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Kinetics, thermodynamic, and adsorption studies on removal of chromium(VI) using Tulsion A-27(MP) resin

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ABSTRACT

The kinetics, thermodynamic, and adsorption studies on removal of chromium(VI) from aqueous and in presence of industrial solvents 2-methoxyethanol and 2-ethoxyethanol with macroporous resin Tulsion A-27 was studied at varying concentration of Cr(VI), adsorbent dosage, pH, contact time, and temperature. Batch shaking sorption experiments were carried out to evaluate the performance of Tulsion A-27(MP) anion exchange resin in the removal of Cr(VI) from aqueous and mixed aqueous solvents, 2-methoxyethanol and 2-ethoxyethanol. The concentrations of Cr(VI) in aqueous and mixed aqueous solvents were determined by UV-Visible spectrophotometer. As the adsorption process is pH dependent, it showed maximum removal efficiency of Cr(VI) in the pH range of 5–6 for an initial chromium concentration of 0.0011 M. Effect of temperature on the equilibrium constant was studied and the thermodynamic parameters were evaluated. Kinetic experiments revealed the dominance of adsorption. The sorption models, Langmuir and Freundlich adsorption isotherms, were discussed on amount of Cr(VI) uptake. The resin was analyzed by infrared spectroscopy and scanning electron microscopy before and after the adsorption process. The sorption of Cr(VI) by the anion exchange resin was reversible and so it has good potential for the removal/recovery of Cr(VI) from aqueous and mixed aqueous solvents. The anion exchange resin can be used for the efficient removal of Cr(VI) from water and wastewater.

Keywords: Chromium removal; Ion exchange resin; Adsorption; Kinetics; Thermodynamic parameters

1. Introduction

Heavy metals are discharged into the environment in large quantities. These metals are of special concern because they are nonbiodegradable posing a number of environmental problems [1]. Among these, Cr, Ni, Zn, Cu, and Cd are considered as priority metals from the point of view of potential health hazards to human beings [2–5]. Chromium and its compounds are widely used in many industrial processes such as chrome plating, textile dyeing, pigmenting, paper and pulp, tanning, rubber, battery, anodizing, photographic material, etc. The wastewater resulting from these processes contain large amounts of chromium which is harmful for human health and environment [6,7]. Industrial effluents from chrome plating, tanning, paper and pulp may contain chromium

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concentration ranging from 10 to 100 mg/L [8]. Chromium exists in various oxidation states from +2 to +6. Among these, +3 and +6 states of chromium compounds are most commonly used in practice [9]. Hexavalent chromium is oncogenic and produces 1,000 times more toxicity than trivalent chromium [8,10]. Hexavalent chromium compounds are classified in water hazard as class three and are very toxic even at low concentrations for living organisms [11]. The mechanism of toxicity is pH dependent. Contrarily, trivalent chromium in small doses is required as a dietary component for human, plant, and animal metabolism. Deficiency of chromium in human beings leads to certain types of diabetes, cardiovascular diseases, and nervous system disorders [12]. Through contaminated food and drinking water, human beings are exposed to excessive amount of Cr(VI). Hexavalent chromium compounds are mobile and hence they readily enter into underground waters [13] and make them toxic. The recommended limit of hexavalent chromium in drinking water is 0.05 ppm [14–18].

Recently, there has been a growing concern with environmental protection and therefore the removal of hexavalent chromium from water and wastewater is of great importance due to its toxicity [19–21]. Several methods are reported in literature for the removal of toxic metal ions from aqueous solutions [22,23]. These include adsorption, precipitation, coagulation, phytoextraction, ultrafiltration, membrane separations, reverse osmosis, solvent extraction, electrodialysis, and evaporation [24–26]. However, most of these methods are not suitable for the treatment of water because of the drawbacks such as high capital and operational costs or the disposal of the residual metal sludge [27]. Among all these techniques, ion exchange is an user-friendly technology for the removal of Cr (VI) [28] as it reduces the problem of sludge disposal. Ion exchange resins have been widely used to remove toxic Cr(VI) ions from water and wastewater. A number of investigators have studied the removal of hexavalent chromium by ion exchange [29,30]. Ion exchange is one of the most efficient and economical methods for the removal of toxic ions [31–33]. Due to high chemical and mechanical stability and high ion exchange capacity, anion exchange resins are used to remove Cr(VI) from water and wastewater.

The objective of the study was to remove Cr(VI) from water and water–organic solvent mixed media using a strong base anion exchanger Tulsion A-27(MP). In addition to kinetic and thermodynamic parameters, the effect of chromium concentration, temperature, pH, agitation time, resin dosage, and dielectric constant of the medium were also studied. The macroporous resin Tulsion A-27 has a greater porosity and hence it was used for separation of Cr(VI). The solvents, 2-methoxyethanol and 2-ethoxyethanol, were used in the present study to understand the effect of organic solvent on removal of Cr(VI) in mixed media as they are widely used as industrial solvents. They are mainly used in the manufacture of paints, varnishes, and dyes as they are easily miscible with water, which makes possible entry into water and wastewater [34,35].

2. Experimental

2.1. Materials

Exchange studies of chromate were carried out using deionized water free from CO_2. Strong base macroporous resin Tulsion A-27(MP) was supplied by Thermax Limited, Pune, India. The physical properties of the resin are presented in Table 1. The resin was reconditioned and air dried before carrying out the experimental work.

All the chemicals and reagents used were of analytical grade. The solvents, 2-methoxyethanol and 2-ethoxyethanol, were obtained from Acros Organics, USA. Molar solutions of K_2CrO_4 were prepared in water and water–organic solvent mixed media.

2.2. Methods

Batch ion exchange studies were carried out by stirring the 30 ml of chromate solutions with 0.025 g of resin Tulsion A-27(MP) for a period of 6 h at controlled temperatures of 303, 313, and 323 K in a thermostatic water bath incubator shaker (Toshiba make) until the equilibrium was reached.

After the equilibration, the resin was separated by filtration and the supernatant liquid was analyzed spectrophotometrically to determine the concentration of Cr(VI) with 1,5-diphenyl carbazide method [30] using a UV-Vis spectrophotometer (Varian Cary 50 Bio) (λ: 540 nm).

Table 1
Characteristic properties of strong base anion exchange resin Tulsion A-27(MP)

Resin	Tulsion A-27(MP)
Type	Strongly basic, Cl^- form
Matrix structure	Styrene–DVB
Functional group	Quaternary ammonium-I
Total exchange capacity	0.82 m.eq./250 g
Moisture content	43.5%
Stability	80°C
pH range	0–14
Screen size	16–50 US mesh

The ion exchange reaction of Cr(VI) can be depicted as:

$$2\mathrm{RCl} + \mathrm{CrO}_4^{2-} \rightleftharpoons \mathrm{R}_2\mathrm{CrO}_4 + 2\mathrm{Cl}^- \quad (1)$$

in which R represents the resin matrix.

Equilibrium distribution coefficient (K_d) was calculated [32] using Eq. (2).

$$K_d = \frac{q_e}{C_e} \quad (2)$$

where q_e is the amount of metal ion adsorbed at equilibrium (mol) and C_e is the equilibrium concentration of metal ion in solution (mol).

Equilibrium distribution coefficients for Cr(VI) on Tulsion A-27(MP) anion exchange resin in water and water-2-methoxyethanol and water-2-ethoxyethanol are represented in Table 2.

Cr(VI) recovery factor was calculated using the Eq. (3).

$$\%R = \frac{C_a}{C_o} \times 100 \quad (3)$$

where C_a is the concentration of Cr(VI) adsorbed on the resin (mol) and C_o is the initial concentration of Cr(VI) (mol).

3. Results and discussion

3.1. Fourier transform infrared spectroscopic analysis

Fourier Transform infrared spectroscopic (FT–IR) spectra of resin Tulsion A-27(MP) before and after adsorption process are shown in Fig. 1. The FT–IR spectra after adsorption process shows changes in the absorption peaks of 3,615, 3,741, and 3,846 cm^{-1} corresponding to –NH and –OH vibrational bands; new peaks were observed at 1,380 and 1,415 cm^{-1} corresponding to vibrational bands of carboxylic groups. These changes in absorptions bands in the FT–IR spectra of resin after adsorption indicated that –OH, –NH, and carboxylic groups of resin play a vital role in the adsorption Cr(VI) [36–38].

3.2. Scanning electron microscopy of Tulsion A-27(MP)

Scanning electron microscopy (SEM) is widely used to study the surface morphology of the adsorbent materials. SEM images of resin Tulsion A-27(MP) were obtained before and after adsorption of Cr(VI) (Figs. 2(a) and 2(b)). The surface morphology of the resin shows that the pore diameter of the resin was from 1 to 5 μm and this pore size was retained after adsorption process. This clearly indicated that the surface morphology was not much affected by the adsorption process.

Table 2
Equilibrium distribution coefficients for chromate/chloride exchange on Tulsion A-27(MP) in water and water–organic solvent mixed media at different temperatures

	Temperature (°C)	Solvent composition in %	log K_d
2-Methoxyethanol	30	00	1.8490
		20	2.1008
		40	2.0688
		60	1.3914
		80	1.2791
	40	00	1.8350
		20	1.9713
		40	1.8557
		60	1.6103
		80	1.2990
	50	00	1.7281
		20	1.9476
		40	1.8627
		60	1.6674
		80	1.3841
2-Ethoxyethanol	30	00	1.8490
		20	1.8869
		40	1.8308
		60	1.4536
		80	1.2450
	40	00	1.8350
		20	2.1845
		40	1.9758
		60	1.5161
		80	1.3448
	50	00	1.7281
		20	2.1333
		40	1.8513
		60	1.6972
		80	1.4721

3.3. Effect of temperature

The effect of temperature on adsorption of Cr(VI) in aqueous and aqueous organic solvent mixed media was investigated in the temperature range of 303–323 K. In general, with an increase in temperature the extent of adsorption decreases in higher solvent compositions (Table 2). At higher solvent compositions (40–80%) with an increase in temperature the adsorption of Cr(VI) decreases. This may be due to decrease in solubility of electrolyte at higher solvent

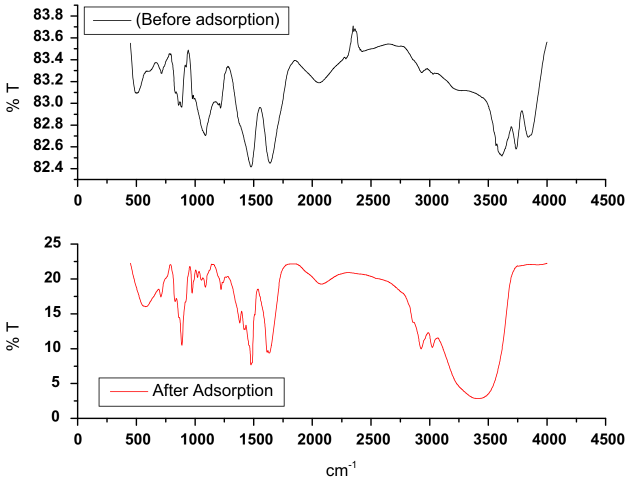
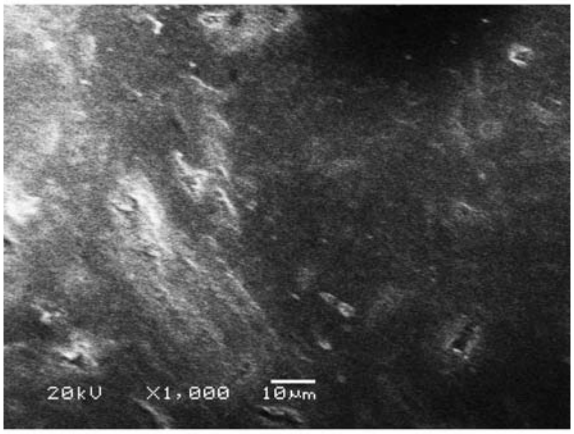


Fig. 1. FT–IR spectra of Tulsion A-27(MP) before and after adsorption of Cr(VI).

(a) Before adsorption



(b) After adsorption

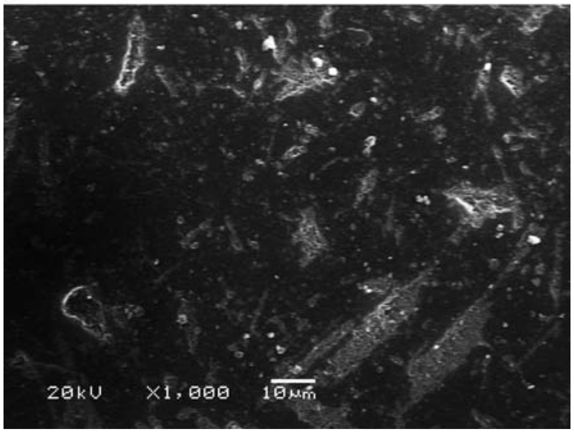


Fig. 2. SEM images of Tulsion A-27(MP) (a) before adsorption of Cr(VI) and (b) after adsorption of Cr(VI).

compositions. There is a decrease in adsorption of Cr (VI) with an increase in temperature indicating the endothermic nature of the process [39]. This may be due to the desorption caused by an increase in thermal energy which in turn increases the mobility of adsorbate [40].

3.4. Evaluation of thermodynamic parameters

The Gibbs free energy change for the chromate/chloride exchange in water-2-methoxyethanol and water-2-ethoxyethanol was calculated in accordance with the following equation:

$$\Delta G = -RT \ln K_d \tag{4}$$

where R is universal gas constant, T is temperature, and K_d is the equilibrium distribution coefficient. With increase in percentage of 2-methoxyethanol and 2-ethoxyethanol in solution, there was an increase in free energy change (Table 3). The negative values of free energy change become less negative with an increase in percentage of 2-methoxyethanol and 2-ethoxyethanol. This implied that adsorption of Cr(VI) was facilitated in lower solvent composition. The change in enthalpy (ΔH) was determined for the exchange process using Van't Hoff equation.

$$\ln \frac{K_2}{K_1} = \frac{-\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{5}$$

where K_1 is the equilibrium distribution coefficient at temperature T_1 and K_2 is the equilibrium distribution coefficient at temperature T_2.

The change in entropy (ΔS) was calculated using the following equation.

$$\Delta G = \Delta H - T\Delta S \tag{6}$$

The values of ΔG, ΔH, and ΔS are represented in Table 3. The negative values of ΔH show exothermic behavior of exchange in aqueous and lower solvent composition. As the concentration of organic solvents increases, the ΔH values become positive indicating the endothermic behavior of exchange. The variation of ΔS along with ΔH, points out changes in enthalpy that brings out randomness in the system. The presence of organic solvent creates a kind of disorder in the structure of water so that the entropy changes in water–organic solvent mixed media. Due to increase in temperature, chemical process such as association of ions in solution was not supported [39] which lead to more randomness.

3.5. Effect of solvent

The present study was carried out to investigate how the increasing percentage of organic solvents

Table 3
Thermodynamic parameters for adsorption of Cr(VI) on Tulsion A-27(MP) in water and water–organic solvent mixed media

	ΔG (kJ mol^{-1})			ΔH (kJ mol^{-1})		ΔS (J K^{-1} mol^{-1})	
	303 K	313 K	323 K	303–313 K	313–323 K	303–313 K	313–323 K
2-Methoxyethanol (%, v/v)							
00	−10.7	−10.9	−10.6	−2.5	−20.6	27.0	−31.0
20	−12.1	−11.8	−12.0	−23.5	−4.5	−37.4	23.1
40	−12.0	−11.1	−11.5	−38.6	1.3	−88.1	39.9
60	−8.0	−9.6	−10.3	39.7	11.0	157.8	66.1
80	−7.4	−7.7	−8.5	3.6	16.4	36.4	77.5
2-Ethoxyethanol (%, v/v)							
00	−10.7	−11.0	−10.6	−2.5	−20.7	27.0	−31.0
20	−10.9	−13.0	−13.2	54.0	−9.9	214.5	10.2
40	−10.6	−11.8	−11.4	−26.3	−24.1	122.0	−39.2
60	−8.4	−9.0	−10.5	11.3	35.0	65.3	141.0
80	−7.2	−8.0	−9.1	18.1	24.6	83.6	104.5

Note: Error ± 5%.

2-methoxyethanol and 2-ethoxyethanol influences the adsorption of Cr(VI). The equilibrium distribution coefficient for chromate/chloride exchange varies with solvent composition as shown in Table 2. The adsorption of Cr(VI) decreases with increase in percentage of organic solvent from 20 to 80%. This may be due to increase in organic solvent composition that decreases the ionization of the electrolyte in solution. As the solvent composition increases, the external solution becomes less water containing and thus decreasing the ionization of the electrolyte causes decrease in adsorption of Cr(VI). This indicates that Cr(VI) prefers more solution phase than resin phase at higher solvent compositions.

There was a continuous decrease in dielectric constant of water from 78.54 to 17.2 and 78.54 to 12.0 upon addition of 2-methoxyethanol and 2-ethoxyethanol, respectively. Accordingly, the magnitude of equilibrium distribution coefficient should decrease with increase in organic solvent content. The experimental data support this context for both the solvents.

3.6. Effect of pH

The adsorption of Cr(VI) depends upon the concentration of hexavalent chromium and pH of the solution. The quaternary ammonium group of strong base anion exchange resin Tulsion A-27(MP) has a significant influence on the adsorption of Cr(VI). The interaction study between 30 ml of 0.0011 M solution of Cr(VI) species and 0.025 g of Tulsion A-27(MP) resin was carried out at various pH values between 4.0 and 8.0. From Fig. 3, it was clear that the removal efficiency of Cr(VI) was maximum (99.55%) in the pH range of 5.0–6.0. At higher pH values, the adsorption of Cr(VI) decreases due to the hindrance caused by OH$^-$ ions by forming a precipitate. At lower pH values, the uptake of Cr(VI) decreases due to the competition between excess of hydrogen ions and Cr(VI) for adsorption sites [41]. In other words, Cr(VI) species at lower pH values forms H_2CrO_4.

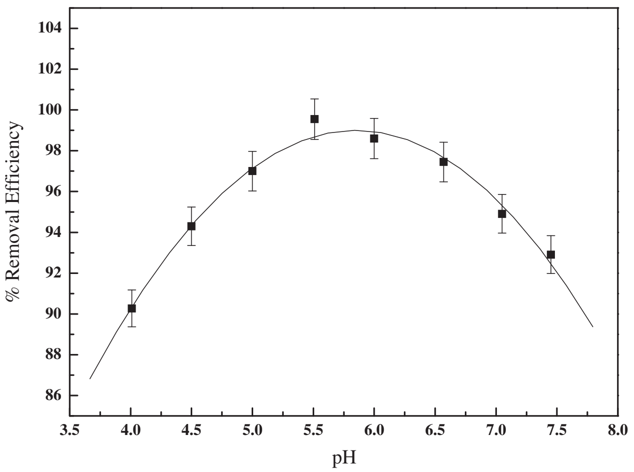


Fig. 3. Effect of pH on adsorption of Cr(VI) by Tulsion A-27(MP).

3.7. Effect of agitation time

An experiment was conducted using 30 ml of 0.0011 M solution of Cr(VI) species to determine the

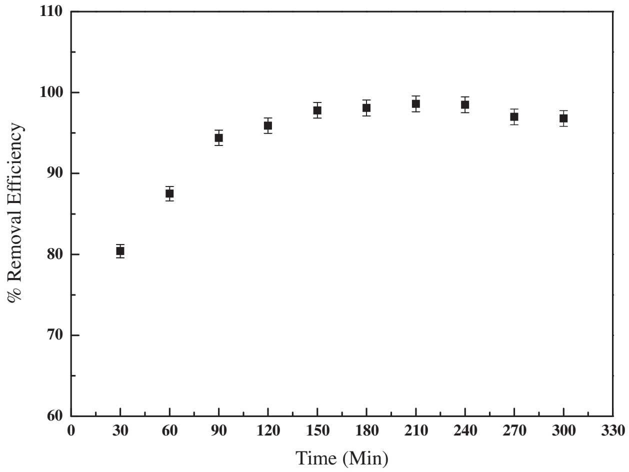


Fig. 4. Effect of agitation time on adsorption of Cr(VI) by Tulsion A-27(MP).

dependence of removal percent of Cr(VI) with time. Fig. 4 shows the uptake of Cr(VI) ions on Tulsion A-27 (MP) as a function of time at neutral pH (7.0). It was observed that the maximum uptake capacity (98.6%) of the resin for Cr(VI) was at 210 min. The adsorption of Cr(VI) increased with time and attained an equilibrium at about 135 min. The percentage of adsorption of Cr (VI) increased rapidly up to 90 min and thereafter, rose gradually before attaining an equilibrium value in 135 min indicating the monolayer coverage of Cr(VI) on the surface of the resin. A further increase in interaction time had a negligible effect on the percentage adsorption of Cr(VI). The removal percentage of Cr(VI) was high in the beginning due to the maximum number of exchange sites available on the resin matrix.

3.8. Effect of resin dosage

An equilibrium capacity study was performed by aliquoting 30 ml of Cr(VI) solutions of concentration 0.0011 M with varying amounts of resin Tulsion A-27 (MP) from 0.010 to 0.060 g and equilibrated for 6 h at neutral pH 7.0. Fig. 5 shows that for the maximum uptake (99.9%) of Cr(VI), the required resin dosage was 0.025 g, beyond which the removal efficiency does not change [33,42]. It may be concluded that by increasing the adsorbent dose the removal efficiency increases but adsorption density decreases, which can be attributed to the fact that some of the adsorption sites remain unsaturated during the adsorption process. It was clear from experimental results that removal of Cr(VI) increases with increase in quantity of the resin because the number of available sites were more and thus providing a greater surface area.

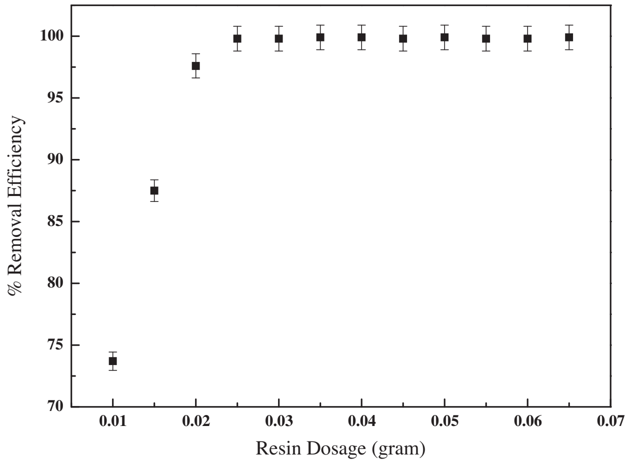


Fig. 5. Effect of resin dosage on adsorption of Cr(VI) by Tulsion A-27(MP).

3.9. Effect of initial concentration

Influence of initial concentration on the removal of Cr(VI) on Tulsion A-27(MP) was studied. The concentration of chromium solution was varied between 0.00077 M and 0.00143 M. It was observed from Fig. 6 that removal of Cr(VI) decreases with an increase in initial concentration of the adsorbate in aqueous medium at 303 K, because in the beginning maximum number of adsorption sites were available for adsorption of Cr(VI) and as the initial concentration increases the resin matrix becomes saturated with adsorption of Cr(VI). Thus results in decrease in removal of Cr(VI). Effect of change in the concentration was observed more in aqueous and lower solvent composition (20 and 40%) whereas effect of concentra-

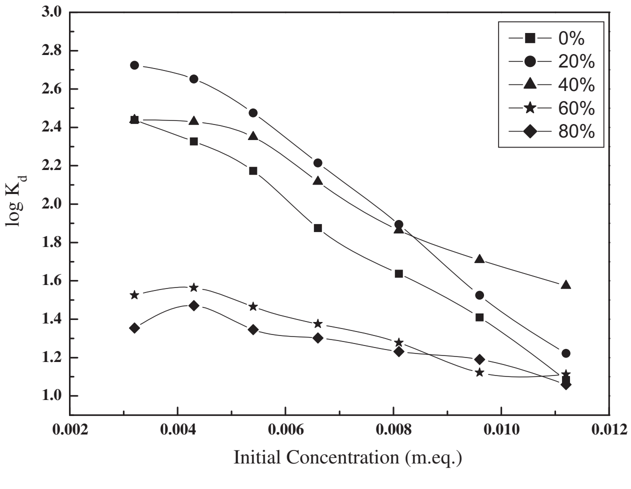


Fig. 6. Effect of initial concentration on adsorption of Cr(VI) from water and water-2-methoxyethanol mixed media by Tulsion A-27(MP) at 303 K.

tion was less on adsorption of Cr(VI) at higher solvent composition (60 and 80%). Similar effect was observed in higher temperature range (Fig. 7).

4. Adsorption isotherms

Sorption process is an interesting topic for the prediction of metal partitioning between a solid and a solution. Langmuir and Freundlich isotherms are useful for the description of heavy metal adsorption by different adsorbents [43,44]. These isotherms relate metal uptake per unit weight of adsorbent, q_e, to the equilibrium concentration of adsorbate in the bulk of the solution, C_e, at constant temperature. The general forms of these models are described below.

The Langmuir isotherm is given as:

$$\frac{C_e}{q_e} = \frac{1}{K_b A_s} + \frac{C_e}{A_s} \tag{7}$$

where A_s (mol/g) and K_b (l/mol) are Langmuir constants related to ion exchange capacity and energy of adsorption, respectively.

The Langmuir isotherm represents one of the first theoretical treatments of nonlinear adsorption. The isotherm is based on the assumptions:

(i) maximum ion exchange depends on the saturation level of a monolayer of adsorbate molecules on the adsorbent surface,
(ii) the energy of ion exchange is constant, and
(iii) there is no transmigration of adsorbate molecules in the plane of the surface [8].

The data for the adsorption of Cr(VI) by the resin were processed in accordance with a linear form of the Langmuir equation. The linear model described the accumulation of a solute by the adsorbent was directly proportional to the concentration of the solution as shown in Fig. 8. The Langmuir isotherm applies to ion exchange on a completely homogeneous surface with negligible interaction between adsorbed molecules. The Langmuir isotherm provided an excellent fit to the equilibrium adsorption data. The obtained results showed that the resin has higher capacity and affinity for the removal of Cr(VI) from the solutions under the studied conditions.

The adsorption of Cr(VI) on the ion exchange resin was described by Freundlich isotherm. The Freundlich isotherm is the most widely used nonlinear sorption model and gives the relationship between the amount of metal adsorbed per unit mass of the adsorbent (x/m) and the concentration of the metal at equilibrium (C_e).

The general form of Freundlich isotherm is:

$$\frac{x}{m} = kC_e^{\frac{1}{n}} \tag{8}$$

where x is the amount of metal adsorbed (mmol), m is the amount of adsorbent (g), C_e is the equilibrium concentration (mmol), and k and n are Freundlich constants representing adsorption capacity and intensity of adsorption, respectively. The logarithmic form of the equation is written as:

$$\log\left(\frac{x}{m}\right) = \log k + \frac{1}{n}\log C_e \tag{9}$$

Using the Freundlich Eq. (9) the relationship between the adsorption capacity of the resin and concentration of Cr(VI) at equilibrium was analyzed (Fig. 9). Param-

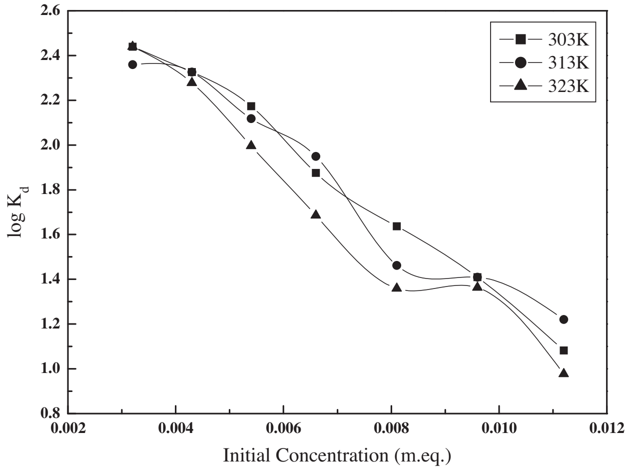


Fig. 7. Effect of initial concentration on adsorption of Cr(VI) from water by Tulsion A-27(MP) at different temperatures.

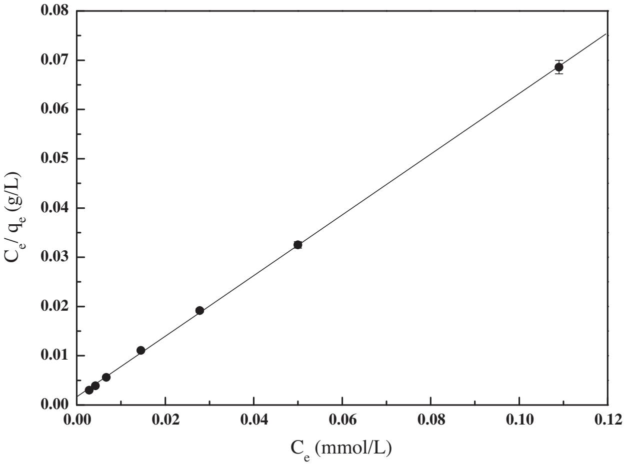


Fig. 8. Langmuir isotherm for the adsorption of Cr(VI) on Tulsion A-27(MP).

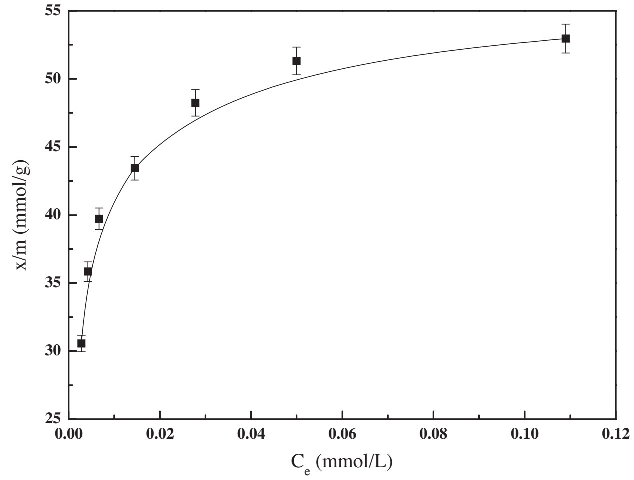


Fig. 9. Freundlich isotherm for the adsorption of Cr(VI) on Tulsion A-27(MP).

eters of Freundlich and Langmuir isotherms are given in Table 4. The Freundlich constant (*k*) was found to be 77.74 and the value of n (6.93) between 1 and 10 indicates strong chemical interaction and ion exchange between the resin and Cr(VI) [45,46]. Similar behavior for the weak base resin Lewatit MP 64 and strong base resin Lewatit MP 500 as reported by Pehlivan et al. in the literature [41]. A further analysis of Langmuir equation can be made on the basis of a dimensionless parameter known as separation factor [47,48] as given below.

$$R_L = \frac{1}{1 + K_b C_0} \tag{10}$$

where K_b is the Langmuir constant and C_0 (mg/L) is the initial concentration of Cr(VI).

The R_L value provides the following information (Table 4).

If

(i) $R_L = 0$, adsorption is irreversible;
(ii) $0 < R_L < 1$, adsorption is favorable;
(iii) $R_L = 1$, adsorption is linear favorable;
(iv) $R_L > 1$, adsorption is unfavorable;

In our study, the R_L value was 0.711 which lies between 0 and 1 indicates that the adsorption was favorable.

5. Adsorption kinetics

Experiment was carried out to understand the kinetics of chromium removal by the resin Tulsion A-27(MP). It is a well established fact that the adsorption of ions in aqueous medium follows reversible first-order kinetics, when a single species is considered on a heterogeneous surface. It must be remembered that the two important physicochemical aspects for parameters evaluation of the adsorption process as a unit operation are the kinetics and the equilibria of the system. Kinetics of adsorption describe the uptake rate of Cr(VI) on the resin and also govern the required residence time of adsorption reaction. Using the kinetic equations, the forward, backward, and the overall rate constants were calculated [45]. The adsorption of hexavalent

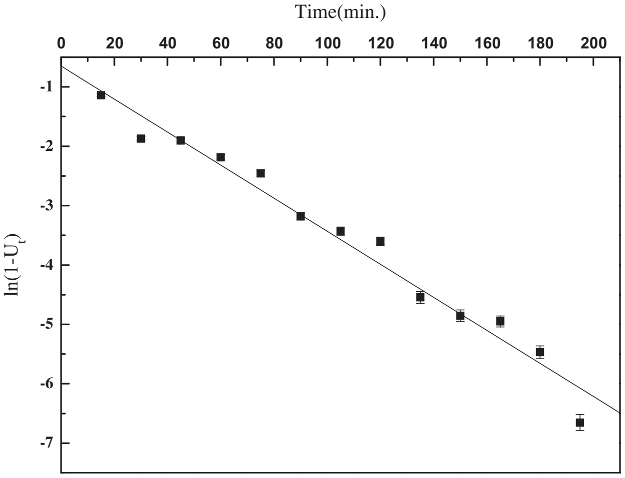


Fig. 10. Kinetic fit for the adsorption of Cr(VI) on Tulsion A-27(MP).

Table 4
Parameters of Freundlich and Langmuir isotherms for adsorption of Cr(VI) on Tulsion A-27(MP)

Freundlich isotherm			Langmuir isotherm			
k	*n*	R^2	K_b	A_S[a]	R^2	R_L
77.74	6.93	0.93	370.12	1.62	0.99	0.711

Note: [a]mmol/g resin.

Table 5(a)
Rate constants for the adsorption of Cr(VI) on Tulsion A-27(MP) at 303 K and resin dosage of 0.025 g

Resin	Cr(VI) amount (mmol)	Overall rate constant, $k = k_1 + k_2$ (min^{-1})	Forward rate constant, k_1 (min^{-1})	Backward rate constant, k_2 (min^{-1})
Tulsion A-27(MP)	1.1	0.0278	0.0274	0.0004

chromium from liquid phase to solid phase may be given as:

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$$

where k_1 is the forward reaction rate constant, k_2 the backward reaction rate constant. By plotting $\ln(1-U_t)$ vs. time t (Fig. 10), the overall rate constant k for given concentration (0.0011 M) of chromium, forward and backward rate constants k_1 and k_2 were calculated and depicted in Table 5(a). The forward rate constant for the removal of Cr(VI) was much higher than the backward rate constant, namely the desorption process. This suggested that the rate of adsorption was clearly dominant.

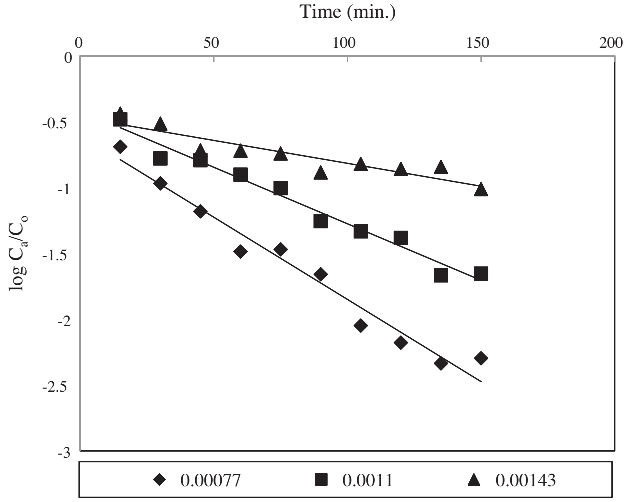


Fig. 11. Langmuir–Hinshelwood model for the adsorption of Cr(VI) on Tulsion A-27(MP) at different concentrations.

Table 5(b)
Pseudo-first-order rate constants at different concentrations of Cr(VI) on Tulsion A-27(MP) at 303 K and resin dosage of 0.025 g

Concentration of Cr(VI) (M)	Rate constants (min^{-1})
0.00077	0.02874
0.00110	0.01977
0.00143	0.00801

Adsorption on ion exchange usually follows the Langmuir–Hinshelwood model as given in Eq. (11).

$$r = -\frac{dc}{dt} = k\theta = k\frac{KC}{1 + KC} \tag{11}$$

where k is the rate constant, K is the adsorption constant, t is the time, and C is the concentration of Cr(VI). For the low initial concentrations of Cr(VI), the term KC, in the denominator, can be neglected and the rate approaches first-order kinetics described by:

$$r = -\frac{dc}{dt} = kKC = k'C \tag{12}$$

where k' the apparent rate constant is also known as the pseudo-first-order rate constant. The integral form of the rate equation is:

$$\ln\frac{C}{C_0} = -k't \tag{13}$$

where C_0 is the initial concentration of Cr(VI).

Plot of ln C/C_0 vs. time gives a straight line (Fig. 11) and k' value was calculated from the slope. The experiment was repeated for different concentrations of Cr(VI) and data are given in table 5(b).

Pseudo-first-order rate constant obtained from the above equation found to decrease with increase in concentration of Cr(VI). This can be attributed to the increase in concentration of Cr(VI) that leads to decrease in the available sites on the resin for the adsorption.

6. Conclusion

The purpose of this study was to assess the performance of the commercial anion exchange resin Tulsion A-27(MP) to reduce trace concentrations of Cr(VI) in aqueous and aqueous organic solvent mixed media. Optimum pH for the maximum removal of Cr(VI) by the ion exchanger was 5–6 for a minimum dosage of 0.025 g of Tulsion A-27(MP). The uptake of Cr(VI) increased with increase in agitation time and equilibrium was attained at about 135 min. Effect of temperature on adsorption Cr(VI) indicated the endothermic nature of the process. Presence of organic solvents influences the adsorption of Cr(VI). Langmuir and Freundlich isotherms provided an excellent fit to the equilibrium adsorption data. Separation factor (R_L) value 0.711 and Freundlich constant (n) value 6.93 indicated favorable adsorption. Kinetic studies revealed the dominance of adsorption of Cr(VI) on Tulsion A-27(MP). Langmuir–Hinshelwood model suggested that the pseudo-first-order rate constant obtained was found to decrease with increase in concentration of Cr(VI). The experimental results have shown that the resin was effective in the removal of hexavalent chromium from aqueous and aqueous organic solvent mixed media. Hence, this anion exchange resin can be successfully employed for the treatment of water and waste water containing traces of hexavalent chromium in the pH range of 5–6 with the maximum removal efficiency by batch treatment technique, even in presence of organic solvents.

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References

[1] M.A. Hanif, R. Nadeem, H.N. Bhatti, N.R. Ahmad, T.M. Ansari, J. Haz, Mater. B39 (2007) 345–355.

[2] S. Babel, E.M. Opiso, Removal of Chromium from synthetic waste water by sorption into volcanic ash soil, Int. J. Environ. Sci. Tech. 4(1) (2007) 99–107.

[3] E.A. Ayuso, A.G. Sanchez, X. Querol, Purification of metal electroplating waste waters using zeolites, Water Res. 37 (2003) 4855–4862.

[4] A. Dabrowski, Z. Hubicki, P. Podkoscielny, E. Robens, Selective removal of the heavy metal ions from waters and industrial wastewaters by ion exchange method, Chemosphere 56 (2004) 91–106.

[5] K. Rouibah, A.-H. Meniai, M.T. Rouibah, L. Deffous, M. Bencheikh Lehocine, Chromium VI and cadmium II removal from aqueous solutions by olive stones, Desalin. Water Treat. 16 (2010) 393–401.

[6] J.W. Patterson, Industrial waste water treatment technology, Butter worths, Boston, 1985.

[7] A.M. Zayed, N. Terry, Chromium in environment: Factors affecting biological remediation, Plant and Soil 249 (2003) 139–156.

[8] S. Rengaraj, C.K. Joo, Y. Kim, J. Yi, Kinetics of removal of chromium from water electronic process wastewater by ion exchange resins: 1500H and IRN97H, J. Hazard. Mater. B102 (2003) 257–275.

[9] A.F Cotton, G. Wilkinson, Advanced Inorganic Chemistry, fifth ed., Wiley, New York, 1988 (680).

[10] S. Marshal, Hazardous and Toxic effects of Industrial Chemicals, NDC Publication, USA,. 137 1979.

[11] Water Quality Association, Technical Application Bulletin: Chromium (Cr), Water Quality Association, Lisle, IL, 2004.

[12] D.M. Ayres, A.P. Davis, P.M. Gietka, Removing heavy metals from waste water, Engineering research center report, University of Maryland, USA, 1994.

[13] M. Malakootian, J. Nouri, H. Hossaini, Removal of heavy metals from paint industry's wastewater using Leca as an available adsorbent, Int. J. Environ. Sci. Tech. 6(2) (2009) 183–190.

[14] I. Marzouk, C. Hannachi, L. Dammak, B. Hamrouni, Removal of chromium by adsorption on activated alumina, Desalin. Water Treat. 26 (2011) 279–286.

[15] L. Rafati, A.H. Mahvi, A.R. Asgari, S.S. Hosseini, Removal of chromium (VI) from aqueous solutions using Lewatit FO36 nano ion exchange resin, Int. J. Environ. Sci. 7(1) (2010) 147–156.

[16] N. Goyal, S.C. Jain, U.C. Banerjee, Comparative studies on the microbial adsorption of heavy metals, Adv. Environ. Res. 7 (2003) 311–319.

[17] EPA (Environmental Protection Agency), "Environmental Pollution Control Alters", EPA/625/5–90/025, EPA/625/4–89/023, Cincinnati, 1990.

[18] Indian Standard, "Drinking water specification", 1st Revision, IS-10500, 1991.

[19] M. Fabbricino, R. Gallo, Chromium removal from tannery wastewater using ground shrimp shells, Desalin. Water Treat. 23 (2010) 194–198.

[20] Lin Tiana, Gang Xie, Rong-xing Li, Yu Xiao-hua, Yan-qing Hou, Removal of Cr (VI) from aqueous solution using MCM-41, Desalin. Water Treat. 36 (2011) 334–343.

[21] B. Singha, T.K. Naiya, A.K. Bhattacharya, S.K. Das, Cr(VI) ions removal from aqueous solutions using natural adsorbents-FT–IR studies, J. Envt. Protection 2 (2011) 729–735.

[22] Chunhua Xiong., Caiping Yao, Li Wang, Jiajun Ke, Adsorption behavior of Cd(II) from aqueous solutions onto gel-type weak acid resin, Hydrometallurgy 98 (2009) 318–324.

[23] N. Balkaya, N. Bektas, Chromium(VI) sorption from dilute aqueous solutions using wool, Desalin. Water Treat. 3 (2009) 43–49.

[24] J. Rivera-Utrilla, M. Sanchez-Polo, Adsorption of Cr(III) on ozonised activated carbon, Importance of C-cation interactions, Water Res. 37 (2003) 3335–3340.

[25] M.D. Lanagan, D.C. Ibana, The solvent extraction and stripping of chromium with Cyanex 272, Miner. Engng. 16 (2003) 237–245.

[26] W. Patterson, Industrial waste water treatment technology, Ann Arbar Science Pub. Inc.: Ann Arbor, Michigam, 53 (1985).

[27] E. Demirbas, M. Kobya, E. Senturk, T. Ozkan, Adsorption kinetics for the removal of chromium(VI) from aqueous solutions on the activated carbons prepared from agricultural wastes, Water SA 30(4) (2004) 533–539.

[28] G. Kabir, S.E. Ogbeide, Removal of Chromate in trace concentration using ion exchange from tannery wastewater, Int. J. Environ. Res. 2(4) (2008) 377–384.

[29] S.H. Lin, C.D. Kiang, Chromic acid recovery from waste acid solution by an ion exchange process: Equilibrium and column ion exchange modelling, Chem. Eng. J. 92 (2003) 193–199.

[30] B. Saha, R.J. Gill, D.G. Bailey, N. Kabay, M. Arda, Sorption of Cr(VI) from aqueous solution by Amberlite XAD-7 resin impregnated with Aliquat 336, React. Funct. Polym. 60 (2004) 223–244.

[31] I. Narin, A. Kars, M. Soylak, A novel solid phase extraction procedure on amberlite XAD-1180 for speciation of Cr(III), Cr (VI) and total chromium in environmental and pharmaceutical samples, J. Hazard. Mater. 150 (2008) 453–458.

[32] E. Pehlivan, T. Altun, Ion-exchange of Pb^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Ni^{2+} ions from aqueous solution by Lewatit CNP 80, J. Hazard. Mater. 140 (2007) 299–307.

[33] S. Rengaraj, K.-H. Yeon, S.-Y. Kang, J.-U. Lee, K.-W. Kim, S.-H. Moon, Studies on adsorptive removal of Co(II), Cr(III) and Ni(II) by IRN77 cation-exchange resin, J. Hazard. Mater. B92 (2002) 185–198.

[34] B.K. Nelson, W.S. Brightwell, J.R. Burg, V.I. Massari, Behavioral and neurochemical alteration in the offspring of rats after maternal or paternal inhalation exposure to the industrial solvent 2-Methoxy ethanol, Pharmacol. Biochem. Behav. 20(2) (1984) 269–279.

[35] J. Lakatos, S.D. Brown, C.E. Snape, Coals as sorbents for the removal and reduction of Cr(VI) from aqueous waste streams, Fuels 81 (2002) 691–698.

[36] D. Park, S.-Y. Yun, J.M. Park, Studies on hexavalent chromium biosorption by chemically treated biomass of *Ecklonia* sp., Chemosphere 60 (2005) 1356–1364.

[37] R.S. Bai, T.E. Abraham, Studies on enhancement of Cr(VI) biosorption by chemically modified biomass of *Rhizopus nigricans*, Water Res. 36 (2002) 1224–1236.

[38] P.X. Sheng, Y.-P. Ting, J.P. Chen, L. Hong, Sorption of lead copper, cadmium, zinc and nickel by marine algal biomass: Characterization of biosorptive capacity and investigation of mechanisms, J. Colloid Interf. Sci. 275 (2005) 131–141.

[39] R. Tomar, P. Sharma, V. Kushwah, Separation of oxoanions from mixed aqueous solvents using strongly basic anion exchanger Amberlite IRA-400 in nitrate form, Ind. J. Chem. 46A (2007) 624–627.

[40] P.K. Pandey, S.K. Sharma, S.S. Sambi, Kinetics and equilibrium study of chromium adsorption on zeolite NaX, Int. J. Environ. Sci. Tech. 7(2) (2010) 395–404.

[41] E. Pehlivan, S. Cetin, Sorption of Cr(VI) ions on two Lewatit-anion exchange resins and their quantitative determination using UV-visible spectrophotometer, J. Hazard. Mater. 163 (2009) 448–453.

[42] S. Rengaraj, S.-H. Moon, Kinetics of adsorption of Co(II) removal from water and wastewater by ion exchange resins, Water Res. 36(7) (2002) 1783–1793.

[43] K. Bedoui, I. Bekri-Abbes, E. Srasra, Removal of cadmium(II) from aqueous solution using pure smectite and Lewatite S 100: The effect of time and metal concentration, Desalination 223 (2008) 269–273.

[44] Q. Yu, P. Kaewsarn, Binary adsorption of copper(II) and cadmium(II) from aqueous by biomass of marine alga Durvillaea potatorum, Separ. Sci. Tech. 34(8) (1999) 1595–1606.

[45] G. McKay, H.S. Blair, J.R. Gardner, Adsorption of dyes on chitin. I. Equilibrium studies, J. Appl. Polymer Sci. 127 (1982) 3043–3057.

[46] S.K. Sahu, P. Meshram, B.D. Pandey, V. Kumar, T.R. Mankhand, Removal of chromium(III) by cation exchange resin, Indion-790 for tannery waste treatment, Hydrometallurgy 99 (2009) 170–174.

[47] P.K. Malik, Dye removal from wastewater using activated carbon developed from sawdust: Adsorption equilibrium and kinetics, J. Hazard. Mater. 113(1–3) (2004) 81–88.

[48] F. Gode, E. Pehlivan, A comparative study of two chelating ion-exchange resins for the removal of chromium(III) from aqueous solution, J. Hazard. Mater. B100 (2003) 231–243.