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Removal of Cr(VI) Oxy-anions from Aqueous Solution by Sorption into Poly(Acrylamide-Co-Maleic Acid) Hydrogels

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Abstract: The dynamic removal of hexavalent chromiuim by poly(acrylamide-co-maleic acid) hydrogels was studied by a batch equilibrium technique at 35°C. Various kinetic and adsorption parameters such as rate constant for sorption, intraparticle diffusion rate constant, Langmuir constant, and adsorption capacity have been evaluated. The sorption process follows the Langmuir-type behavior and extent of sorption of Cr(VI) ions depends upon the composition of co-polymeric gels, presence of other ions in the solution, and temperature of the system. Relatively higher temperature favors the sorption process. The activation energy was found to be $-20.369\,\mathrm{kJ\,mol^{-1}}$. Finally, various thermodynamic parameters have also been calculated to elucidate the mechanism involved in the sorption process. The positive enthalpy change indicates the endothermic nature of the process. The presence of fluoride ions causes a decrease in the degree of sorption of Cr(VI). Finally, the sorption of Cr(VI) into the copolymeric sorbent has been explained on the basis of coordination between electron rich O and N atoms of sorbent molecules and the Cr(III) molecules. Moreover, H-bonding interactions also seem to contribute to the sorption process.

Keywords: Sorption, Langmuir isotherm, ion-exchange, activation energy

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INTRODUCTION

Heavy metal contamination has gained much attention due to increasing industrialization and urbanization activities. These activities are polluting water resources with huge amounts of waste water containing organic compounds, coloring materials, and heavy metals. The discharge of toxic and polluting metal ions into the environment and municipal sewers by the mining, metallurgical, electroplating, electronic, nuclear, textile-dyeing, cement, and other industries constitutes one of the major causes of ground water contamination (1).

Chromium, which is one of the most toxic of metals, exists in two stable oxidation states viz., Cr(III) and Cr(VI). The Cr(VI) oxidation state is more toxic and mutagenic (2). Chromium (VI) requires intracellular reduction for activation, and this *in vivo* reduction can produce several reactive intermediates such as chromium (V) and chromium (IV) that can target and damage DNA (3). It is very essential to remove Cr(VI) from industrial effluents before it is mixed with drinking water sources. Conventional methods for the removal of Cr(VI) from waste water include chemical precipitation, electrochemical precipitation, ion-exchange, reverse osmosis, solvent extraction, (4), and membrane separation (5). However, owing to the operational difficulties and high capital and operational costs, attempts have been made to develop new technologies for cost effective and safe methods to remove toxins from industrial effluents such as polymer assisted ultra filtration, (6, 7), sorption onto fire clay (8), polysaccharides (9, 10), wood pulp (11), wood pulp (N), brown coals (12) and polymeric hydrogels (13–15). Out of these, synthetic polymers have been the focus of research for environmental scientists and polymer chemists due to their characteristic properties like renewable origin, environmental friendly behavior, cost–effectiveness and the ability to carry out almost complete removal. These materials normally function through adsorption, ion-exchange, and chelation mechanisms.

Recently we synthesized poly(acrylamide-co-maleic acid) hydrogels and reported a detailed investigation of their water uptake behavior (16). In this connection, this paper describes the sorption of Cr(VI) ions by the equilibration method onto these hydrogels.

EXPERIMENTAL

Materials

The monomers acrylamide (AAm; purity 99.8%) and maleic acid (MA; analytical reagent grade) were obtained from Hi Media, Mumbai, India. The cross linker N,N′-methylene bisacrylamide (MB), initiator potassium persufate (KPS; analytical reagent grade), and sodium hydroxide flakes (NaOH) were obtained from Research Lab., Pune, India. The monomer acrylamide (AAm) was recrystallized in methanol to remove the inhibitor. The double distilled water was used throughout the investigations.

Synthesis of polymeric hydrogels

The free radical aqueous co-polymerization of AAm and MA in the presence of a cross linker MB and initiator KPS yielded co-polymeric gels as described previously (16). In brief, to synthesize the control set, 20.00 mM of AAm and 0.86 mM of MA and 0.097 mM of crosslinker MB were dissolved in distilled water to give a clear solution with final volume of 5.0 ml. Finally, 0.072 mM of the initiator KPS was added and the resultant solution was transferred into the petri dish and kept in an electric oven (Tempstar, India) at 60°C for a period of 2 h. The gel, so formed, 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 powder of hydrogel was passed through a standard sieve of mesh size 100, having a geometrical mean particle diameter of 150 μm.

All the sorption studies were carried out with these grinded gels. The sample shall be designated as HG (3.92), where the number in parenthesis is the percent mole fraction of the monomer MA in the feed mixture.

FTIR Spectral Analysis

The FTIR spectra of the sorbent was recorded on a Shimadzu 8201 PC spectrophotometer using KBr pallets.

Sorption Studies

Batch mode sorption studies were carried out by agitating 20 ml of $Cr_2O_7^{2-}$ solution of desired concentration with 0.10 g of grinded 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 pre-determined time–intervals, the sorbent was separated by filtration and the supernatant was analyzed spectrophotometrically (17) for the remaining concentration of chromium in solutions.

RESULTS AND DISCUSSION

Mechanism of Cr(VI) Uptake

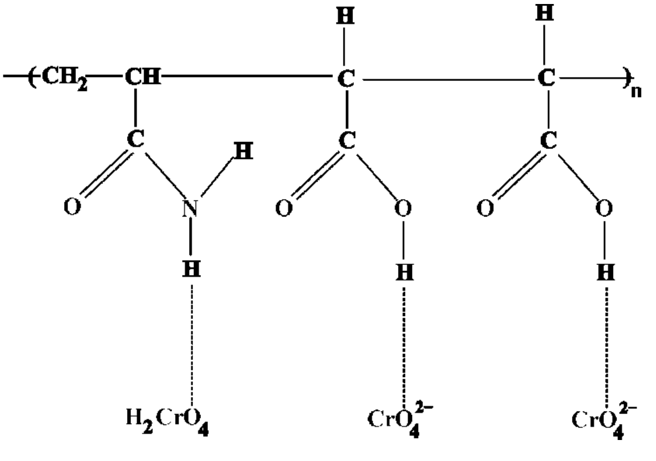
In the present investigation, since the highly acidic solution of potassium dichromate (pH 2.0) has been brought into contact with the poly(acrylamide-co-maleic acid) gel particles, the H-bounding interactions seem to be responsible for the uptake of chromium. It is well known that dichromate ions exist in different equilibria depending upon the pH of the solution (18); for example the following equilibrium exists at pH range 2–6:

$$H_2C_rO_4 \leftrightharpoons 2H^+ + CrO_4^{2-}$$

Therefore, in the light of the above fact, the binding of chromium with co-polymeric gel particles may be due to the following:

(i) The highly electronegative oxygen atoms present in the sorbate molecules may bind with corresponding H-atoms of sorbent molecules through H-bonding interactions as shown in Scheme 1. It can be seen clearly that electronegative oxygen atoms of H_2CrO_4 and CrO_4^{2-} binds through H-bonding with hydrogen atoms present in carboxylic and amide groups of macromolecular chains of copolymeric gels.

(ii) One more reason for the uptake of chromium seems to be the binding of electron rich O and N species of sorbent molecules with Cr^{3+} in the highly acidic region. It has been a well established fact (19) that the presence of organic species in the sorbent system results in the partial conversion of $Cr_2O_7^{2-}$ into Cr^{3+} in the pH range 2–6. Therefore, in the present study the binding of electron rich O and N atoms with Cr^{3+} can not be ruled out. However, in order to confirm this, we carried out FTIR spectral analysis of plain and chromium–loaded sorbent (see Fig. 1). It can be seen clearly that in the finger print region of 400 cm^{-1}–600 cm^{-1}, presence of Cr(III)-N and Cr(III-O stretching vibrations confirm the binding between -COOH and



Scheme 1. Interactions between chromium (VI) and hydrogel.

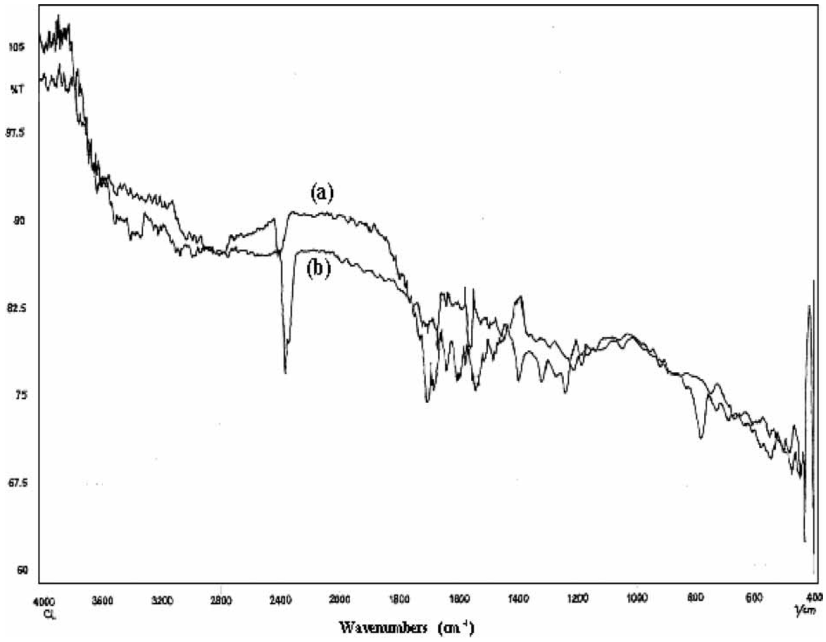


Figure 1. FTIR spectrum of (a) plain and (b) chromium – loaded polymers.

-CONH$_2$ group with Cr(III). In this way, the chemical sorption seems to be the major cause for the observed chromium uptake.

Effect of Contact Time and Temperature

Figure 2 depicts the dynamic sorption of Cr(VI) into a co-polymeric absorbent as a function of time at three different temperatures, namely 15, 35, and 50°C, with initial Cr(VI) concentration of 20 mg l^{-1}. It is clear that the amount of Cr(VI) sorbed increases with contact time and finally attains maximum value. At 15°C the chromium uptake attained saturation value in 300 min while it took almost 540 min to obtain equilibrium sorption at 35 and 50°C (data has been shown for only 350 min). Moreover, the sorption increases with increase in temperature, thus indicating an endothermic sorption process and, the equilibrium time is observed to be independent of temperature. It is also worth mentioning that the removal of Cr(VI) ions increases from 27.00% to 74.00% with the increase in temperature from 15 to 50°C. The observed increase in sorption with temperature may be attributed to the increased coordination between Cr^{3+} and electron rich N and O atoms of sorbent molecules. Here it is worth mentioning that if the H-bonding interactions were the major cause for the sorption process then with the rise of the temperature the extent of the sorption should have been

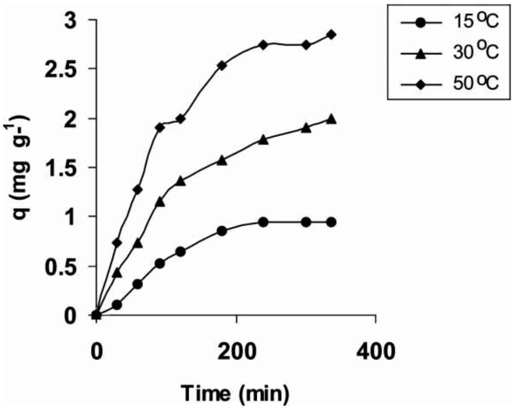


Figure 2. Effect of contact time and temperature on the Cr(VI) uptake by copolymeric sorbent.

decreased. However, the observed increase in extent of the sorption with temperature indicates that coordination between chromium and the electron rich species of sorbent molecules seems to be the governing factor in the present case.

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 (20) of an equilibrium type:

$$\text{Sol.} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{Sorb} \tag{1}$$

where both the reactions are of the first order. The resultant Lagergren rate equation (21) for the overall sorption process may be given as

$$\ln(1 - q/q_e) = -K't \tag{2}$$

where q and q_e are amount (mg/g) of Cr(VI) sorbed at time 't' and at equilibrium respectively. Moreover, K′ is overall rate constant for sorption and

$$K' = k_1(1 + 1/K_c) = k_1 + k_2 \tag{3}$$

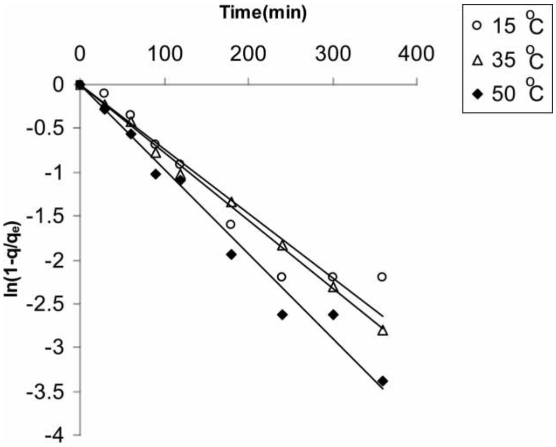


Figure 3. First order reversible kinetic fit of Cr(VI) uptake by poly(AAm-co-SA) gels at different temperatures.

where

$$K_c = \frac{[C_0 - C_e]}{[C_e]} = \frac{k_1}{k_2} \tag{4}$$

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 the ratio of equilibrium concentration of the metal ion in the sorbent to that in the solution phase.

The overall rate constants of sorption (i.e. K') at different temperature were determined from the slopes of the linear plots of ln $(1-q/q_e)$ versus t (see Fig. 3) and are given in Table 1. The values obtained clearly indicate that high temperature favors the sorption of Cr(VI) into 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 have been given in Table 1.

Table 1. Various kinetic parameters for Cr(VI) uptake at different temperatures

Temp. (°C)	K' (min^{-1}) × 10^2	K_1 (min^{-1}) × 10^3	K_2 (min^{-1}) × 10^3	K_{id} (mg g^{-1} min$^{-0.5}$) × 10^2	D (cm^{2}s^{-1}) × 10^{11}
15	0.73	1.94	5.36	1.68	2.68
35	0.77	4.06	3.64	2.98	2.98
50	0.97	7.15	2.55	4.26	3.50

Due to the porous nature of hydrogel, pore diffusion is also expected in addition to surface adsorption. The rate constant of intraparticle diffusion (K_{id}) may be calculated according to the following equation given by Weber and Morris (22),

$$\frac{C_t}{C_0} = K_{id}t^{0.5} \tag{5}$$

where C_t and C_o are the concentrations (mg l^{-1}) of Cr(VI) 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_o and $t^{0.5}$, as shown in Fig. 4. We also calculated the activation energy of sorption E_s, using the logarithmic Arrhenius plot.

$$\ln K_{id} = \ln A - \frac{E_s}{RT} \tag{6}$$

For this, ln K_{id} values were plotted against $1/T$ and E_s was calculated from the slope of the linear plot as shown in Fig. 5. The value of E_s was found to be -20.369 kJ mol^{-1}.

The pore diffusion coefficient $\bar{D}$ for the intraparticle transport of Cr(VI) was calculated assuming the spherical geometry of the sorbent (23) using the following equation:

$$\overline{D} = \frac{0.03r_0^2}{t_{1/2}} \tag{7}$$

where r_o 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.

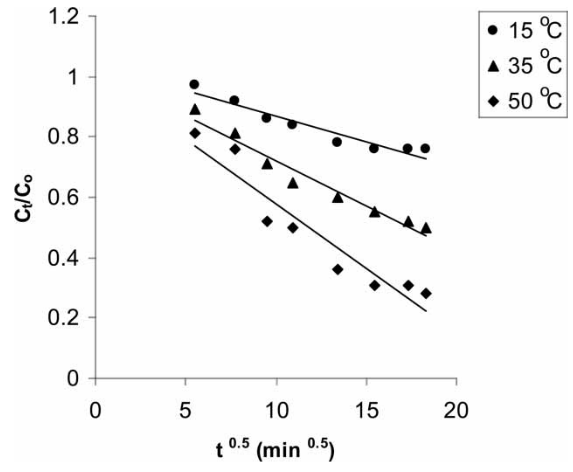


Figure 4. Variation of fractional uptake of Cr(VI) with under root of time at 30°C.

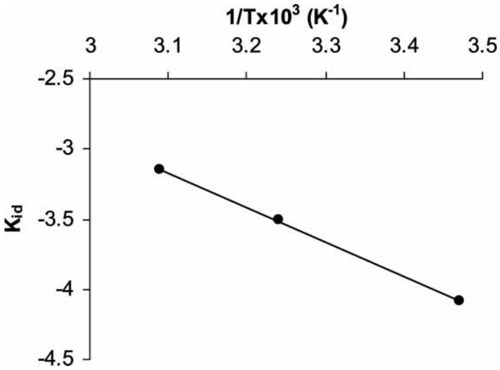


Figure 5. Variation of pore diffusion constant K_{id} of Cr(VI) with reciprocal of temperature (Arrhenius plot).

Sorption Isotherm

The uptake of Cr(VI) by copolymeric sorbent has been analyzed with the help of the Langmuir model. The 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 (see Fig. 6) at three different temperatures, namely 15, 35, 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:

$$\frac{C_e}{q_e} = 0.314C_e + 10.95 \quad \text{at } 15^\circ\text{C} \tag{9}$$

$$\frac{C_e}{q_e} = 0.218C_e + 4.54 \quad \text{at } 35^\circ\text{C} \tag{10}$$

$$\frac{C_e}{q_e} = 0.214C_e + 1.82 \quad \text{at } 50^\circ\text{C} \tag{11}$$

By using these equations, the values of Q_o and b were determined and have been found to be in close agreement with the graphical values as shown in Table 2. The R^2 values for the three temperatures, namely 15, 35, and 50°C, were 0.9759, 0.9905, and 0.9975 respectively. As the latter two values are

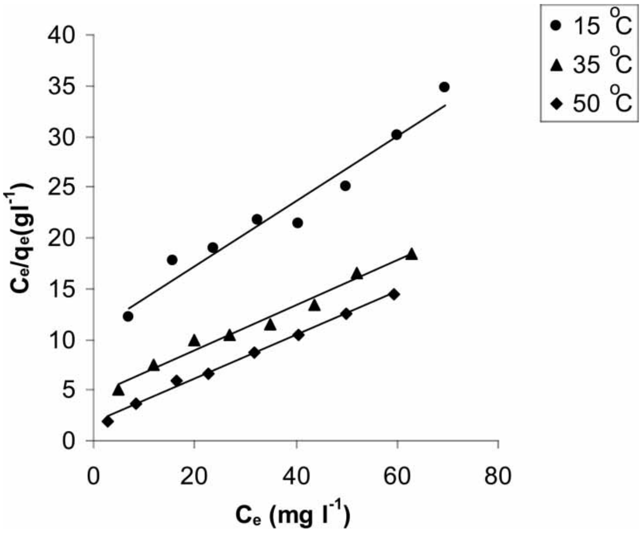


Figure 6. Langmuir isotherm plots for Cr(VI) sorption by copolymeric sorbents.

greater than 0.99, they confirm the suitability of the Langmuir model. However, the model does not appear to fit the experimental data satisfactorily at 15°C.

The apparent heat of sorption ΔH (24) 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.

Table 2. Values of Langmuir constants for Cr(VI) sorption at different temperatures

	Values of Q_o and b at different temperatures			
	Graphical values		Regression values	
Temp. (°C)	Q_o (mg g^{-1})	b (l mg^{-1})	Q_o (mg g^{-1})	b (l mg^{-1})
15	3.12	0.029	3.18	0.028
35	4.52	0.049	4.58	0.048
50	4.67	0.117	4.67	0.117

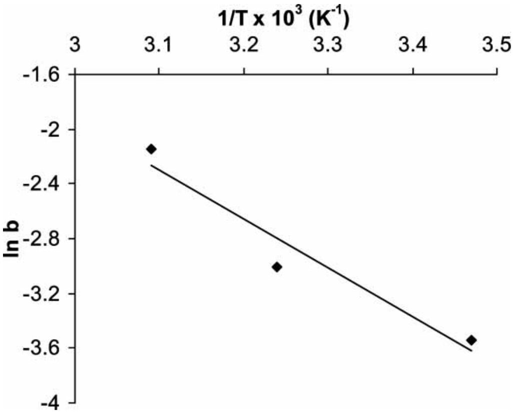


Figure 7. Plot for calculation of apparent heat of sorption ΔH.

The values of ΔH was calculated from the slope of the linear plot between ln b and 1/T (see Fig. 7), and was found to be 29.67 kJ mol^{-1}. The positive value of ΔH indicates the endothermic nature of the sorption process.

Thermodynamic Parameters

We also calculated various thermodynamic parameters (Table 3) with the help of the following equations:

$$\Delta G^\circ = -RT \ln K_c \tag{14}$$

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

and $$\Delta S^\circ = \Delta H^\circ - \Delta; G^\circ/T \tag{16}$$

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.

Table 3. Thermodynamic parameters at different temperatures

Temp. (°C)	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1})
15	2.44	36.87	119
35	−0.26	50.96	166
50	−2.76		

A close look at the values of various thermodynamic parameters reveals some interesting indications about the nature of the sorption process. The value of standard free energy change ΔG° is positive (Table 3) for the sorption process at 15°C while for the higher temperatures 35 and 50°C, negative standard free-energy changes are observed. The positive free-energy change at 15°C suggests the non-spontaneous nature of adsorption process. This may be attributed to the fact that at low temperature coordination between electron rich atoms (N and O) and chromium does not seem to be feasible and the chromium uptake may be due to H-bonding interactions only. However, when the temperature is raised to 35 and 50°C, the standard free energy change acquires a negative value, thus suggesting the spontaneous nature of the sorption. This may simply be attributed to the greater chances of the formation of coordination linkage to higher temperatures. Moreover, positive enthalpy change is indicative of the endothermic nature of the process. The positive value of ΔS° suggests some structural changes in the sorbate and the sorbent, and also reflects the affinity of the sorbent for chromium. In addition, the positive values of ΔS° indicates the increased randomness during the sorption process also. During the uptake of chromium, the sorbed water molecules which are displaced by H_2CrO_4 species, gain more translational entropy than is lost by the sorbate molecules, thus allowing the prevalence of randomness in the system (25).

Effect of Composition of Gels on Cr(VI) Uptake

The composition of co-polymeric hydrogels, used as a sorbent, affects the metal ions uptake in a significant way. The change in composition not only affects the number of binding sites available for sorbate molecules but it also influences the degree of swelling of sorbent gels which, in turn, affects the extent of sorption. In order to investigate this aspect, we synthesized a number of hydrogels by varying the concentration of maleic acid in the range 0.17 to 1.03 mM, and studied uptake of Cr(VI) from its solutions of initial concentration 20 mg l^{-1} at 35°C. The results, as depicted in Fig. 8, clearly indicate that the amount of Cr(VI) sorbed into hydrogels increases with maleic acid content upto 0.86 mM and with further increase in concentration of maleic acid, the uptake of Cr(VI) is observed to decrease. The observed findings can be explained in the following way:

Initially, when the concentration of maleic acid is increased, the chromium uptake increases due to increase in the number of electron rich oxygen atoms present in carboxylic groups, which serve as binding sites for sorbate species. At the same time, the increase in carboxylic groups also results in a greater number of H-bonding interactions as discussed previously. These two factors ultimately enhance the chromium uptake. However, when the maleic acid content is increased beyond 0.86 mM, the degree of sorption of Cr(VI) decreases. This may be attributed to the fact

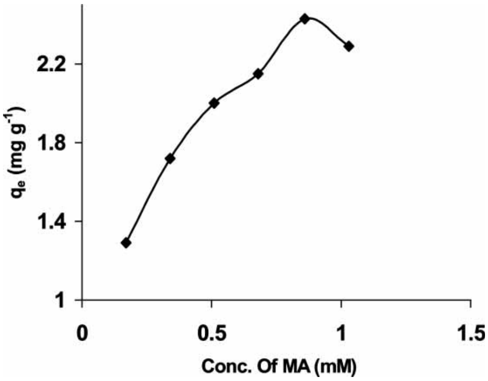


Figure 8. Effect of variation in maleic acid content in the gel on the Cr(VI) uptake.

that as the sorption studies have been conducted in the medium of pH 2.0, the undissociated -COOH groups form intermolecular H-bondings and hence serve as additional crosslinks. This highly crosslinker polymer network not only retards the diffusion of the solvent but it also hinders the diffusion of sorbate species into the network. As a result, the uptake of Cr(VI) begins to decrease. Hence it can be concluded that 0.86 mM of monomer acid seems to be the optimum concentration in the feed mixture for the co-polymeric gels to have the maximum retention efficiency of Cr(VI).

Sorption in the Presence of Fluoride Ions

In order to investigate the effect of the presence of fluoride ions in the aqueous solution on the sorption of Cr(VI) ions into the copolymeric gels, we prepared various 20 mg l^{-1} solutions of Cr(VI) ions containing different concentrations of fluoride ions and studied the sorption of Cr(VI) ions into the gels. The results, as depicted in Fig. 9 clearly indicate that as the concentration of fluoride ions in the solutions increases, the extent of sorption of Cr(VI) ions decreases. This may be attributed to the fact that fluoride ions, being highly electronegative, bind strongly with the sorbent through H-bonding interactions. This results in the decrease in the number of binding sites available for sorbate molecules, thus finally causing decrease in the degree of sorbtion.

Concentration Effect

The dependence of the process of removal of Cr(VI) from the aqueous solution of varying initial concentrations (10–80 mg l^{-1}) is shown in the bar diagram (Fig. 10). It is clear that at very low concentrations sorption is highly effective

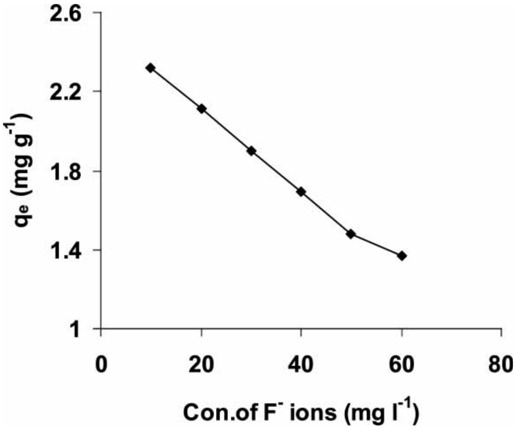


Figure 9. Effect of presence of fluoride ions in the solution on the Cr(VI) uptake.

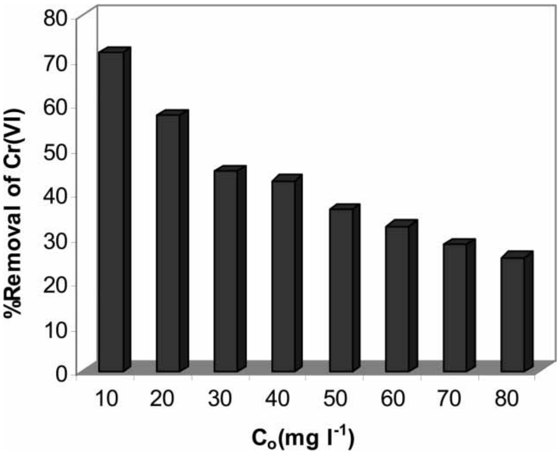


Figure 10. Percent removal of Cr(VI) ions.

and the percent Cr(VI) sorbed decreases with increase in the initial concentration. This may simply be attributed to the fact that for lower concentrations, the ratio of the 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 Cr(VI) decreases.

CONCLUSION

From the above study it can be concluded that poly(acrylamide-co-maleic acid) hydrogels prove to be efficient (72.00% removal of Cr(VI) from

20 mg l^{-1} solution by gel containing 3.9 mole percent of maleic acid) for the removal of Cr(VI) ions by sorption through coordination between O and N atoms of sorbent molecules and Cr^{3+} species. In addition, H-bonding interactions also contribute to the sorption process. The higher temperature favors the sorption process. The positive value of enthalpy change also confirms endothermic nature of the sorption process. Similarly, the positive value of entropy change is indicative of non-spontaneous nature of the process. The presence of other competing ions (e.g. F^- ions) in the solution causes a decrease in the extent of sorption of Cr(VI). The sorption process is found to be highly dependent on the concentration of maleic acid in the copolymeric sorbent.

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