



Chromium (III) removal by weak acid exchanger Amberlite IRC-50 (Na)

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ABSTRACT

Chromium (III) sorption on a weakly macroporous cation exchanger Amberlite IRC-50 (Na) is studied as a function of time and temperature. The rate constant values for chromium (III) sorption are calculated both for film and particle diffusion processes. The temperature is found to have a positive effect on both the diffusional processes. The high values of energy of activation confirm the particle diffusional nature of the process. The pH changes in the system show a competition between the $\text{Cr}(\text{OH})_2^{2+}$ and H^+ ions for the exchange sites of the adsorbent. Equilibrium data are explained with the help of Langmuir equation. Various thermodynamic parameters (ΔH° , ΔS° and ΔG°) from chromium (III) exchange on the resin are calculated.

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1. Introduction

Heavy metals like Cr, Cu, Pb, Mn, Hg, and Cd are common pollutants in soil as well as in water. Due to the greater stability they cannot be degraded and removed from the environment. They are harmful to aquatic life, and also remain a serious public health problem.

Chromium, one of the above toxic metals consists of two stable oxidation states, Cr (III) and Cr (VI) where the later is very toxic to human beings [1]. It is extensively used in pigments and paints, leather tanning, fungicides, ceramic and glass industries. Cr (III) is an essential nutrient for human health also. However, the presence of strong oxidants can change it to harmful Cr (VI) [2].

A lot of work is present in literature on Cr (VI) removal but very limited research work is done on the removal of chromium (III) from aqueous solutions [3]. Many separation techniques have been proposed for the removal of chromium (III) from aqueous solutions, which include solvent extraction, ion exchange, co-precipitation, membrane processes and sorption. Among these methods, ion exchange is highly popular and has been widely practiced for metal ions removal [4,5].

Organic ion exchange resins are found more suitable for the removal of toxic elements due to their faster kinetics, ease of regeneration and high exchange capacity [6]. While a number of studies have been reported for the exchange removal of monovalent and divalent metal cations from aqueous solutions [7–9], very little is

reported about the exchange of trivalent metal cations like Cr^{3+} , Al^{3+} , Fe^{3+} , etc. [10,11]. It was recently studied [5,12,13] that solutions containing Cr^{3+} ions were treated with strong cation exchanger Amberlite IR-120 and the result obtained showed that the resin has a strong affinity for these ions.

The present study, thus, reports a detailed investigation of Cr (III) removal from aqueous solutions using a macroporous weak cation exchange resin, Amberlite IRC-50 under different experimental conditions of metal ion concentration (0.962–19.231 mmol/l) and temperature (293–313 K) using the initial pH values between 2.50 and 3.50.

2. Experimental

All the analytical grade reagents were used without further purification. All the solutions were prepared in doubly distilled water, using Pyrex glass vessels.

Amberlite IRC-50 (H^+) is a macroporous weak acid cation-exchange resin having methacrylic acid-DVB structure and is available in the form of spherical beads. The maximum temperature it can tolerate is 120 °C. It works in the pH range of 5–14. The particle size varies from 0.3 to 1.18 mm. The exchange capacity of the resin is 9.5 meq/g. The moisture content is 10% by weight.

2.1. Conversion of Amberlite IRC-50 (H^+) into Na^+

10 g of Amberlite IRC-50 (H^+) was taken in a burette provided with a glass wool plug. The resin was converted into Na^+ form by treating it with 0.1 M NaCl. The treatment continued until the concentration of the effluents also became equal to 0.1 M. The resin

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was washed with triply distilled water and then placed in air to dry for 24 h. Finally, it was stored in glass-stoppered bottles for further study.

2.2. Ion exchange studies

After air-drying, an exactly weighed amount (0.2 g) of Amberlite IRC-50 (Na) was mixed with 30 ml of CrCl₃·6H₂O solution having concentrations ranging from 0.162 to 19.231 mmol/l which had attained the desired temperature (293–313 K) in a shaker bath for 2 h with the initial pH between 3.50 and 4.50. The stirring rate was 120 rpm. The concentration of Cr (III) in the aqueous phase was analyzed by oxidizing it into Cr (VI) using H₂O₂ as an oxidizing agent in alkaline medium using the method described in the literature [2,14]. The concentration of Cr (III) was also determined using atomic absorption spectrophotometer (PerkinElmer A Analyst 800). The results obtained by the two methods were very close to each other.

Infinite bath method was used to study the kinetics of sorption of Cr (III). An exactly 10 g of Amberlite IRC-50 (Na) was poured in 300 ml solution of Cr (III) having concentration 19.231 mmol/l in a double glass wall cell attached to the water-circulating bath at the desired temperature with the stirring rate of 120 rpm. After different time intervals, 1.0 ml from the mixture was taken in the test tube and analyzed for chromium (III) according to the methods described above.

3. Results and discussion

3.1. Kinetics studies

The results of kinetic study are represented in Fig. 1. The equilibrium is attained within 120, 90 and 60 min at 293, 303 and 313 K respectively indicating that the rate of reaction increases with the rise in temperature.

The kinetics of the chromium sorption on Amberlite IRC-50 (Na) can be described with the help of two types of equations, film diffusion and particle diffusion equations. The expression for the film diffusion equation [12] is given below,

$$-\ln(1 - F) = K_u t \tag{1}$$

where *F* is the ratio of amount adsorbed after time *t* to the amount adsorbed at equilibrium and *K_u* is the rate constant. According to Eq. (1), when the kinetic data obtained for a series of *F* values are plotted against *t*, a straight line is obtained having a slope equal to rate constant as shown in Fig. 2. This indicates that on Amberlite IRC-50 (Na) resin, the mechanism of chromium sorption is the dif-

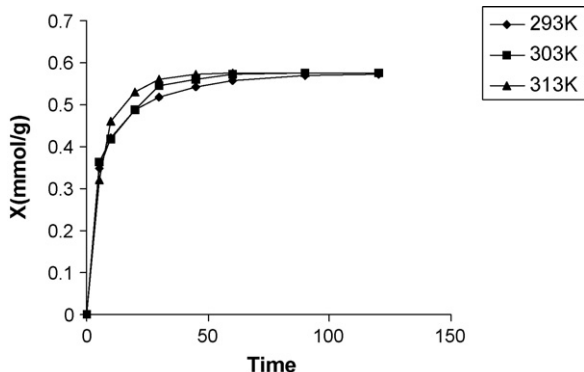


Fig. 1. Amount of chromium (III) adsorbed as a function of time on Amberlite IRC-50 (Na) at different temperatures, (concentration = 19.231 mmol/l).

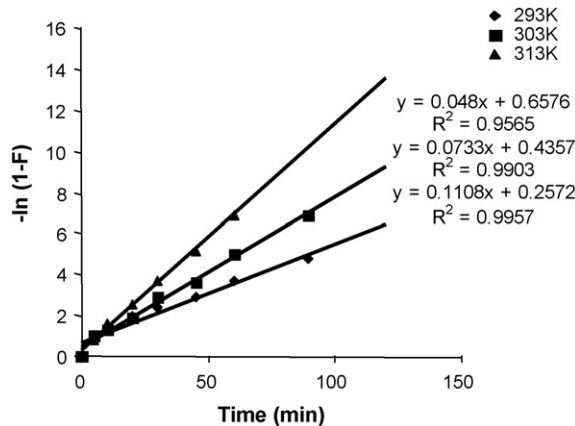


Fig. 2. Film diffusion plots for Amberlite IRC-50 (Na) at different temperatures, (concentration = 19.231 mmol/l).

fusion of chromium through a thin covering liquid film. Similarly for particle diffusion equation, the *Bt* values can be calculated by using the equations given below,

$$Bt = -2.30258 \log(1 - F) - 0.49770 \tag{2}$$

$$Bt = 6.28318 - 3.2899F - 6.28318(1 - 1.0470F)^{1/2} \tag{3}$$

where *B* is equal to $D\pi^2/r^2$, \bar{D} being the particle diffusion coefficient and *r*² its radius.

Eq. (3) is used for values of *F* from 0 to 0.85 and Eq. (2) for values of *F* from 0.86 to 1 according to simplification given by Reichenberg [15]. The *Bt* values calculated from Eqs. (2) and (3) are plotted against *t* and again a straight line is obtained. The values of rate constant *B* are calculated from the slope in Fig. 3. This shows that sorption is also limited due to the diffusion inside the resin particle. The values of *K_u* and *B* obtained from both diffusional equations at different temperatures are presented in Table 1.

The energy of activation (*E_a*) of both diffusional processes can be calculated using Arrhenius equation as,

$$\ln K = \ln A - \frac{E_a}{RT} \tag{4}$$

where *K* is either film (*K_u*) or particle diffusion (*B*) rate constant, *A* is Arrhenius factor, *T* is the absolute temperature and *R* is the molar gas constant.

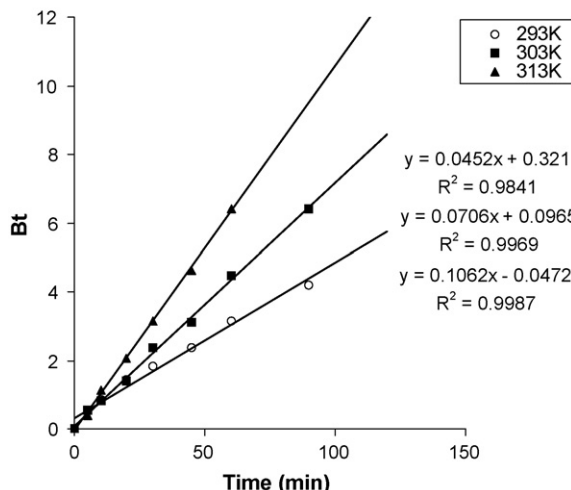


Fig. 3. Particle diffusion plots for Amberlite IRC-50 (Na) at different temperatures, (concentration = 19.231 mmol/l).

Table 1
Values for film and particle diffusion process on Amberlite IRC-50 (Na)

Temperature (K)	Rate constants (min ⁻¹)		Activation energies, E _a (kJ/mol)	
	Film diffusion (K _u)	Particle diffusion (B)	Film diffusion	Particle diffusion
293	0.048	0.045		
303	0.073	0.071	31.90	32.60
313	0.111	0.106		

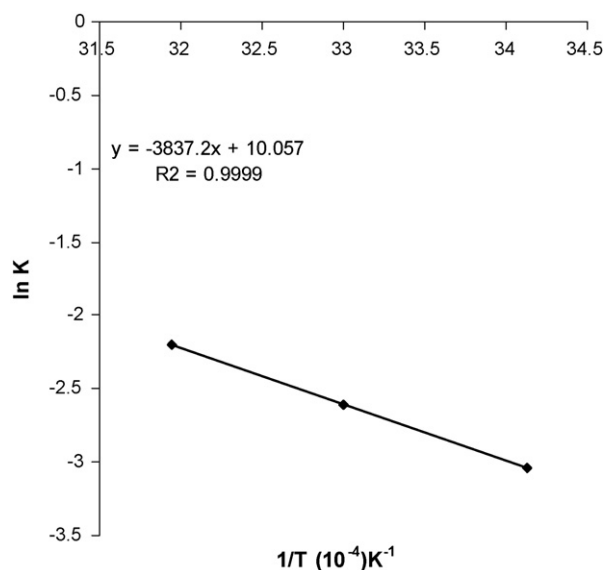


Fig. 4. Arrhenius plots for film diffusion process on Amberlite IRC-50 (Na) at different temperatures.

The plots of $\ln K$ versus $1/T$ according to Eq. (4) for film diffusion process are shown in Fig. 4 where a straight line is obtained with a slope and intercept equal to E_a/R and $\ln A$. Similar behavior was also observed for particle diffusion process. The values of activation energies for the diffusion processes are also given in Table 1. The rate constants and activation energies obtained both for the film and particle diffusion are very close to each other, which indicates that kinetics of chromium sorption on Amberlite IRC-50 (Na) is governed by a mixed diffusion process, i.e. both the film and particle diffusions. Kocaoba and Akcin [14] recently proposed similar mixed diffusion during kinetic investigation of Cr (III) removal from aqueous solutions using cation exchanger Amberlite IRC-718.

In order to determine the exact mechanism of the process, the interruption test was performed by separating the resin beads from the Cr (III) solution after a time interval of 20 min and remixing again after 10 min. The results shown in Fig. 5 reveal an increase in

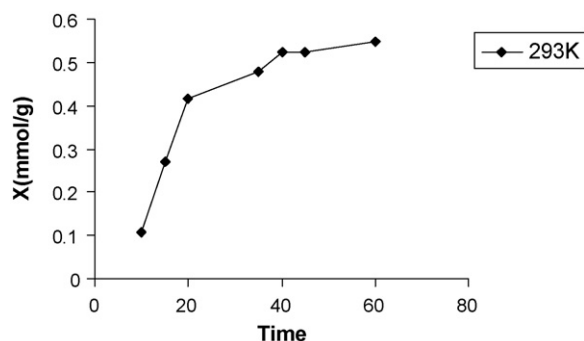


Fig. 5. Interruption test for Cr (III) ions removal.

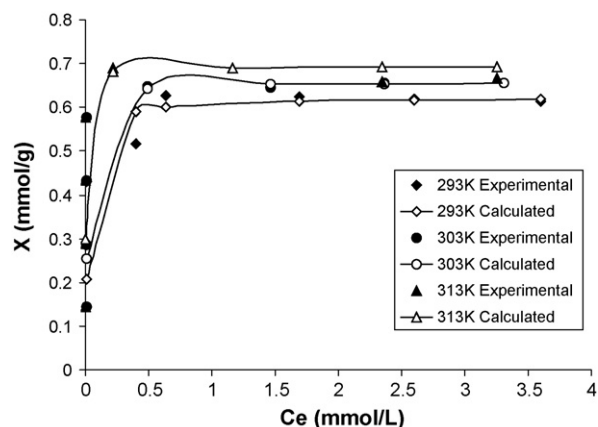


Fig. 6. Chromium (III) sorption isotherm on Amberlite IRC-50 (Na) at different temperatures.

uptake after the interruption, indicating the predominance of the particle diffusion as suggested elsewhere [16].

3.2. Equilibrium studies

Sorption of chromium (III) on Amberlite IRC-50 (Na) is studied at different temperatures (293, 303 and 313 K) employing concentrations in the range of 0.962–19.231 mmol/l. The results of the study are shown in Fig. 6, which shows that Cr (III) sorption on Amberlite IRC-50 (Na) increases with increase in the initial concentration and temperature. The maximum exchange capacity is found to be 0.694 mmol/g at 313 K, which is higher than 0.588 and 0.610 mmol/g for Diaion CR 11(Na) and Amberlite IRC-86 (Na) respectively reported by Sofia et al. [17] for the removal of Cr (III).

The increase in chromium (III) sorption is accompanied by the increase in equilibrium pH of the solution with respect to initial pH. The pH changes shown in Table 2 indicate the decrease in initial pH of the Cr (III) solutions with concentration before contact with the resin, which shows the hydrolysis of chromium (III) according to reaction (5). This reaction forms protons and divalent $\text{Cr}(\text{OH})^{2+}$ ions, which results in an increase in the acidity of solutions. However, the increase in equilibrium pH after sorption reveals that both H^+ and $\text{Cr}(\text{OH})^{2+}$ ions are sorbed by the resin. This pH increase after sorption is particularly greater in solutions, which contain low concentrations of Cr (III). It reveals that H^+ are taken preferentially by the resin in solutions that contain low concentrations of Cr (III).

The uptake of H^+ along with $\text{Cr}(\text{OH})^{2+}$ by the resin was also confirmed by the following experiments. 30 ml of 100 mg/l of Cr (III) solution were taken in three different conical flasks to which 0.2 g of the resin Amberlite IRC-50 (Na) was added. In one of the flask, the pH was adjusted to 3 after 2 h when sorption of the Cr (III) was almost complete. In the second flask, after putting the resin, the pH

Table 2
Temperature effect on pH changes during chromium (III) sorption on Amberlite IRC-50 (Na)

pH _i	pH _e		
	293 K	303 K	313 K
3.447	6.616	6.449	6.637
3.244	5.779	6.342	6.028
3.157	5.690	5.790	6.014
3.100	4.847	5.182	5.348
2.922	4.381	4.458	4.129
2.783	4.067	4.210	3.991
2.670	3.992	4.136	3.768
2.580	3.789	3.828	3.671

pH_i, initial pH; pH_e, final pH.

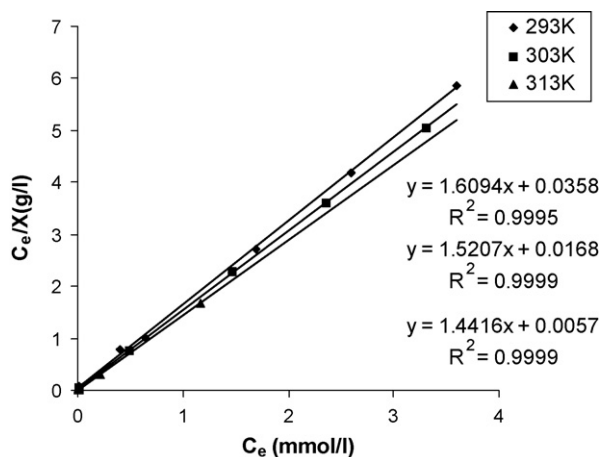
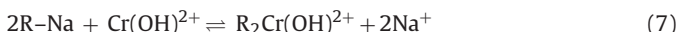
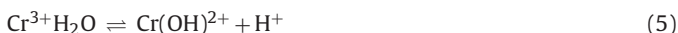


Fig. 7. Langmuir plots for chromium (III) sorption on Amberlite IRC-50 (Na) at different temperatures.

was adjusted immediately to 3, while the third flask was left without adjustment for 2 h. The amount of Cr (III) sorption was found to be the highest (0.287 mmol/g) in the third flask where no pH adjustment was made. Similarly, the sorption was higher (0.242 mmol/g) in the system where the pH was adjusted after 2 h than in the system where pH was adjusted immediately after the resin addition (0.188 mmol/g). The amount of Cr (III) adsorbed in the three different systems shows clearly the competition between Cr (III) and H⁺ ions for the resin phase. As such, the following mechanisms can be proposed for the sorption of chromium (III) by Amberlite IRC-50 (Na),



Similar competition was also observed by Mohan et al. [18] and Chanda and Rempel [13] while studying Cr (III) sorption on weak acid exchangers.

The Langmuir equation was applied to the present data to determine the maximum exchange capacity at different temperatures. As is evident from Fig. 7, the experimental data fitted to the linear form of the Langmuir equation expressed in the form [19,20].

$$\frac{C_e}{X} = \frac{1}{K_b X_m} + \frac{C_e}{X_m} \quad (8)$$

where C_e is the equilibrium concentration of metal ions in the solution, X is the amount of metal ions sorbed per unit weight of the resin, X_m is the maximum sorption, K_b is the binding constant, computed from the slope and intercept of the lines in Fig. 7. It can be seen from Table 3, the values of X_m are in close agreement with the experimental data which show the Langmuir model is the best applicable. The K_b values are found to increase with temperature showing the greater interaction of the chromium (III) ions with the resin. The data given in Fig. 6 show that the experimental values of sorption are close to the calculated values using the Langmuir constants obtained from Fig. 7.

Table 3
Maximum adsorption capacities (X_m) and binding energy constants (K_b) according to Eq. (8) at different temperatures

Temperature (K)	X_m (mmol/g)	K_b (l/g)	R^2
293	0.621	44.96	0.999
303	0.658	90.52	0.999
313	0.694	252.91	0.999

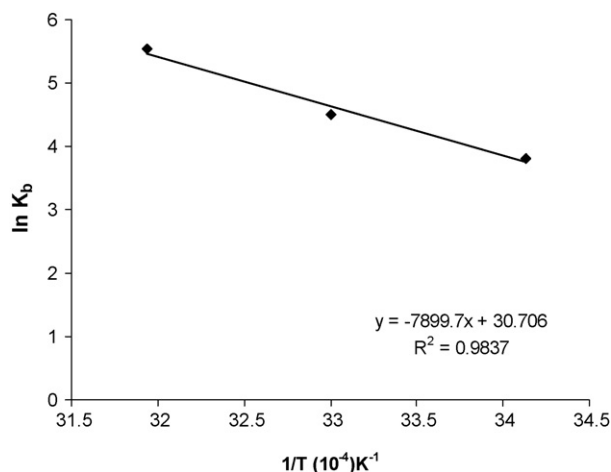


Fig. 8. Plots of $\ln K_b$ versus $1/T$ for the sorption of Cr (III) onto Amberlite IRC-50 (Na).

Table 4
Gibbs free energy, enthalpy and entropy changes for Cr (III) sorption on Amberlite IRC-50 (Na)

Temperature (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol)
293	-9.122		
303	-11.675	65.68	255.29
313	-14.228		

The standard enthalpy and entropy changes for metal ion removal can be estimated by using the well-known thermodynamic equation

$$\ln K_b = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (9)$$

where K_b is the binding energy constant (l/g), T is the absolute temperature (K), R is the molar gas constant (J/K mol). The standard free energy change (ΔG°) of the process can be calculated by the equation,

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (10)$$

The plots of $\ln K_b$ versus temperature according to Eq. (9) give a straight line with slope and intercept equal to $\Delta H^\circ/R$ and $\Delta S^\circ/R$ as shown in Fig. 8. The values of ΔS° , ΔH° and ΔG° thus determined are reported in Table 4. The negative values of ΔG° are obtained at different temperatures, which increase with the increase in temperature (Table 4). The increase in negative values of ΔG° with increasing temperature shows that sorption of chromium (III) becomes more spontaneous at higher temperatures. The positive values of ΔH° and ΔS° indicate the process of Cr (III) sorption is endothermic and also spontaneous in nature. The positive values of ΔS° show the dehydration of the metal cations before their sorption by the resin Amberlite IRC-50 (Na). Similar trends for the values of ΔH° , ΔS° and ΔG° were also observed using wine processing waste and bentonite for Cr (III) removal elsewhere [21,22].

4. Conclusions

From the discussion above, it may be concluded that the weak acid exchanger Amberlite IRC-50 (Na) has high exchange capacity towards the Cr (III) ions in the acidic medium. The resin prefers the H⁺ ions at low concentration of Cr (III) in the aqueous solutions. The energy of activation shows the process to be diffusional in nature. The thermodynamic parameters illustrate that the process is endothermic and spontaneous.

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