half sorption. The values of K_{id} and $\bar{D}$ have also been summarized in Table 1.

3.2 Mechanism of Ni(II) Sorption

When the hydrogel particles are put in the solution of Ni^{2+} ions, the sodium ions that are bound to the charged carboxylate groups (i.e., -COO$^-$) via electrostatic binding in the sorbent particles undergo ion−exchange with Ni^{2+} ions present in the outer solution. This occurs due to a stronger tendency of Ni (II) to form a complex with changed carboxylate groups. These divalent ions also serve as additional crosslinks, thus not allowing the particles to undergo appreciable swelling. This can be shown in the following scheme:
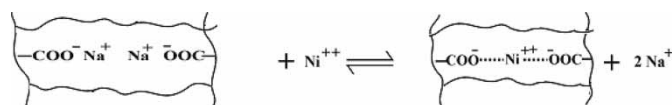
3.3 Sorption Isotherm

The uptake of Ni (II) by copolymeric sorbent has been analyzed with the help of the Langmuir model. The

Table 1. Various kinetic parameters for Ni (II) uptake at different temperatures

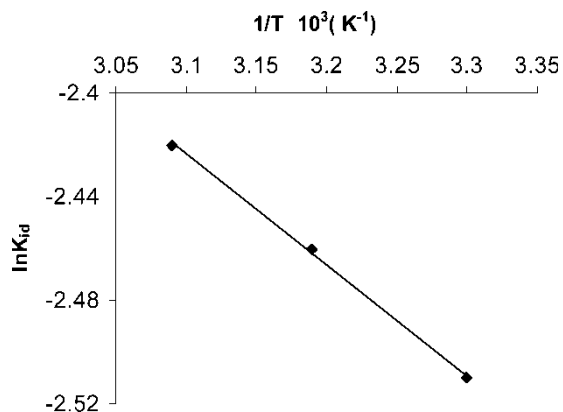| Temp. (°C)	K' (min^{-1}) $\times 10^2$	K_1 (min^{-1}) $\times 10^3$	K_2 (min^{-1}) $\times 10^3$	K_{id} (mg g^{-1}min$^{-0.5}$) $\times 10^2$	D (cm^{2}s^{-1}) $\times 10^7$
30	8.40	82.50	1.40	8.12	2.75
40	7.70	72.50	4.42	8.47	1.80
50	6.60	54.70	11.60	8.81	1.50

Fig. 4. Variation of pore diffusion constant K_{id} of Ni (II) with reciprocal of temperature (Arrhenius plot).

modified Langmuir model used in this study is:

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_0} \tag{8}$$

where C_e is the equilibrium concentration (mg l^{-1}) of metal ions in the solutions, Q_o is the Langmuir constant related to the sorption capacity (mg g^{-1}) and b is the Langmuir constant related to the energy sorption (l mg^{-1}). The values of Q_o and b were determined from the slopes and intercepts of the linear plots obtained between C_e/q_e and C_e (Figure 5) at three different temperatures, namely 30, 40, and 50°C.

The validity of the Langmuir isotherm was confirmed by regression analysis of the equilibrium data at different temperatures and are presented in the form of straight line equations as shown below:

$$\frac{C_e}{q_e} = 0.248C_e + 0.414 \quad \text{at } 30°C \tag{9}$$

$$\frac{C_e}{q_e} = 0.232C_e + 0.824 \quad \text{at } 40°C \tag{10}$$

Table 2. Values of Langmuir constants for Ni(II) sorption at different temperature

	Values of Q_o and b at different temperature			
	Graphical Values		Regression Values	
Temp. (°C)	Q_o (mg g^{-1})	b (l mg^{-1})	Q_o (mg g^{-1})	b (l mg^{-1})
30	4.52	0.646	4.03	0.599
40	4.30	0.283	4.31	0.281
50	3.41	0.258	3.42	0.253

$$\frac{C_e}{q_e} = 0.292C_e + 1.15 \quad \text{at } 50°C \tag{11}$$

By using intercept and slopes of these equations, the values of Q_o and b were determined at different temperatures and have been found to be in close agreement with the graphical values as shown in Table 2.

The apparent heat of sorption (21) ΔH is related to the Langmuir constant b, as shown below:

$$b \sim b' \cdot e^{\Delta H/RT} \tag{12}$$

or

$$\ln b = -\frac{\Delta H}{R} \cdot \frac{1}{T} + \ln b' \tag{13}$$

where b' is a constant.

The values of ΔH was calculated from the slope of the linear plot between ln b and $1/T$ (see Figure 6), and was found to be -36.62 kJ mol^{-1}. The negative value of ΔH indicates the exothermic nature of the sorption process.
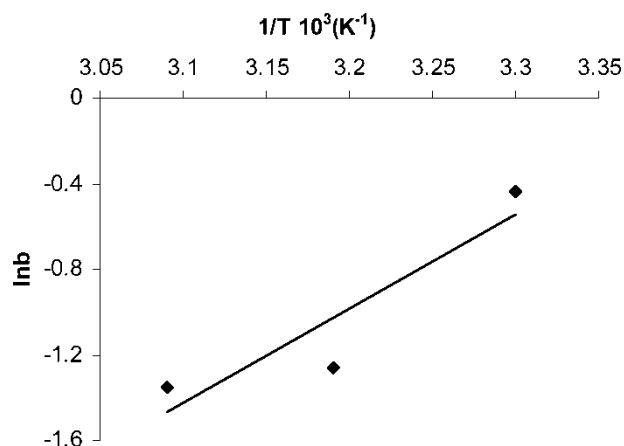

Fig. 5. Langmuir isotherm plots for Ni (II) sorption by copolymeric sorbents.

Fig. 6. Plot for calculation of apparent heat of sorption ΔH.

3.4 Thermodynamic Parameters

We also calculated various thermodynamic parameters with the help of the following equations:

$$\Delta G^\circ = -RT \ln K_c \qquad (14)$$

$$\Delta H^\circ = R\left(\frac{T_2 \cdot T_1}{T_2 - T_1}\right) \ln K_{C2}/K_{C1} \qquad (15)$$

and:

$$\Delta S^\circ = \Delta H^\circ - \Delta G^\circ / T \qquad (16)$$

The equilibrium constants K_c, K_{c1} and K_{c2} (ratio of k_1 and k_2) were obtained from the values of k_1 and k_2 (Table 1) at different temperatures. The negative value of the free energy change, ΔG° (Table 3) is indicative of spontaneity of the sorption process. The negative value of the enthalpy (ΔH°) change shows the exothermic nature of the process. The negative entropy change ΔS° indicates faster interaction with the active sites of the sorbent.

3.5 Effect of Gels Composition on Sorption

As the proposed sorbent hydrogel removes the Ni^{++} ions from the aqueous solution by an ion–exchange process, which takes place between the nickel ions of the solution and sodium ions of the copolymeric gel, the amount of sodium acrylate present within the gel may affect the sorption process significantly. In order to investigate the latter aspect, we synthesized a number of copolymeric gels containing varying concentrations of sodium acrylate and studied the sorption of Ni^{2+} ions into them under similar conditions. The results, as shown in Figure 7, clearly indicate that as the amount of sodium acrylate in the feed mixture increases, the amount of Ni^{2+} sorbed into gel particles increases, indicating that with an increase in SA content in the gel, the amount of Ni^{2+} ions sorbed increases. This may simply be attributed to the fact that with the increase in SA content in the copolymeric gels, the extent of ion–exchange between Na^+ ions and Ni^{2+} ions increases, thus causing an enhancement in the degree of sorption of Ni (II) into the gels. In this way, it can be concluded that sorption of Ni^{2+} ions depends upon the concentration of sodium acrylate in the gels. It is also worth mentioning that the sorption of Ni^{2+} (although minimum) into the gel without sodium acrylate (i.e., hydrogels composed of polyacrylamide) may

Table 3. Thermodynamic parameters at different temperatures

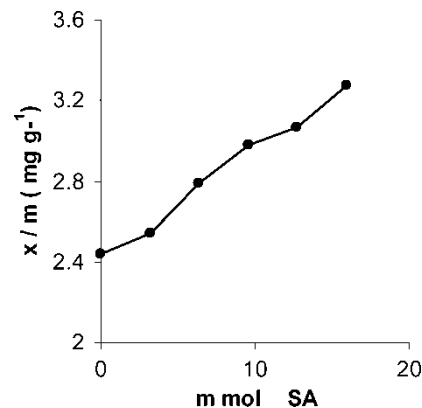| Temp. (°C)	$-\Delta G^\circ$ (kJ mol^{-1})	$-\Delta H^\circ$ (kJ mol^{-1})	$-\Delta S^\circ$ (J mol^{-1})
30	10.14	26.17	52.9
40	7.27	37.23	95.6
50	4.60		

Fig. 7. Effect of variation in sodium acrylate content in the gel on the Ni (II) uptake.

be attributed to the finding of Ni^{2+} ions to nitrogen, as well as to amide oxygen atoms of the polymeric sorbent.

3.6 Sorption in the Presence of Cu^{2+} Ions

In order to investigate the effect of the Cu^{2+} ions presence in the aqueous solution on the sorption of Ni^{2+} ions into the copolymeric gels, we prepared various 20 mg l^{-1} solutions of Ni^{2+} ions containing different concentrations of Cu^{2+} ions and studied sorption of Ni^{2+} into the gels.

The results, shown in Figure 8, clearly indicate that as the concentration of Cu^{2+} ions in the solutions increases, the extent of sorption of Ni^{2+} ions decreases. This may be attributed to the fact that both Cu^{2+} and Ni^{2+} ions compete for the sorption into the copolymeric gels via the ion–exchange process. Therefore, as the concentration of Cu^{2+} ions in the solutions increases, the ion–exchange process between Cu^{2+} and Na^+ ions becomes more and more prominent, ultimately resulting in a decrease in sorption of Ni^{2+} ions into the gels.
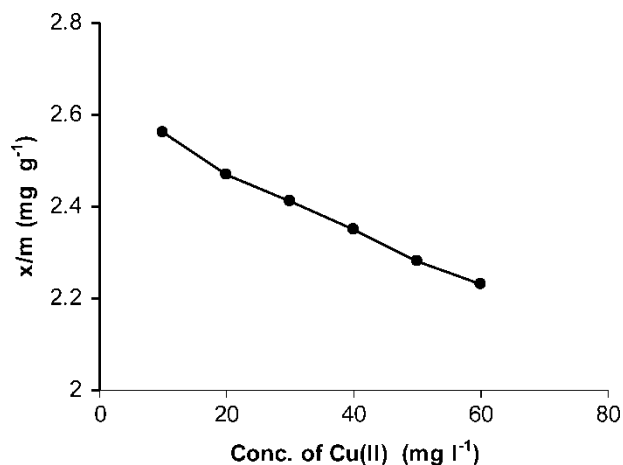

Fig. 8. Effect of presence of Cu (II) ions in the solution on the Ni (II) uptake.
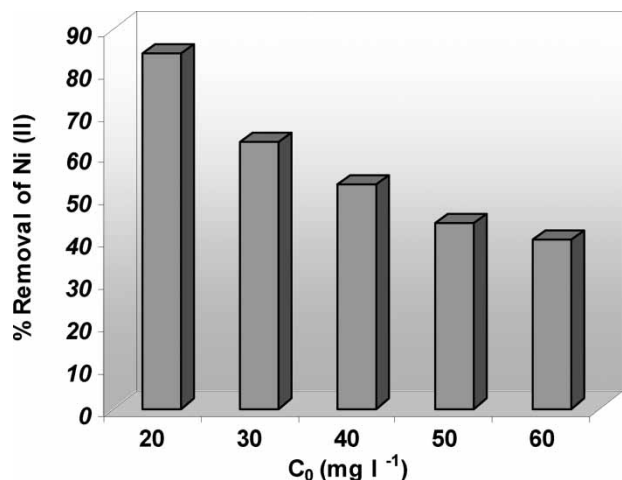
Fig. 9. Percent removal of Ni (II) ions.

3.7 *Concentration Effect*

The dependence of the process of Ni(II) removal from aqueous solution of varying initial concentrations (20–60 mgl^{-1}) is shown in the Figure 9 bar diagram. It is clear that at very low concentrations, sorption is highly effective and the percent Ni(II) sorbed decreases with an increase in the initial concentration. This may simply be attributed to the fact that for lower concentrations, the ratio of surface area available to the number of moles of metal is quite high. However, at higher concentrations, the available sites for sorption becomes fewer and subsequently, the percent removal of Ni(II) decreases.

4 Conclusions

From the above study, it can be concluded that poly(acryl-amide−co−sodium acrylate) hydrogels prove to be highly efficient (84.00% removal of Ni^{2+} from 20 mg l^{-1}solution by gel containing 44 mole percent of sodium acrylate) for the removal of Ni^{2+} ions via ion−exchange mechanism. The lower temperature favors the sorption process. The negative value of enthalpy change also confirms exothermic nature of the sorption process. Similarly, the negative value of entropy change is indicative of spontaneous nature of the process. The presence of other competing ions (e.g. Cu^{2+} ions) in the solution causes a decrease in extent of Ni (II) sorption. The sorption process in highly dependent on the concentration of sodium acrylate in the copolymeric

sorbent, thus suggesting an ion-exchange mechanism for sorption process.

6 References

1. Harrison, R.M. and Laxen, D.P.H. (1980) *Chem. Br.*, **16**, 316−320.
2. Low, K.S. and Lee, C.K. (1991) *Bioresor. Technol.*, **38**, 1−6.
3. Wild, J. (1987) Liquid wastes from the metal finishing industries. In *Survey in Industrial Waste Water Treatment*; Barnes, D., Forster, C.F., Hurdey, S.E. (eds.); John Wiley and Sons, New York, 1987, pp. 21−62.
4. Dupont, A., Vidonne, A., Dejeu, J., Fievet, P. and Foissy, A. (2006) *Water Research*, **40(6)**, 1303−1309.
5. Molinari, B., Argurio, P. and Poerio, T. (2004) *Desalination*, **162**, 217−228.
6. Karthikeyan, G., Anbalagan, K. and Andol, N.M. (2004) *J. Chem. Sci.*, **116(2)**, 119−127.
7. Nomanbhay, S.M. and Palanisamy, K. (2005) *Ele. J. Biotechnol.*, **8(1)**, 44−53.
8. Zhao, L., Mitomo, H., Yoshii, F. and Kume, T.J. (2003) *Appl. Polym. Sci.*, **91(1)**, 556−562.
9. Say, R., Yilmaz, N. and Denizli, A. (2003) *Ads. Sci. Technol.*, **21(7)**, 643−650.
10. Kovacevic, Z.F., Sipos, L. and Briski, F. (2000) *Food Technol., Biotechnol.*, **38(3)**, 211−216.
11. Nastasovi, A., Jovanovic, S., Dordevic, D., Onjia, A., Jakovljevi, D. and Novakovic, T. (2004) *React. Funct. Polym.*, **58(2)**, 139−147.
12. Ali, A.E., Shawki, H.A., Rehim, H.A.A. and Hegazy, E.A. (2003) *Eur. Polym. J.*, **39(12)**, 2337−2344.
13. Essawy, H.A. and Ibrahim, H.S. (2004) *React. Funct. Polym.*, **61(3)**, 421−432.
14. Jouad, E.M., Jourjon, F., Guillanton, G.L. and Elothmani, D. (2005) *Desalination*, **180(1−3)**, 271−276.
15. Kara, A., Uzun, L., Beirli, N. and Denizli, A. (2004) *J. Hazardous Mater*, **106(2−6)**, 93−99.
16. Bajpai, S.K. and Johnson, S. (2005) *React. Funct. Polym.*, **62**, 271−283.
17. Bajpai, S.K. (1999) *Asian J. Chem.*, **11(1)**, 171−180.
18. Yadav, K.P., Tyagi, B.S. and Singh, V.N. (1991) *J. Chem. Technol. Biotechnol.*, **51**, 47−60.
19. Weber, W.J., Morris, J.C. and Sanit, J. (1963) *Eng. Dov., ASCE*, **89(SA2)**, 31−39.
20. Helfferch, F. Ion Exchange. McGraw-Hill Book Co. Inc: New York, 1962.
21. Langmuir, I. (1918) *J. Chem. Soc.*, **40**, 1361.