

Ion Exchange Removal of Chromium (III) from Tannery Wastes by Using a Strong Acid Cation Exchange Resin Amberlite IR-120 H⁺ and its Hybrids

^{1,2}Tauqeer Ahmad*, ²Syed Mustafa, ²Abdul Naeem, ¹Farooq Anwar
¹Tahir Mehmood and ²Khizar Hussain Shah²

¹Department of Chemistry, University of Sargodha, Sargodha-40100, Pakistan.

²National Centre of Excellence in Physical Chemistry, University of Peshawar, Peshawar-25120, Pakistan.
tskp72@yahoo.com*

(Received on 7th June 2013, accepted in revised form 4th February 2014)

Summary: A strong acid cation exchange resin Amberlite IR-120 H⁺ and its hybrids with Mn(OH)₂, Cu(OH)₂ and Fe(OH)₃ are used for the removal of chromium (III) from spent tannery bath. The experimental data give good fits with the Langmuir sorption model. The thermodynamic parameters entropy (ΔS°), enthalpy (ΔH°) and free energy (ΔG°) changes are computed, which reveal that the chromium removal from tannery wastes by ion exchangers is an endothermic, physical sorption and entropically driven process. The rate of sorption is found to increase with the increase of resin dosage, stirring speed and temperature. Different kinetic models such as film diffusion, particle diffusion and Lagergren pseudo first order are used to evaluate the mechanism of the process. It is found that the hybrid ion exchange resins have better removal capacity as compared to the parent ion exchanger. The increase in the removal capacity is found to be in the order of the corresponding PZC values of the hybrid ion exchangers. Further, it is suggested that the higher exchange capacity is the result of Donnan effect and specific adsorption of chromium by the oxides / hydroxides present inside the matrix of the organic cation exchanger.

Keywords: Chromium (III), hybrid cation exchangers, ion exchange, kinetics, spent tanning bath, thermodynamics.

Introduction

Chromium solutions are extensively used in many industrial processes like leather tanning, paper and pulp, pigments production, wood preservation, production of steel and other metal alloys etc. Of these, the effluents discharged from the tanneries contain chromium (III) in abundance and is the main source of pollution in the aquatic system because about 30–40 % of chromium remains unreacted in the tanning process. The chromium concentration in tanning effluent varies from 2500 to 8000 mg L⁻¹ [1], while that of chromium (VI) 1300 to 2500 mg L⁻¹ [2]. The Environmental Protection Agency (EPA) US has set the maximum level of 0.1 mg L⁻¹ for total chromium in the drinking water, while World Health Organization (WHO) has set it to be 0.05 mg L⁻¹ for chromium (VI) [3]. National Environmental Quality Standards of Pakistan have also set the maximum level of total chromium to 1.0 mg L⁻¹ in the effluents [4, 5]. Therefore, the control of chromium level in the industrial effluents is necessary.

Chromium usually exists in two forms chromium (III) and chromium (VI) in the tannery wastes. Chromium (III) is considered as an essential element playing an important role in the metabolism of glucose, lipid and protein, while chromium (VI) is reported to be the toxic to the biological systems [6]. The presence of strong oxidants in soil and water can change chromium (III) to harmful chromium (VI) [7]

as a result of oxidation. According to Apte *et al.* (2005) [8] a considerable concentration of chromium (VI) was found in fresh sludge samples dumped at a site in India. The reason for this conversion was due to the presence of solid MnO₂ and oxygen pressure greater than 10⁻⁶ atm. Therefore, the removal of chromium is necessary, whether it exists in chromium (III) or (VI) forms.

Removal of heavy metal ions in general and chromium in particular from wastewater can be achieved by the application of various methods such as precipitation, solvent extraction, electrochemical processes, and adsorption, ion exchange, filtration and membrane processes [9]. From these methods, ion exchange adsorption is a promising technique for the treatment of wastewaters containing heavy metals as it is rapid, cheap, effective, versatile and demands less skill among others. The method is technologically simple and enables efficient removal of even traces of impurities from solutions [10–15].

Over the past several years, oxides and hydroxides of polyvalent metals; aluminum, iron, silicon, titanium and zirconium have been used as adsorbents for metal ions and exhibited ligand sorption properties [16–18]. Ion exchange resins have also been frequently used for the removal of chromium ions from aqueous solutions [19–24].

*To whom all correspondence should be addressed.

Recently, researchers developed a new class of ion exchange resins known as hybrid ion exchange (HIX) resins which are based on the Donnan membrane effect of the host material and the metal hydroxides nanoparticles. Host materials are usually the commercially available ion exchange resins. Each hybrid sorbent particle is a spherical bead within which agglomerates of nanoparticles of the hydrated metal oxides are uniformly and irreversibly dispersed using chemical and thermal processes. These hybrid ion exchangers have excellent attrition resistance and sorption properties [25, 26]. However, these hybrid ion exchange resins have not been previously reported in the literature for the removal of chromium. The present investigation describes thermodynamic and kinetic parameters for the removal of chromium (III) from tannery wastes by using strong acid cation exchange resin Amberlite IR-120 H⁺ and its hybrids with Mn(OH)₂, Cu(OH)₂ and Fe(OH)₃.

Results and Discussion

Characterization of hybrid cation exchangers

The metal contents and the BET surface areas of the exchangers are given in Table-1. It is observed that the surface areas of the hybrid exchangers are greater than the virgin one and are almost independent of the nature of the cation present inside the resin. Further the PZC values of the hybrid exchanger when the number of positive charges on the surface are equal to the number of negative charge are found to be 6.8, 7.1 and 7.7 for the hybrid resins with Mn(OH)₂, Cu(OH)₂ and Fe(OH)₃ respectively. These PZC values are very close to the values reported by Kosmulski [27].

Table-1: The characteristic properties of hybrid cation exchangers.

Resin type	Metal contents	BET surface area (m ² /g)
IR-120 H ⁺	-	38.46
HIX IR-120 Mn(OH) ₂	7.91 % Mn	54.33
HIX IR-120 Cu(OH) ₂	9.84 % Cu	53.53
HIX IR-120 FeOOH	7.89 % Fe	57.36

Effect of pH

The effect of solution pH on the sorption of chromium was investigated by varying the initial pH (2–10) of the synthetic spent tannery bath solution containing 1.923 mmol L⁻¹ of chromium and the results are shown in Fig. 1. It can be observed that with the increase of pH the removal of chromium decreases. The maximum removal is found to be in the range of pH 2–4. Further, it was observed that at pH values > 5 the precipitates appeared in the

process, probably due to the formation of chromium hydroxide. Similar results were found in the literature about the decrease in the recovery of chromium (III) with the increase in pH and the optimum pH value reported for the removal was 4.5 from aqueous chromium nitrate solutions by Amberlite IR-120 H⁺ [28]. Sahu *et al.* [29] found that the sorption of chromium (III) in the pH range 0.5–3.5 was almost constant, but beyond pH 3.5, the sorption decreased due to the hydrolysis of chromium (III) ion forming Cr(OH)SO₄ and Cr(OH)₃. The maximum sorption of chromium (III) ions at pH 3.5 by cation exchangers Lewatit S-100, IRN-77 and SKN-1 was also reported by Gode and Pehlivan [19] and Rengaraj *et al.*, [30]. As the pH values of the chromium solutions lie in the range of 3–3.5 at which maximum removal of chromium is observed to take place, therefore, further experiments were performed without altering the pH of the solution.

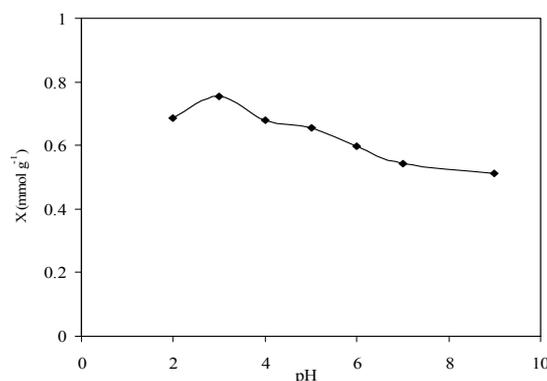


Fig. 1: Effect of initial pH (2–10) on the removal of Cr (III) by Amberlite IR-120 H⁺ at 303 K.

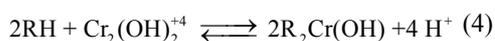
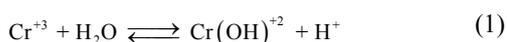
Effect of Temperature

The effect of temperature on the sorption of chromium (III) by cation exchanger Amberlite IR-120 H⁺ in the concentration range of 1.923–84.615 mmol L⁻¹ is shown in Fig. 2, which indicates that the chromium (III) sorption on Amberlite IR-120 H⁺ increases with the increase of temperature. The maximum exchange capacity of the resin at 293K is found to be 0.758 mmol g⁻¹ which increases to 0.858 mmol g⁻¹ at 323 K. The initial and equilibrium pH values of the solutions after sorption are given in Table-2. It is observed from the data that the pH of chromium (III) solutions decrease with the increase of the chromium concentration and temperature, due to the hydrolysis of chromium in water according to reaction (1) [22]. However, the equilibrium pH values are found to decrease further at all the temperatures after their contact with the resin. This effect is the result of the exchange reactions 2–4.

Table-2: pH values (± 0.001) for sorption of chromium (III) on Amberlite IR-120 H⁺.

C ₀ (mmolL ⁻¹)	pH _i	pH _e			
		293 K	303 K	313 K	323 K
1.923	3.656	1.999	2.802	2.801	2.792
3.846	3.419	1.999	1.996	1.991	1.974
5.769	3.322	1.974	1.973	1.971	1.939
7.692	3.164	1.952	1.960	1.946	1.939
9.615	3.131	1.952	1.966	1.964	1.940
19.231	3.103	1.951	1.964	1.968	1.980
28.846	3.092	1.979	1.986	2.008	2.021
38.462	3.071	2.007	2.020	2.032	2.039
57.692	3.063	2.154	2.161	2.166	2.179
84.615	3.000	2.213	2.231	2.247	2.263

pH_i = Initial pH and pH_e = Equilibrium pH



where R is the polymeric part of the resin. The pH values of the tanning bath solutions are in the range of 2.0 to 3.0. Therefore, the sorption of both the species Cr³⁺ and CrSO₄⁺ can be postulated by the resins. The sorption of Cr³⁺ and CrSO₄⁺ is postulated, as applying the computer speciation programme visual Minteq to the spent tannery bath solution revealed that these are the two predominant chromium species present. The details of the chromium speciation are provided in Table-3. It can be seen that at 293 K both the pH values 2 and 3 the major chromium species present in the tannery bath are Cr³⁺ and CrSO₄⁺ ions. However by increase the temperature to 323 K the major chromium species become Cr³⁺, CrSO₄⁺ and Cr₂(OH)₂⁺⁴, indicating an increase in the hydrolysis reaction as

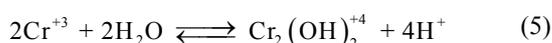


Table-3: Chromium speciation in the synthetic spent tannery bath with visual Minteq.

Species	% Speciation			
	pH = 2		pH = 3	
	293 K	323 K	293 K	323 K
Cr ⁺³	35.907	29.781	26.686	4.155
Cr(OH) ⁺²	0.239	0.942	1.779	1.524
CrOHSO ₄ (aq)	0.088	1.278	0.877	4.704
CrSO ₄ ⁺	61.727	42.000	61.757	15.563
CrCl ⁺²	1.913	3.348	1.428	0.559
Cr ₂ (OH) ₂ SO ₄ ⁺²	-	0.272	0.125	2.202
Cr ₂ (OH) ₂ (SO ₄) ₂ (aq)	-	0.057	0.035	1.050
Cr ₂ (OH) ₂ ⁺⁴	0.125	22.11	6.897	59.882
Cr ₃ (OH) ₄ ⁺⁵	-	0.211	0.415	10.421

The hump observed in the isotherms at low temperature in Fig. 2, which vanishes with the increase in temperatures above 313 K also points

towards the fact that two different chromate species are being sorbed by the resin. At lower concentrations and temperatures the sorption of Cr³⁺ ions are favored over CrSO₄⁺ by the resin due to electro-selectivity, while at higher concentrations and temperatures the sorption of Cr(OH)⁺² and Cr₂(OH)₂⁺⁴ is favoured due to an increase in the hydrolysis of chromium. The increase in equilibrium pH when the initial concentration increases beyond 19.231 mmol L⁻¹ is also clear manifestation of the switch in the sorption of Cr³⁺ by the exchanger to CrSO₄⁺. Mohan *et al.* [31] also reported that in acidic pH predominant chromium species sorbed were Cr³⁺ and Cr(OH)⁺². Similar results were found by Mustafa *et al.* [22] for the removal of chromium (III) by weak acid exchanger Amberlite IRC-50 (Na).

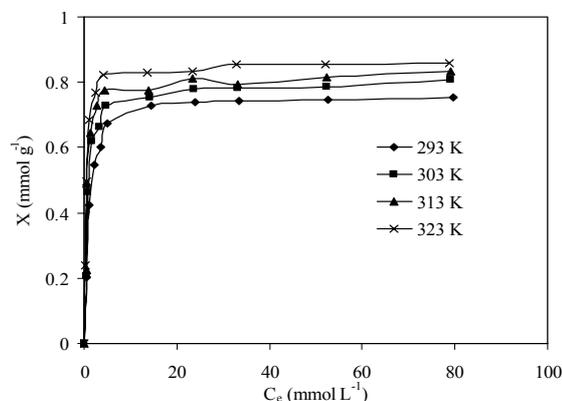


Fig. 2: Sorption isotherms of Cr (III) removal by Amberlite IR-120 H⁺ at different temperatures.

Sorption Isotherm

Sorption isotherm is a suitable approach for presenting the extent of sorption as a function of concentration of the adsorbate in the solution at constant temperature. Langmuir isotherm is frequently used to describe the equilibrium ion exchange relationship between the solid and liquid

phases. The linear form of Langmuir isotherm is described as [32, 33]:

$$\frac{C_e}{X} = \frac{1}{K_b X_m} + \frac{C_e}{X_m} \quad (6)$$

where C_e is the equilibrium adsorbate concentration in the solution, X is the amount of adsorbate sorbed per unit weight of adsorbent, X_m is the maximum sorption capacity and K_b is the binding constant. The numerical values of X_m and K_b , given in Table-4 are computed from the slope and intercept from the plot of C_e versus C_e/X (Fig. 3) with R^2 values 0.999. The increase in X_m values is observed with the increase in temperature indicating that the exchange capacity of resin increases with the increase in temperature. The K_b values are also found to increase with the temperature indicating the greater strength of the bond formed by the metal ions with the sulfonic acid groups of the resin. However, the effect of temperature on the K_b values is much higher as compared to the X_m values, indicating that the higher temperatures lead to stronger interaction of chromium species with the resin. The reason may be the sorption of poly nuclear products of chromium (III) like: $Cr_2(OH)_2^{4+}$, $Cr_3(OH)_6^{+3}$, $Cr_3(OH)_4^{5+}$, $Cr_2(OH)_2SO_4^{2+}$ and $Cr_2(OH)_2(SO_4)_2(aq)$ at higher chromium concentrations and temperatures. Gode and Pehlivan [34] had also reported a slight increase in the sorption of chromium with temperature by the resins Lewatit TP 207 and Chelex-100.

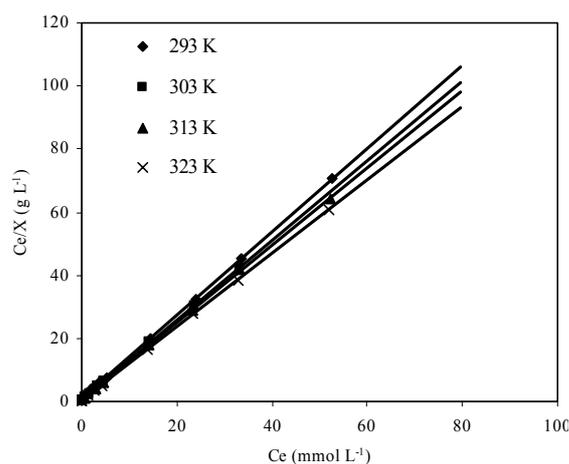


Fig. 3: Langmuir isotherm for Cr (III) removal by Amberlite IR-120 H⁺ at different temperatures.

Table-4: Langmuir parameters for chromium (III) removal by Amberlite IR-120 H⁺.

Temperature (K)	X_m (mmol g ⁻¹)	K_b (L mmol ⁻¹)	R^2
293	0.758	1.481	0.9999
303	0.792	2.155	0.9999
313	0.816	2.738	0.9998
323	0.858	3.108	0.9999

Thermodynamic Studies

The standard enthalpy change (ΔH^0) and entropy change (ΔS^0) are calculated from van't Hoff equation (7) while, the free energy change (ΔG^0) for chromium removal by ion exchange are calculated by using the well-known thermodynamics equation (8).

$$\ln K_b = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (7)$$

$$\Delta G^0 = \Delta H^0 - T \cdot \Delta S^0 \quad (8)$$

The plot of $\ln K_b$ vs. $1/T$ according to equation (7) gave a straight line with R^2 value 0.952. ΔS^0 and ΔH^0 values are computed from the slope ($\Delta H^0/R$) and intercept ($\Delta S^0/R$) of the straight line of Fig. 4 and are the values are given in Table-5. The positive ΔH^0 value shows the process to be endothermic in nature while, the positive ΔS^0 value shows that the randomness increases in the system due the dehydration of chromium (III) ions during the sorption by the resin. The small value of ΔH^0 indicates that the sorption of chromium (III) ions by cation exchange resin Amberlite IR-120 H⁺ is physical in nature. The ΔG^0 values are negative and increase with the increase in temperature. This shows that the sorption of chromium (III) ions is spontaneous, entropy driven and becomes more favorable at higher temperatures. Similar behaviour of ΔH^0 , ΔS^0 and ΔG^0 values for chromium (III) sorption were reported in literature [19, 35–37].

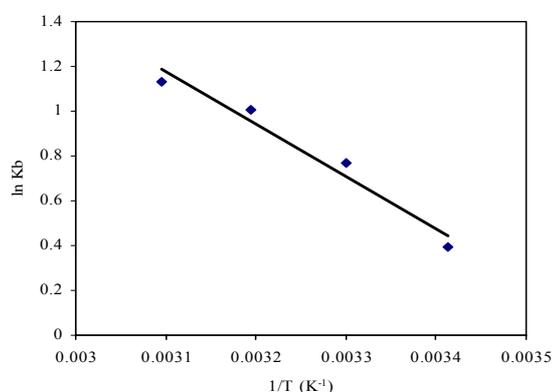


Fig. 4: $\ln K_b$ vs. $1/T$ for the adsorption of Cr (III) by Amberlite IR-120 H⁺.

Table-5: Thermodynamic parameters for the removal of chromium (III) by Amberlite IR-120 H⁺.

Temperature (K)	ΔG° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔS° (J k ⁻¹ mol ⁻¹)
293	-1.086		
303	-1.788		
313	-2.491	19.49	70.24
323	-3.193		

Kinetic Studies

The results of kinetic experiments of chromium (III) removal from simulated tannery bath by Amberlite IR-120 H⁺ are shown in Fig. 5. It can be observed from the Fig that the rate of sorption increases with the increase of temperature. However the equilibrium at all the temperatures is attained approximately within 90 min.

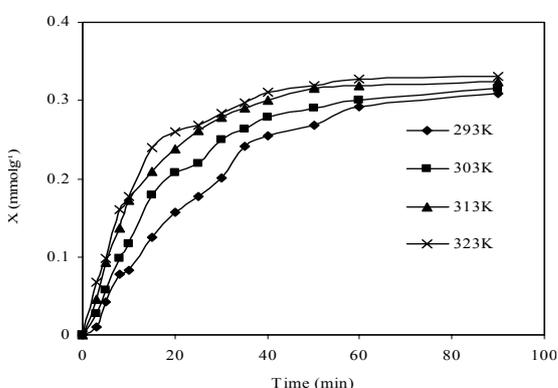


Fig. 5: Amount of Cr (III) adsorbed as a function of time on Amberlite IR-120 H⁺ at different temperatures.

The pH of the solution is noted after different time intervals during the exchange process. It can be seen from Fig. 6 that the greater change in pH is observed only in the first 10 min of the contact, after which it remains almost constant during the entire period of the experiment and is almost independent of the temperature. As the pH of the synthetic tannery bath lies in the range 3 to 3.5 the chromium therefore, mostly exists as Cr³⁺ and its cationic species CrSO₄⁺ [22, 29]. However, as the concentration of Na⁺ is very high in the tanning bath, therefore it can be assumed that the initial high drop in the pH is the result of H⁺ ions exchange from the exchanger with Na⁺ ions from the bath according to reaction (9). After this initial exchange reaction, the chromium ions replace the Na⁺ from the exchanger according to the reaction (10), which would then result in constant pH as shown in Fig. 6.

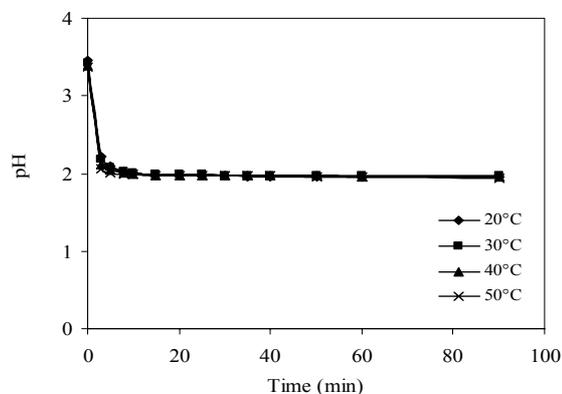
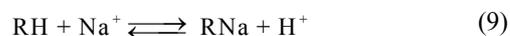


Fig. 6: Effect of temperature on the pH of the adsorbate solutions.

Effect of Resin Dosage

Fig. 7 shows that the rate of chromium removal increases considerably with the increase in the adsorbent dosage. For example after 30 min contact, the chromium removal is found to be 34.01, 64.82 and 79.99% for resin dosage of 0.2, 0.5 and 1.0 g respectively. It is observed that an increase in adsorbent dose resulted in a decrease in the contact time required to reach the equilibrium. This increase in removal is due to an increase in the number of sorption sites and greater surface area for a fixed adsorbate concentration [30].

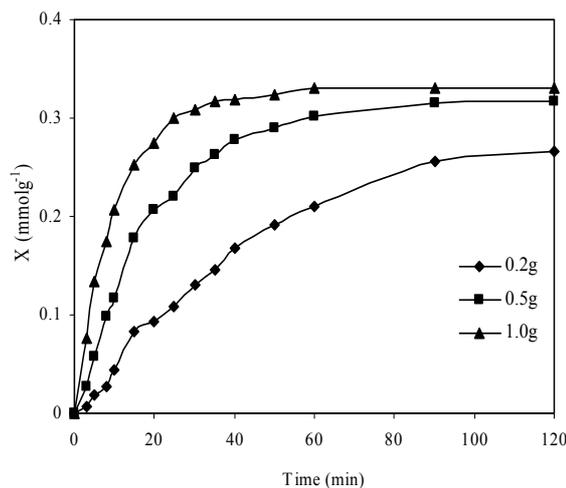


Fig. 7: Amount of chromium (III) sorbed as a function of resin dosage on Amberlite IR-120 H⁺.

Effect of Stirring Speed on Sorption Kinetics

The effect of stirring speed on the removal of chromium from the spent tannery is shown in Fig. 8. It is observed that the rate of sorption increases with an increase in the stirring speed from 100 rpm to 1000 rpm and the equilibrium in the system is also attained much earlier. At 100 rpm stirring speed the equilibrium is reached within 120 min, which is reduced to 90 min by increasing the stirring speed to 1000 rpm. This increase in the uptake is an indication of the diffusional nature of the process.

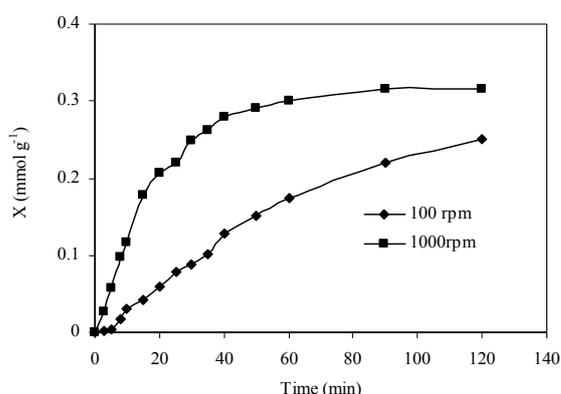


Fig. 8: Amount of chromium (III) sorbed as a function of stirring rate on Amberlite IR-120 H⁺.

Application of Kinetics Models

Different kinetic models are applied to the data and are discussed below:

Film Diffusion Model

The expression for film diffusion is written as [38];

$$\ln(1 - F) = -k_u t \tag{11}$$

where F is the ratio of amount adsorbed after time t to the amount adsorbed at equilibrium and k_u is the rate constant. The value of k_u is obtained from slope of the plot ln(1-F) vs. t given in Fig. 9. The values of rate constants thus calculated at various temperatures are reported in Table-6. The energy of activation (E_a) is calculated by using the Arrhenius equation as:

$$\ln k_u = \ln A - \frac{E_a}{RT} \tag{12}$$

where k_u is the rate constant, A is the Arrhenius factor, R is the molar gas constant (8.314 J K⁻¹ mol⁻¹)

and T is the absolute temperature. Energy of activation is computed from the Arrhenius plot (ln k versus 1/T) from Fig. 10 and is given in Table-6.

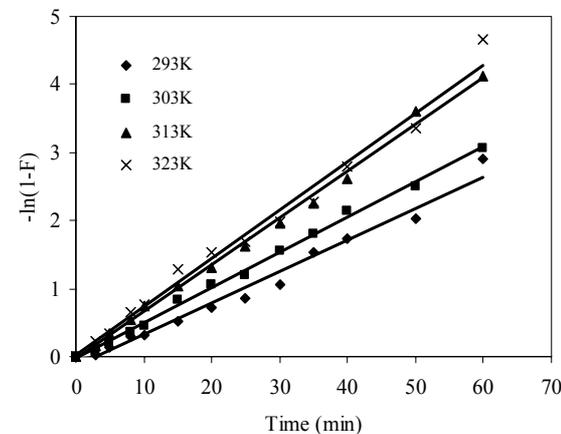


Fig. 9: Film diffusion plots for chromium (III) removal by Amberlite IR-120 H⁺ at different temperatures.

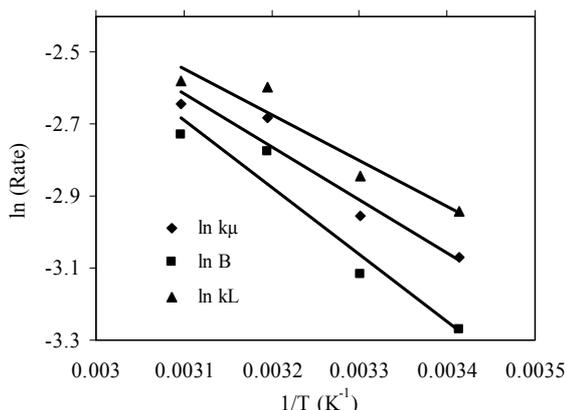


Fig. 10: Arrhenius plots for the sorption of chromium (III) by Amberlite IR-120 H⁺.

Particle Diffusion Model

The expression for particle diffusion is

$$Bt = -2.30258 \log(1-F) - 0.4977 \quad \text{for } F > 0.85 \tag{13}$$

$$Bt = 6.28318 - 3.2899F - 6.28318(1 - 1.047F)^{1/2} \quad \text{for } F < 0.85 \tag{14}$$

where B is the rate constant and is equal to $D\pi^2/r^2$, D is the particle diffusion coefficient and r is its radius [39]. The Bt values are plotted versus t as shown in Fig. 11. The values of rate constants (B) and the respective activation energy are reported in Table-6. Energy of activation was calculated by using the Arrhenius equation (10) and is given in Table-6.

Table-6: Kinetic parameters for the removal of chromium (III) by Amberlite IR-120 H⁺.

Temperature (K)	Film Diffusion Model		Particle Diffusion Model		First Order Lagergren Model	
	k _f	R ²	B	R ²	(k _L)	R ²
293	0.046	0.979	0.038	0.931	0.053	0.925
303	0.052	0.997	0.044	0.986	0.058	0.934
313	0.069	0.996	0.062	0.983	0.075	0.957
323	0.071	0.984	0.065	0.973	0.076	0.861
Activation Energy (kJ mol ⁻¹)	12.316		15.524		10.609	

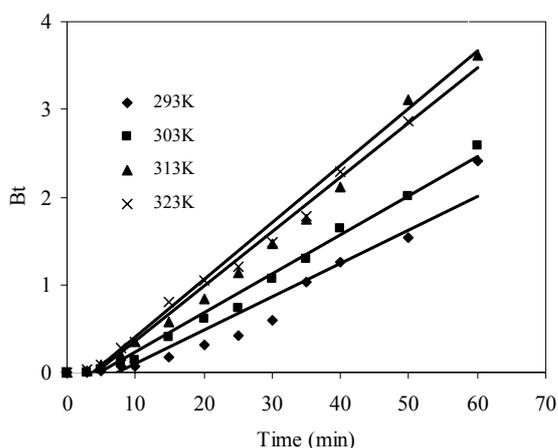


Fig. 11: Particle diffusion plots for chromium (III) removal by Amberlite IR-120 H⁺ at different temperatures.

Lagergren Adsorption Kinetic Model

The pseudo first order rate expression derived by Lagergren was applied to the data for the determination of rate constant values [40]. The most popular form of Lagergren equation is [41]

$$\ln (q_e - q_t) = \ln q_e - k_L t \tag{15}$$

where q_e and q_t are equilibrium concentration and concentration at time t, while, k_L is the Lagergren rate constant. The results are graphically shown in Fig. 12, while the rate constant values are reported Table-6. The calculated activation energy is given in Table-6.

In order to determine the mechanism of the process, the equilibrium sorption values are calculated using the rate constants derived from the different kinetic models and are compared with experimental ones in Table-7. It can be observed from this table that Film diffusion and Lagergren

models are the best fit to the exchange process, as their calculated q_e values are very close to experimental q_e values. As the Lagergren equation can be transformed to film diffusion equation by simple mathematical manipulation therefore, it can be assumed that the sorption process is limited by the film diffusion process. Similar conclusions can be drawn by comparing the R² values given in Table-7.

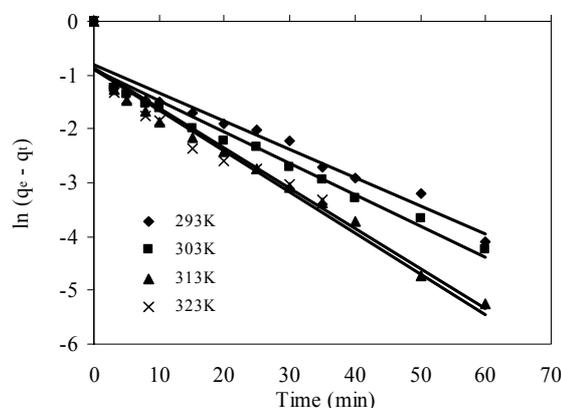


Fig. 12: Lagergren plots for chromium (III) removal by Amberlite IR-120 H⁺ at different temperatures.

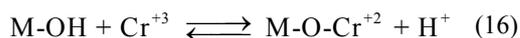
The values of activation energies calculated from the different kinetic models are found to be in the range of 10.61–15.524 kJ mol⁻¹. It was reported in the literature [42] that if the activation energies are below 21 kJ mol⁻¹ then film diffusion took place, for pore diffusion these values are between 20–40 kJ mol⁻¹ and above 84 kJ mol⁻¹ for the chemisorption. Therefore, the low activation energies also points towards the fact that the kinetics of chromium sorption is a controlled by the film diffusion mechanism. The increase in the rate of sorption with stirring speed also points towards the same fact. Similar conclusions were drawn elsewhere [43].

Table-7: Comparison of the equilibrium concentration values of different models.

Temperature (K)	Experimental q _e (mmol g ⁻¹)	Film Diffusion q _e (mmol g ⁻¹)	Particle Diffusion q _e (mmol g ⁻¹)	Lagergren q _e (mmol g ⁻¹)
293	0.306	0.313	0.315	0.311
303	0.316	0.319	0.319	0.317
313	0.325	0.326	0.326	0.325
323	0.330	0.331	0.331	0.331

Sorption Studies on Hybrid Ion Exchangers

Sorption of chromium (III) on hybrid ion exchange resins of Amberlite IR-120 with Mn(OH)₂, Cu(OH)₂ and Fe(OH)₃ is studied at 293 and 323 K. The maximum sorption capacities of these resins are given in Table-8. It can be observed from the table that the hybrid cation exchangers have better chromium removal capacities as compared to the virgin exchanger. The order of removal capacity is found to be HCIX-Mn(OH)₂ > HCIX-Fe(OH)₃ > HCIX-Cu(OH)₂ > IR-120 H⁺ at both temperatures. It is also observed that temperature has very promising effect on the maximum sorption capacity of the exchangers and the effect on sorption capacity for Mn(OH)₂ hybrid form is much pronounced at 323 K. The higher sorption capacities of the HIX are due to Donnan effect and the specific adsorption by oxides / hydroxides. Metal oxides / hydroxides are known to develop surface -OH groups, which are responsible for the uptake of chromium cations according to reaction (14) [36].



where M stands for Mn, Fe and Cu. The pH values of the tannery bath solutions being below the PZC values, the following protonation reaction may be assumed to take place in the hybrid ion exchangers in addition to the chromium sorption by the organic and inorganic part of the hybrid exchanger according to reactions 16 and 2.



The pH values accompanying the sorption reactions by hybrid ion exchangers are given in

Table-8: Comparison of maximum sorption values for the removal of chromium (III) by different forms of Amberlite IR-120 H⁺.

Temperature (K)	Amberlite IR-120 H ⁺	HIX IR-120 Cu(OH) ₂	HIX IR-120 Fe(OH) ₃	HIX IR-120 Mn(OH) ₂
293	0.758	0.886	0.912	1.045
323	0.858	0.966	1.125	1.841

Table-9: Equilibrium pH values (± 0.001) for the sorption of chromium (III) by HIX.

C ₀ (mmol L ⁻¹)	pH _i	pH _e					
		IR-120 Mn(OH) ₂		IR-120 Cu(OH) ₂		IR-120 Fe(OH) ₃	
		293 K	323 K	293 K	323 K	293 K	323 K
1.923	3.656	5.125	6.989	4.900	6.009	5.126	6.957
3.846	3.419	4.356	4.682	4.321	5.155	4.597	4.051
5.769	3.322	4.199	4.139	4.123	4.615	4.173	3.588
7.692	3.164	3.952	4.188	3.971	4.301	3.782	3.347
9.615	3.131	3.842	3.876	3.804	4.069	3.681	3.234
19.231	3.103	3.457	3.376	3.585	3.783	3.288	3.039
28.846	3.092	3.275	3.205	3.343	3.593	3.107	2.989
38.462	3.071	3.165	3.084	3.275	3.404	3.050	2.914
57.692	3.063	3.054	3.003	3.166	3.104	3.003	2.900
84.615	3.000	2.983	2.939	2.947	2.989	2.973	2.893

pH_i = Initial pH and pH_e = Equilibrium pH

Table-9, which indicate that at low concentrations of chromium and at 293 K the chromium sorption reaction (16) predominates the surface protonation reaction (17), while the converse is true when the temperature is increased to 323 K. further at higher concentration of chromium the increased hydrogen ions released from the exchanger are almost completely compensated their sorption by reaction (17). Therefore, as can be seen from Table-9 very small changes are observed in the pH of the equilibrium solutions irrespective of the changes in the amount of the chromium sorbed and temperature of the system. Further, it is interesting to note that the increase in the sorption is in the same order as the PZC of the corresponding hydroxides. This also indicates that the increased sorption of chromium by the HIX is the result of the specific adsorption of chromium by the hydroxides in addition to the ion exchange sorption by the organic part of the hybrid ion exchangers. Similar findings were reported for the sorption of lead and cadmium on MnO₂ loaded resin recently by Dong *et al.* [44].

Experimental

Materials

All chemicals used were analytical grade and used without further purification. All the solutions were prepared in deionized water (Milli-Q water purification system, Millipore-USA), using Pyrex glass vessels. The average composition of synthetic spent tanning bath used in the present investigation reported in Table-10 was prepared according to the method reported elsewhere [23, 24]. The working solutions were prepared from the synthetic spent tanning bath by diluting it with respect to the chromium concentration.

Table-10: Average composition of the Spent Tanning Bath [23, 24].

Items	Real Spent Tanning Bath (mg L ⁻¹)	Synthetic Spent Tanning Bath (mg L ⁻¹)
Cr(III)	3500–4500	4400
Fe(III)	40–100	45
Al(III)	80–150	110
SO ₄ ²⁻	10000–12000	11000
Total (Organic Carbon)	1200–1800	1300 (as CH ₃ COOH)
NaCl	50000–70000	58000
pH	3.0–3.5	3.0

Ion Exchange Resin and Preparation of Hybrid Ion Exchange Resin

A strong acid cation exchange resin Amberlite IR-120H⁺ was used in this study. The physicochemical properties of the resin are given in Table-11. Hybrid ion exchange (HIX) resins were prepared by using Amberlite IR-120 H⁺ as host material and hydroxide particles were dispersed in it. The preparation consisted of the following three steps [25, 26];

Table-11: Physicochemical properties of Amberlite IR-120 H⁺ ion exchange resin.

Parameter	Remarks
Polymer matrix	Styrene-DVB
Functional group	Sulfonic acid
Ionic form	H ⁺
Exchange capacity	4.4 meq g ⁻¹ (dry)
Effective size	16–45 mesh
Operating temperature	120 °C (maximum)
Swelling	5–7%
pH range	0–14

Step 1: Loading of metal ions on to the exchanger by passing 4% metal chloride solution at an approximate pH of 2.0;

Step 2: Precipitation of metal hydroxides within the gel of the exchanger, by passing a solution containing both NaCl and NaOH, each at 5% w/v concentration through the column;

Step 3: Rinsing and washing the column content with a 50/50 ethanol-water solution followed by a mild thermal treatment (323–333 K) for 60 minutes.

Three different forms of hybrid exchangers were prepared i.e., Mn(OH)₂, Cu(OH)₂ and Fe(OH)₃. The metal salts used were chlorides of manganese, copper and iron.

Total metal contents loaded on the hybrid exchangers were determined by digestion of the exchanger in 10% sulfuric acid and were analyzed by atomic absorption spectrophotometer (Model: Perkin-Elmer A Analyst800). The surface areas of the

exchangers were measured by using surface area and pore size analyzer Nova 1200e (Quantachrome Model No. N12-25E, USA). The PZC values of the HIX were determined by salt addition method reported elsewhere [45, 46]. Chromium speciation of spent tannery bath solution at working pH was done with MINTEQA2 version 3.11.

Equilibrium Studies

Sorption of chromium from spent tannery bath solutions by the ion exchangers was studied as a function of temperature (293, 303, 313 and 323K) in the concentration range of 1.923–84.615 mmol L⁻¹ through batch experiments. Briefly 30 mL of chromium solution was added into 50 mL conical flasks containing 0.2 g of resin. The flasks were sealed and placed in a shaking water bath at desired temperature (293–323 K) at 100 rpm for 4 h. The resins were separated by filtration after 4h and the aliquots were analyzed for chromium concentration in solution using visible spectrophotometer (Model: Vis-1100) and atomic absorption spectrophotometer [22, 47].

Kinetic Studies

For kinetics studies, the spent tannery bath was diluted to obtain 1.923 mmol L⁻¹ with respect to chromium. 100mL of this solution was transferred in a double walled glass cell attached to the water-circulating bath. After attaining the desired temperature, 0.5 g of resin was poured into it, while the stirring speed of magnetic bar was adjusted to 1000 rpm. After different time intervals 1.0 mL solution was drawn in to test tube and analyzed for total chromium concentration. pH of the solutions were measured with a pH-meter (BOECO BT-600, Germany) using a combination glass electrode and automatic temperature compensation (ATC) temperature probe NTC30K.

Conclusions

Based on the results obtained, Amberlite IR-120 H⁺ is found to be a suitable sorbent for removal of chromium (III) from tannery wastes. The maximum removal of chromium is achieved at pH range of 2–4 and the sorption capacity increases with the increase in temperature. The Langmuir sorption isotherm is found fit to the data at all temperatures studied. The X_m values increases with temperature increase indicate that the process is endothermic. On the basis of thermodynamic parameters (ΔG° , ΔH° and ΔS°) it can be concluded that the process is spontaneous, endothermic and physical sorption in

nature. Sorption kinetics of chromium ions from tannery wastes by Amberlite IR-120 H⁺ is dependent upon the resin dosage, stirring speed and temperature. It is concluded that the sorption of chromium removal is controlled by a film diffusion process. The activation energy values obtained are small and indicative of the fact that the diffusion is the rate determining step in the process. Hybrid ion exchanger are prepared with Mn(OH)₂, Cu(OH)₂ and Fe(OH)₃ using Amberlite IR-120 H⁺ as host material. The dissolution of metal content of these exchangers is negligible but has higher sorption capacity than parent exchanger due to Donnan exclusion and specific adsorption by the corresponding hydroxide. Therefore, it is concluded that hybrid ion exchangers are very effective for chromium removal from tannery wastes.

Acknowledgments

This work was supported by National Centre of Excellence in Physical Chemistry, University of Peshawar, Peshawar-Pakistan.

References

- M. A. Chaudry, S. Ahmad and M. T. Malik, *Waste Management*, **17**, 211 (1998).
- A. I. Hafez, M. S. El-Manharawy and M. A. Khedr, *Desalination*, **14**, 237 (2002).
- I. Narin, A. Kars and S. Soylak, *Journal of Hazardous Materials*, **150**, 453 (2008).
- M. Bosnic, J. Buljan and R. P. Daniels, *Pollutants in tannery effluents*; UNIDO (2000).
- The Gazette of Pakistan: Government of Pakistan ministry of environment, local government and rural development notification. S.R.O. 549 (1)/2000, (2000).
- B. Wen, X. Q. Shan and J. Lian, *Talanta*, **56**, 681 (2002).
- I. Tadesse, S. A. Isoaho, F. B. Green and J. A. Puhakka, *Bioresource Technology*, **97**, 529 (2006).
- D. A. Apte, S. Verma, V. Tare and P. Bose, *Journal of Hazardous Materials*, **121**, 215 (2005).
- D. Mohan and C. U. Pittman Jr., *Journal of Hazardous Materials*, **B137**, 762 (2006).
- A. Dabrowski, Z. Hubicki, P. Podkoscielny and E. Robens, *Chemosphere*, **56**, 91 (2004).
- L. Khezami, R. Capart, *Journal of Hazardous Materials*, **123**, 223 (2005).
- S. Kocaoba and G. Akcin, *Talanta*, **57**, 23 (2002).
- E. Korngold, N. Baelayev and L. Aronov, *Separation and Purification Technology*, **33**, 179 (2003).
- D. Zhao, A. K. Sengupta and L. Stewart, *Industrial and Engineering Chemistry Research*, **37**, 4383 (1998).
- S. Mustafa, K. H. Shah, A. Naeem, T. Ahmad and M. Waseem, *Desalination*, **264**, 108 (2010).
- S. Debnath and U. C. Ghosh, *Journal of Chemical Thermodynamics*, **40**, 67 (2008).
- D. M. Roundhill, *Extraction of metals from soils and waters*, Plenum, New York. (2001).
- J. A. Schwarz, C. I. Contescu, *Surfaces of nanoparticles and porous materials*, Marcel Dekker, New York, (1999).
- F. Gode and E. Pehlivan, *Journal of Hazardous Materials*, **B136**, 330 (2006).
- A. S. Cavaco, S. Fernandes, M. M. Quina and L. M. Ferreira, *Journal of Hazardous Materials*, **144**, 634 (2007).
- S. Yalcin, R. Apak, J. Hizal and H. Afar, *Separation Science and Technology*, **36** 2181 (2001).
- S. Mustafa, K. H. Shah, A. Naeem, M. Waseem and M. Tahir, *Journal of Hazardous Materials*, **160**, 1 (2008).
- S. Mustafa, T. Ahmad, A. Naeem, K. H. Shah and M. Waseem, *Water Air Soil Pollution*, **210**, 43 (2010).
- D. Petruzzelli, M. Santori, R. Passino and G. Tiravanti, Cr (III) recovery and separation from spent tannery baths by carboxylic ion exchange resins "New Developments in Ion Exchange" Proceedings of the international conference on ion exchange resins, Kodansha, Tokyo, Japan, pp.383 (1991).
- L. Cumbal and A. K. SenGupta, *Environmental Science and Technology*, **39**, 6508 (2005).
- M. J. DeMarco, A. K. SenGupta and J. E. Greenleaf, *Water Research*, **37**, 164 (2003).
- M. Kosmulski, *Journal of Colloid and Interface Science*, **353**, 1 (2011).
- S. Kartal, S. Tokahoglu and B. Ozkan, *Bulletin of the Korean Chemical Society*, **27**, 694 (2006).
- S. K. Sahu, P. Meshram, B. D. Pandey, V. Kumar and T. R. Mankhand, *Hydrometallurgy*, **99**, 170 (2009).
- S. Rengaraj, C. K. Joo, Y. Kim and J. Yi, *Journal of Hazardous Materials*, **102**, 257 (2003).
- D. Mohan, K. P. Singh and V. K. Singh, *Journal of Hazardous Materials*, **135**, 280 (2006).
- G. Barassi, A. Valdés, C. Araneda, C. Basualto, J. Sapag, C. Tapia and F. Valenzuela, *Journal of Hazardous Materials*, **172**, 262 (2009).

33. D. Q. L. Oliveira, M. Goncalves, L. C. A. Oliveira and L. R. G. Guilherme, *Journal of Hazardous Materials*, **151**, 280 (2008).
34. F. Gode and E. Pehlivan, *Journal of Hazardous Materials*, **B100**, 231 (2003).
35. N. K. Lazaridis and C. Charalambous, *Water Research*, **39**, 4385 (2005).
36. Y. S. Li, C. C. Liu and C. S. Chiou, *Journal of Colloid and Interface Science*, **273**, 95 (2004).
37. S. S. Tahir and R. Naseem, *Separation and Purification Technology*, **53**, 312 (2007).
38. G. E. Boyd, A. W. Adamson and L. S. Jr. Myers, *Journal of American Chemical Society*, **69**, 2836 (1947).
39. D. Reichenberg, *Journal of American Chemical Society*, **75**, 589 (1953).
40. S. Lagergren, *Handlingar*, **24**, 1 (1898).
41. Y. S. Ho, *Scientometrics*, **59**, 171 (2004).
42. S. Ayoob, A. K. Gupta, P. B. Bhakat and V. T. Bhat, *Chemical Engineering Journal*, **140**, 6 (2008).
43. F. J. Alguacil, M. Alonso and L. J. Lozano, *Chemosphere*, **57**, 789 (2004).
44. L. Dong, Z. Zhu, H. Ma, Y. Qiu and J. Zhao, *Journal of Environmental Sciences*, **22**, 225 (2010).
45. D. J. Kinniburgh, J. K. Syres and M. L. Jacksow, *Soil Science Society of America Proceedings*, **39**, 161 (1975).
46. S. Mustafa, M. Waseem, A. Naeem, K. H. Shah and T. Ahmad, *Desalination*, **255**, 148 (2010).
47. M. A. Awan, M. A. Baig, J. Iqbal, M. R. Aslam and N. Ijaz, *Journal of Applied Science and Environmental Management*, **7**, 5 (2003).