



Removal of Hexavalent Chromium from Water and Organic Solvent Mixed Media by Adsorption Using Weak Base Anion Exchanger Tulsion A-2X (MP)

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The removal of a most common toxic, environmental pollutant and carcinogen chromium(VI) was studied by batch technique for the adsorption and ion exchange method from water and organic solvent mixed media under various conditions like interaction time, pH, effect of organic solvents and temperature. Maximum adsorption of chromium(VI) on Tulsion A-2X (MP) was in the optimum pH range of 5.0-5.5. Increase in temperature decreased the adsorption of chromium(VI). Interaction time indicated that about 70 % removal of chromium(VI) was within 15 min. Chromium(IV) adsorption was discussed based on first order kinetics and adsorption isotherms.

Keywords: Hexavalent chromium, Adsorption and ion exchange, Kinetics, Thermodynamics, Anion exchanger Tulsion A-2X.

INTRODUCTION

Chromium is commonly used in electroplating, tanning, photography, steel, ceramic, fungicides, glass, paint and pigment manufacturing units. Wastewaters generated from these industries having chromium(VI) which is very toxic [1]. Usually its concentration in water medium varies from 10-100 mg L⁻¹. Studies have indicated that in biological systems Cr(VI) can behave as carcinogenic, mutagenic and teratogenic [2]. Removal of Cr(VI) has become today a major concern due to its hazardous effects on health and environment such as high risk of lung cancer, damages to liver, kidney, nervous system and modification of DNA transcription [3,4]. Permissible limit for total chromium in water is 0.05 mg L⁻¹ [5]. Proper treatment of chromium(VI) is very much essential prior discharge of chromium containing water into natural water sources. Various physico-chemical methods have been suggested in the literature for the removal of chromium(VI) such as precipitation, electrolysis, ion exchange, reverse osmosis, adsorption, solvent extraction, *etc.* [6]. However, these methods have either expensive, require technical knowledge or they have considerable disadvantages including the generation and disposal of solid residues which causes a secondary pollution [7]. Simple and eco-friendly method among the available is ion exchange and adsorption. The technique ion exchange and adsorption gives an effective treatment of chromium(VI) from water and organic solvent mixed media.

Presently, the purpose of this work is to remove hexavalent chromium from water and organic solvent mixed media using weak base resin Tulsion A-2X (MP). For removing chromium(VI)

from aqueous media under acidic conditions, generally weak base ion exchange resins are used [8]. Mixed water-organic solvents media is specially considered as the solvents are widely used in paint and pigment industries and hence there is a possibility of presence of solvents in water medium for the adsorption of chromium(VI) [9]. The resin efficiency in adsorption of chromium(VI) is described under various conditions like, effect of temperature, effect of pH, effect of interaction time and effect of organic solvents. Adsorption isotherms, thermodynamic and kinetic parameters have also been evaluated.

EXPERIMENTAL

Analytical reagent grade chemicals and reagents were used in the experiments and procured from Himedia Company, India. 2-Methoxyethanol and 2-ethoxyethanol solvents were procured from Acros Organics, USA. Weak base ion exchange resin Tulsion A-2X (MP) used in the present study was supplied by Thermax Ltd., Pune, India. The physico-chemical properties of Tulsion A-2X (MP) are listed in Table-1. Reconditioned and air dried resin was used in the experimental work. Known molar concentrations of K₂CrO₄ solutions were prepared in water and organic solvent mixed media.

Equilibrium studies: Adsorption experiments were made by stirring 30 mL of potassium dichromate solutions and 0.025 g of resin Tulsion A-2X (MP) in water and organic solvent mixed media for 6 h using batch technique at constant temperatures of 303, 313 and 323 K in a thermostatically controlled

TABLE-1
PHYSICO-CHEMICAL CHARACTERISTICS OF
WEAK BASE ION EXCHANGE RESIN

Resin	Tulsion A-2X (MP), Cl ⁻ form
Resin type	Anionic weak base exchanger with macroporous structure
Matrix	Polystyrene copolymeric
Functional group	Tertiary amine
Resin bead size (mm)	0.3-1.2
Percentage of moisture	47
Exchange capacity per 250 g	0.90 meq.
Stability	80 °C
pH range	0-9
Screen size	16-40 US mesh

laboratory shaker and after equilibration chromium(VI) concentration in solution was measured by UV-visible spectrophotometer (Varian Cary 50 Bio) at 540 nm using 1,5-diphenylcarbazide method [10,11]. Distribution coefficient (K_d) values were determined using the following equation [9]:

$$K_d = \frac{q_e}{C_e} \quad (1)$$

where q_e (mol g⁻¹) is the quantity of metal ions adsorbed at equilibrium and C_e (mol L⁻¹) is the concentration of metal ions in the solution at equilibrium.

Percentage of removal of chromium(VI) from water and organic solvent mixed media was calculated using eqn 2:

$$R (\%) = \frac{(C_o - C_e)}{C_o} \times 100 \quad (2)$$

where C_o and C_e are the initial and equilibrium concentrations of chromium(VI) in mol L⁻¹.

RESULTS AND DISCUSSION

Effect of interaction time: The effect of interaction time on adsorption of chromium(VI) on Tulsion A-2X (MP) at neutral pH and temperature 303 K is represented in Fig. 1. It revealed that adsorption of chromium(VI) increases with increase in period of contact. About 70 % adsorption of chromium(VI) was achieved within 15 min [8]. A maximum of 97.2 % adsorption of chromium(VI) was at 225 min. The percentage adsorption of chromium(VI) was rapid upto 120 min because of the existence of greater percentage of resin sites for the exchange. Later there was a gradual increase in the adsorption rate upto 225 min. Further increase in interaction time decreases the adsorption of chromium(VI) due to lack of available sites on the resin phase.

Effect of pH: The influence of pH on the adsorption of chromium(VI) by Tulsion A-2X (MP) was studied in pH range of 4 to 8. Fig. 2 showed that adsorption of chromium(VI) was maximum (95.91 %) at pH 5 for an initial chromium concentration of 0.0011 M. On increasing the pH more than 5, a continuous decrease in the adsorption of chromium(VI) was observed by Tulsion A-2X (MP). This decrease at higher pH may be attributed to the competition between hydroxyl ions and chromate ions to occupy the active sites of Tulsion A-2X (MP) [12]. Hence, it is concluded that the percentage of adsorption of Cr(VI) is maximum on weak base resin in the pH values between 5.0 - 5.5.

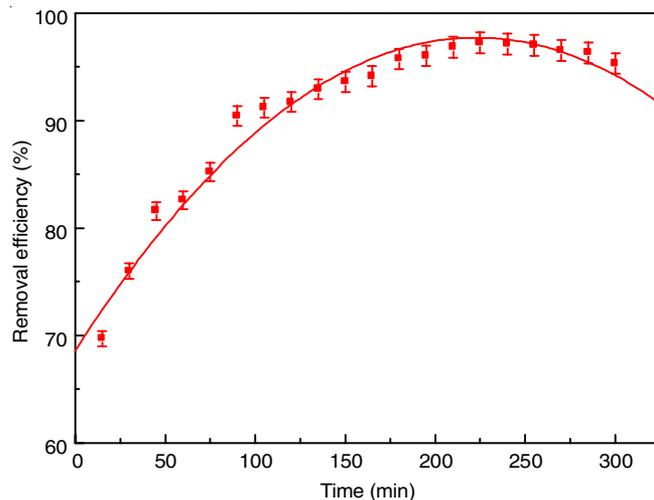


Fig. 1. Effect of interaction time on the adsorption of chromium(VI) by Tulsion A-2X (MP)

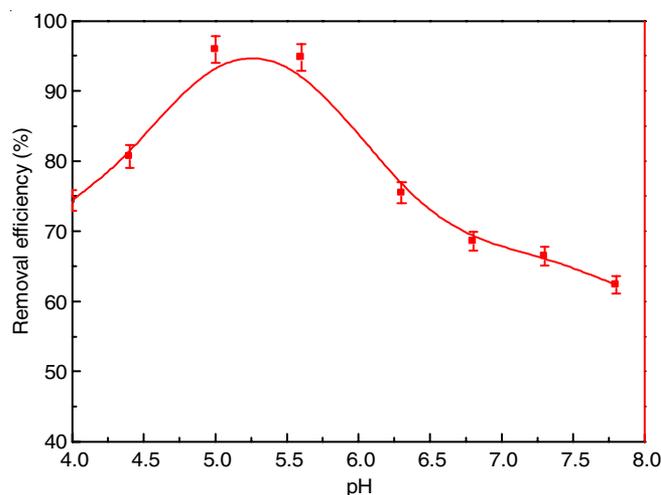


Fig. 2. Variation of pH for of adsorption of chromium(VI) by Tulsion A-2X (MP)

Effect of temperature: Adsorption of chromium(VI) on Tulsion A-2X (MP) was studied as a function of temperature in the range 303 K to 323 K (Table-2). The decrease in adsorption rate with rise in temperature may be due to the desorption process caused by an increase in the available thermal energy. The desorption process is influenced by higher temperature and is due to higher mobility of adsorbate [13,14].

Thermodynamic parameters *viz.*, change in Gibbs free energy (ΔG), change in enthalpy (ΔH) and change in entropy (ΔS) are required to predict the nature of adsorption of chromium(VI) on Tulsion A-2X (MP). The free energy change for the adsorption of chromium(VI) has been calculated by eqn 3.

$$\Delta G = -RT \ln K_d \quad (3)$$

where R is the universal gas constant, T is the temperature and K_d is the equilibrium distribution coefficient.

The ΔH values are calculated using van't Hoff equation (eqn. 4) and the change in entropy values are calculated using eqn. 5.

$$\ln \frac{K_2}{K_1} = \frac{-\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (4)$$

TABLE-2
EQUILIBRIUM DISTRIBUTION COEFFICIENTS FOR
ADSORPTION OF CHROMIUM(VI) ON TULSION A-2X (MP)
IN WATER AND ORGANIC SOLVENT MIXED MEDIA
AT 303, 313 AND 323 K

Solvent	Temperature (K)	Organic solvent (%)	log K _d
2-Methoxyethanol	303	00	1.8077
		20	1.6674
		40	1.4513
		60	1.0194
		80	0.9224
	313	00	1.7975
		20	1.6011
		40	1.2752
		60	0.9510
		80	0.7889
	323	00	1.6874
		20	1.5621
40		1.2351	
60		0.9184	
80		0.7481	
2-Ethoxyethanol	303	00	1.8077
		20	1.5531
		40	1.2129
		60	0.8694
		80	0.7937
	313	00	1.7975
		20	1.5006
		40	1.1972
		60	0.8126
		80	0.7694
	323	00	1.6874
		20	1.4721
40		1.1495	
60		0.8121	
80		0.6742	

$$\Delta G = \Delta H - T\Delta S \quad (5)$$

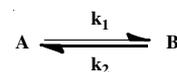
where K₁ and K₂ are the values of equilibrium distribution coefficients at constant temperatures of T₁ and T₂ respectively.

The values of enthalpy change (ΔH) in negative sign revealed that energy was released as the adsorption of chromium(VI) on Tulsion A- 2X (MP) proceeds [15]. As there is increase in temperature and organic solvent contents from 20 to 80 % (w/w)

the values of ΔG also increase (Table-3). This indicates that adsorption was less favored at high temperatures and higher solvent compositions. Spontaneity of the process was confirmed by the negative values of ΔG . The variation in ΔS showed that organic solvent compositions can produce a kind of disorder in the water structure. Change in negative entropy may be due to the decreased randomness on the resin-solution interface and the positive entropy change may be due to the release of water during the adsorption of chromium(VI) [16,17].

Effect of organic solvents: The study was made to investigate the effect of solvents and dielectric constant of the media on the adsorption of chromium(VI). From Table-2, the adsorption of chromium(VI) decreases with increase in percentage of organic solvents from 20 to 80 % at all temperatures studied. This may be attributed to the decrease in the ionization of inorganic salt in solution. Upon addition of organic media, 2-methoxyethanol and 2-ethoxyethanol, the extent of equilibrium distribution coefficient decreases due to decrease in dielectric constant of the medium and thus causing decrease in adsorption process of chromium(VI).

Kinetics studies: Weak base anionic exchanger Tulsion A-2X (MP) was used in present work to understand the effect of change in resin fixed ion on kinetics of exchange of chromium(VI). The sorption of chromium(VI) from solution phase to resin phase may be given as:



where k₁ and k₂ are the rate constants for forward and backward reactions. Using the equation mentioned in Gode and Pehlivan [18] and the plot of ln(1-U_i) against time t (Fig. 3), the overall kinetic rate constant k, forward and backward kinetic rate constants k₁ and k₂ were determined [18,19]. It was observed from Table-4 that k₁ was much better than k₂. This depicts the predominance of adsorption of chromium(VI) on Tulsion A-2X (MP).

Adsorption isotherms: The dispensation of solute across two regions of liquid and solid sorbent is the assessment of adsorption process and can popularly be described using Freundlich and Langmuir models.

Freundlich isotherm is represented by eqn. 6 as follows:

TABLE-3
THERMODYNAMICAL PARAMETERS FOR THE ADSORPTION OF CHROMIUM(VI) IN
WATER AND ORGANIC SOLVENT MIXED MEDIA ON TULSION A-2X (MP)

	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	-10.5	-10.8	-10.4	-1.85	-21.3	28.5	-33.7
20	-9.7	-9.6	-9.5	-12.0	-11.4	-7.8	-5.8
40	-8.4	-7.6	-7.6	-32.0	-7.8	-77.8	-0.4
60	-5.9	-5.7	-5.7	-12.4	-6.3	-21.5	-1.9
80	-5.4	-4.7	-4.6	-24.2	-7.9	-62.4	-10.1
2-Ethoxyethanol (% v/v)							
00	-10.5	-10.8	-10.4	-1.85	-21.3	28.5	-33.7
20	-9.0	-8.9	-9.1	-9.6	-5.5	-2.0	11.1
40	-7.0	-7.2	-7.1	-2.9	-9.2	13.8	-6.6
60	-5.0	-4.9	-5.0	-10.3	-0.1	-17.4	15.3
80	-4.6	-4.6	-4.2	-4.4	-18.4	0.63	-44.1

Error \pm 10 %

TABLE-4
KINETIC PARAMETERS FOR THE ADSORPTION OF CHROMIUM(VI) ON TULSION A-2X (MP)

Adsorbent	Amount of chromium(VI) (mmol)	Overall kinetic rate constant, $k = k_1 + k_2$ (min^{-1})	Forward kinetic rate constant, k_1 (min^{-1})	Backward kinetic rate constant, k_2 (min^{-1})
Tulsion A-2X (MP)	1	0.0225	0.0216	0.0009

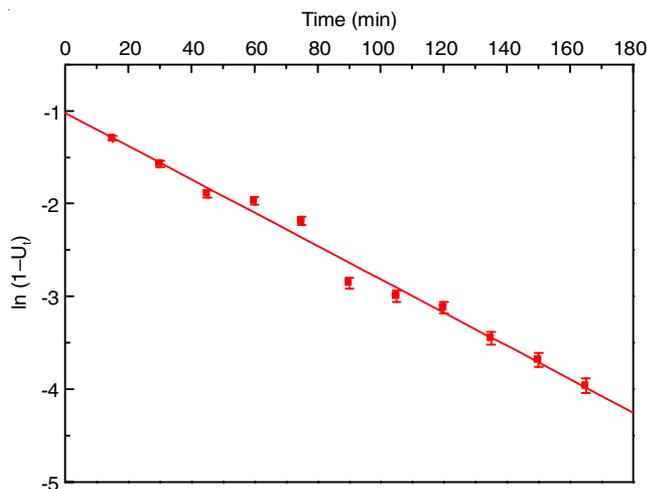


Fig. 3. Kinetic plot for the adsorption of chromium(VI) on Tulsion A-2X (MP)

$$\left(\frac{x}{m}\right) = kC_e^{1/n} \quad (6)$$

where x/m (mg g^{-1}) is the quantity of chromium(VI) adsorbed per unit weight of the adsorbent, C_e (mg L^{-1}) is the concentration at equilibrium, k and n are Freundlich constants indicating adsorption capacity and intensity, respectively.

Freundlich model (Fig. 4) shows the favourable adsorption of chromium(VI) and the values of Freundlich constants are given in Table-5. Higher value of n shows the adsorption rate of chromium(VI) on resin phase [20].

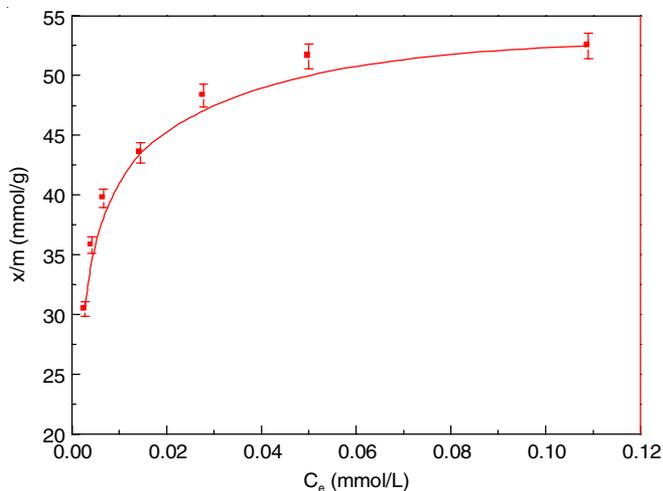


Fig. 4. Freundlich adsorption isotherm for chromium(VI) on Tulsion A-2X (MP)

Langmuir isotherm is represented by eqn. 7 as follows:

$$\frac{C_e}{q_e} = \frac{1}{K_b A_s} + \frac{C_e}{A_s} \quad (7)$$

where q_e is amount of adsorption of chromium(VI) per unit weight of the resin, A_s (mol g^{-1}) and K_b (L mol^{-1}) are the constants representing capacity and energy, respectively. Fig. 5 shows the validity of adsorption of chromium(VI) on Tulsion A-2X (MP).

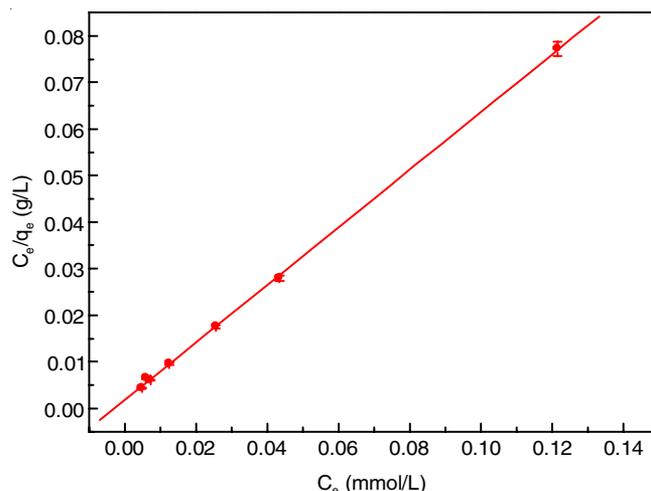


Fig. 5. Langmuir adsorption isotherm for chromium(VI) on Tulsion A-2X (MP)

Langmuir isotherm is expressed as separation factor R_L , an essential dimensionless parameter [21,22] as per the eqn 8.

$$R_L = \frac{1}{1 + K_b C_0} \quad (8)$$

where C_0 is initial concentration of chromium(VI) in mg/L . The calculated value of R_L is 0.728 indicated the favourable ($0 < R_L < 1$) adsorption [23] of chromium(VI) on Tulsion A-2X (MP).

Conclusion

The present study revealed that the Tulsion A-2X (MP) is an effective adsorbent for the adsorption of chromium(VI) from water and organic solvent mixed media. The optimum pH for the maximum adsorption of chromium(VI) on Tulsion A-2X (MP) was between 5.0-5.5. Interaction time indicated that about 70 % removal of chromium(VI) was within 15 min and maximum of 97 % removal was achieved within 225 min. The change in Gibbs free energy with negative values showed

TABLE-5
PARAMETERS OF FREUNDLICH AND LANGMUIR MODELS FOR ADSORPTION OF CHROMIUM(VI) ON TULSION A-2X (MP)

Freundlich adsorption isotherm			Langmuir adsorption isotherm			
k	n	R ²	K _b	A _s (mmol/g resin)	R ²	R _L
77.62	6.95	0.92	340.16	1.62	0.99	0.728

that ion-exchange and adsorption processes on Tulsion A- 2X (MP) were favourable with spontaneity. Kinetics and adsorption models gave the best feasibility data of chromium(VI) and it was well interpreted by separation factor R_L between 0 to 1. Thus, it is concluded that the ion-exchange resin Tulsion A-2X (MP) could be employed in the removal of chromium(VI) from water and organic solvent mixed media.

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