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Evaluation of chromium(VI) sorption efficiency of modified Amberlite XAD-4 resin



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KEYWORDS

Chromium; Sorption; Amberlite XAD; Solid phase extraction; Isotherms **Abstract** The present work deals with the removal of Cr(VI) from aqueous media by modified Amberlite XAD-4 (MAX-4) resin through the solid phase extraction method. Different parameters such as pH, dosage and temperature were optimized during the batch experiment. The experimental data were analyzed by Freundlich, Langmuir, Dubinin-Radushkevich (D-R) and Temkin equilibrium isotherms. Each characteristic parameter of isotherms was determined. The kinetic sorption experiments show that the sorption process follows pseudo second order kinetics. The sorption mechanism was investigated by Reichenberg (R-B) and Morris–Weber equations. From the thermodynamic parameters, it could be concluded that the sorption process is endothermic and spontaneous in nature. The interference and desorption studies were also performed. The results show that MAX-4 resin has the capability to remove Cr(VI) significantly from aqueous media even in the presence of interfering ions.

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1. Introduction

Many industries such as leather tanning, dye and electroplating extensively use chromium as alloy or trivalent or hexavalent salt. As a result, these industries release a large quantity of chromium without treatment to our environment, which causes great hazard to humans and aquatic life (Goyal et al.,

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2003; Yusof and Malek, 2009; Raji and Anirudhan, 1998). In aqueous systems, chromium mainly exists in two forms, i.e. Cr(III) and Cr(VI) subsequently; toxicity and reactivity mainly depend on the chemical form or oxidation state of the chromium. In trace amounts, Cr(III) is an essential nutrient for humans and to mammals for their maintenance of normal glucose tolerance factor, lipid and protein metabolism (Kocaoba and Akcin, 2002). Cr(VI) is a well known carcinogen and due to its high solubility in water, high oxidation potential and relatively small size enable it to penetrate through biological cell membrane and being mutagenic and genotoxic causes different types of DNA damages (Ertul et al., 2010). Cr(VI), i.e. CrO_4^{2-} and $Cr_2O_7^{2-}$ mainly exist as divalent anions with oxide functionalities at the periphery, which are potential sites for hydrogen bonding (Yilmaz et al., 2007). As it has been mentioned that Cr(VI) is highly soluble in water as compared

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to Cr(III) and the maximum permissible level for Cr(VI) in potable and industrial wastewater is 0.05 and 0.25 mg/L, respectively (Sayin et al., 2010; Deligöz et al., 2008). Therefore, there is an essential need of treatment of wastewater containing Cr(VI) as compared to Cr(III).

Solid phase extraction (SPE) has been favored by many researchers and preferred over liquid-liquid extraction (Oureshi et al., 2009; Ozcan et al., 2009). In SPEs, chelating resins have often been used because they provide good thermal stability and high sorption capacity toward ions with better flexibility in working conditions however; insignificance in selectivity and regenerability makes them unsuitable. Among them 5-palmitoyl oxine-functionalized XAD-2 resin (Filik et al., 2003), Amberlite XAD-16 (Elci et al., 2000), Amberlite XAD-2000 (Narin et al., 2001), Amberlite IRC-718, 4-vinyl pyridine-divinylbenzene/acrylonitrile-divinylbenzene copolymer, Amberlite IRA-400, silica based C-18 Dowex A-26 have been employed for sorption of Cr(VI) (Mondal, 2003). Besides these resins, Amberlite XAD-4 has been known as non-ionic polymeric sorbent material with superior physical properties, economical, easily available, thermally stable and can be easily modified (Uzun et al., 2001; Soylak et al., 2001). Previously, we have modified Amberlite XAD-4 by introducing amino groups into the aromatic ring for the removal of fluoride ion from aqueous environment (Solangi et al., 2010). Therefore, keeping in view the above observations and results, in this study we have used the same resin, i.e. modified Amberlite XAD-4 for the removal of Cr(VI) ion from aqueous media using the solid phase extraction method by optimizing various parameters.

2. Experimental

pH meter (781-pH/Ion meter, Metrohm, Herisau Switzerland) with glass electrode and internal reference electrode was used for pH measurements. The pH of the solution was adjusted by mixing an appropriate amount of 0.1 M (HCl/KOH). Janke and Kunikel automatic shaker model KS 501 D Singapore was used at ambient temperature ($25 \pm 2 \,^{\circ}$ C). All chemicals used were of analytical or equivalent grade. Stock standard solution (1000 mg/L) was prepared using K₂Cr₂O₇ purchased from Sigma (St. Loius, MO, USA). Calibration standards were prepared by diluting stock solution. Amberlite XAD-4TM (surface area of 825 m²/g, pore diameter 14.4 nm and bead size 20.50 mesh) was procured from Fluka, Germany. The surface area, pore diameter and mesh size were quoted by the supplier.

All glassware were thoroughly washed and soaked overnight in 5 M HNO₃, and rinsed with de-ionized water before use. All aqueous solutions were prepared with deionized water that had been passed through a Millipore milli-Q Plus water purification system (ELGA Model CLASSIC UVF, UK).

2.1. Synthesis

Amberlite XAD-4[™] has been modified (Scheme 1) by using previously developed method (Solangi et al., 2010). The modification of the resin was confirmed by FT-IR spectroscopy.

2.2. Sorption procedure

Batch experiment was carried out for the sorption process of Cr(VI) on MAX-4 resin at ambient temperature. A 10 ml sample solution containing Cr(VI) (5 mg/L) was taken in a 25 mL Erlenmeyer flask and MAX-4 resin (0.1 g) was added. The mixture was equilibrated for a fixed period of time (1 h). The mixture was filtered and the concentration of Cr(VI) was analyzed by UV–Visible spectrophotometer. The percent sorption of Cr(VI) ion was calculated as follows:

$$\% \text{Sorption} = \frac{C_i - C_f}{C_i} \times 100$$

where C_i and C_f (mol/L) are the initial and final concentrations of solution before and after the sorption of the Cr(VI), respectively.

3. Results and discussion

3.1. Effect of sorbent dosage

Sorbent dosage is an important parameter because this concludes the ability of a sorbent for given initial concentration of the sorbate at the operating conditions (Solangi et al., 2009). The effect of sorbent dosage on the sorption of Cr(VI) is represented in Fig. 1. It was observed that as the amount of MAX-4 resin increases, the sorption of Cr(VI) increases due to more surface area available for sorption. Maximum sorption (98.7 %) was achieved at 0.1 g of the MAX-4 resin and sorption remained almost constant up to 0.2 g. There is no significant change in removal efficiency of sorbent after 0.1 g due to the availability of large number of sorption sites. Keeping in



Scheme 1 Modification of Amberlite XAD-4 resin.



Figure 1 Effect of sorbent dosage on the percent sorption (10 ml of Cr(VI) with concentration 1×10^{-4} mol/L, 60 min contact time).

view the above results further study was processed at 0.1 g of sorbent.

3.2. pH effect on sorption of Cr(VI)

Effect of pH on sorption of Cr(VI) on MAX-4 resin was also checked because in the sorption experiment pH plays a vital role (Memon et al., 2008). Surface binding sites of sorbent and aqueous chemistry are widely affected with change in pH. At a fixed concentration of Cr(VI), sorption behavior was observed at various pH values as shown in Fig. 2 and it has been found that the maximum sorption ($q_{max} = 1.08$ mmol/g) was achieved at pH 6.9.

3.3. Sorption isotherms

Optimizing the design of a sorption system to evaluate the most appropriate correlations for equilibrium curves is important. The sorption isotherms may be applied to predict the sorbate behavior that has not been experimentally investigated. Langmuir, Freundlich, D-R and Temkin isotherm models were applied to experimental data (Langmuir, 1918; Clayton, 1926; Kamboh et al., 2011). These nonlinear isotherm models can be recast as linear equations (Ruthven, 1984; McKay et al., 1982; Abdelwahab, 2007).

The Langmuir isotherm (Eq. (1)) is based on the assumption of monolayer surface coverage, equivalent sorption sites, and independent sorption sites.



Figure 2 Effect of pH on sorption of Cr(VI) on MAX-4 resin (10 ml of Cr(VI) with concentration 1×10^{-4} mol/L, 60 min contact time).

$$\frac{C_e}{C_{ads}} = \frac{1}{Qb} + \frac{C_e}{Q} \tag{1}$$

The linear plot of C_e/C_{ads} versus C_e indicates the experimental data follow the Langmuir sorption isotherm very well (Fig. 3). The separation factor R_L , a dimensionless constant, which describes the type of isotherm, is an essential characteristic of Langmuir isotherm and can be expressed by $R_L = 1 + (1/bC_i)$, where C_i is the initial concentration of Cr(VI) ion. The values of R_L calculated were between 0.522 and 0.108, the R_L values indicate favorability ($0 < R_L < 1$) of isotherm (Eagleton et al., 1966).

The Freundlich isotherm (Eq. (2)) is useful to identify sorption phenomena with the heterogeneous sorbent media. This isotherm is derived from the assumption that the sorption sites are distributed exponentially with respect to the heat of sorption (Helfferich, 1995).

$$\ln C_{\rm ads} = \ln A + \frac{1}{n} \ln C_e \tag{2}$$

where A and 1/n are the Freundlich constants, obtained from the slope and intercept of plot of $\ln C_{ads}$ versus $\ln C_e$, indicating the sorption capacity and sorption intensity, respectively (Fig. 4). The value of 1/n < 1 (Table 1), indicates that Cr(VI) is favorably adsorbed by resin at low concentration. Greater value of A also suggests that there is a greater Cr(VI) uptake by the resin.

The Dubinin-Radushkevich, (D-R) isotherm (Eq. (3)) model is more general than the Langmuir isotherm as its deviations are not based on ideal assumptions such as equipotential of sorption sites, absence of steric hindrances between adsorbed and incoming particles and surface homogeneity on microscopic level (Itodo and Itodo, 2010).

$$\ln C_{\rm ads} = \ln X_{\rm m} - \beta \varepsilon^2 \tag{3}$$

where $\varepsilon = RT \ln(1 + 1/C_e)$, C_{ads} is the amount of sorbate adsorbed per unit mass of the sorbent and C_e is the amount of Cr(VI) ion in the liquid phase at equilibrium (Fig. 5). X_m and β are D–R isotherm constants. The constant gives an idea about the mean free energy E (kJ/mol) of sorption per molecule of the sorbate when it is transferred to the surface of the solid from infinity in the solution and can be calculated using the relationship:

$$E = \frac{1}{\sqrt{-2\beta}} \tag{4}$$



This parameter gives information about sorption mechanism as chemical ion exchange or physical sorption depending on

Figure 3 Langmuir isotherm (Conc. 1.0×10^{-4} – 1.0×10^{-3} mol/L, 0.1 g sorbent per 10 mL of sorbate with 60 min shaking time at 25 °C).

Parameters	Langmuir	Freundlich	D-R	Temkin
Q mmol/g	1.581 ± 0.054	_	_	-
A mmol/g	-	0.526 ± 0.094	-	-
$X_{\rm m} {\rm mmol/g}$	-	_	13.72 ± 0.034	-
A mol/g	_	_	-	1.08 ± 0.000034
$b \times 10^2 \text{ L/mol}$	91.32	_	-	-
1/ <i>n</i>	-	0.746	_	-
E kJ/mol	-	_	9.449	-
b J/mol	-	_	_	680.1
R _L	0.522-0.108	_	-	-
n	-	1.338	-	-
R^2	0.994	0.991	0.990	0.980

Table 1 Isotherm parameters for sorption of Cr(VI) on MAX-4 resin.



Figure 4 Freundlich isotherm (Conc. 1.0×10^{-4} – 1.0×10^{-3} mol/L, 0.1 g sorbent per 10 mL of sorbate with 60 min shaking time at 25 °C).



Figure 5 D-R isotherm (Conc. 1.0×10^{-4} - 1.0×10^{-3} mol/L, 0.1 g sorbent per 10 mL of sorbate with 60 min shaking time at 25 °C).

the value of E, i.e. 0–8 or 8–16 corresponding to physical or chemical sorption, respectively. Herein, the magnitude of E is between 8 and 16 kJ/mol that reveals the sorption process follows chemical ion exchange (Andal and Sakthia, 2010).

Temkin isotherm, assumes that the heat of sorption decreases linearly with the coverage due to sorbent-sorbate interaction.



Figure 6 Temkin isotherm (Conc. 1.0×10^{-4} – 1.0×10^{-3} mol/L, 0.1 g sorbent per 10 mL of sorbate with 60 min shaking time at 25 °C).



Figure 7 Reichenberg (R-B) plot at different temperatures for the sorption of Cr(VI) on MAX-4 resin.

$$q_e = B \ln A + B \ln C_e \tag{5}$$

$$b = \frac{RT}{B} \tag{6}$$

Table 2 Kinetic parameters for sorption of Cr(VI) on MAX-4 resin.						
Temperature	Pseudo-first order kinetic model			Pseudo-second order kinetic model		
	$K_1 \min^{-1}$	$q_e \operatorname{mol/g}$	R^2	K_2 g mol/min	$q_e \operatorname{mol/g}$	R^2
303	0.1602	2.300	0.951	162.08	0.00772	0.999
308	0.1183	1.568	0.963	43.971	0.00946	0.996
313	0.1325	2.244	0.987	47.529	0.00911	0.997

where A (μ mol/g) is Temkin isotherm constant, b (J/mol) is a constant related to heat of sorption, R is the gas constant (8.314 Jmol/K) and T the absolute temperature (K). A plot of q_e versus ln C_e enables the determination of the isotherm constants A, b from the slope and intercept (Fig. 6). The data are listed in Table 1. The value of b is quite higher that reveals the strong ionic interaction of sorbate and sorbent.

3.4. Sorption kinetics

The batch experiment plays a key role in designing and evolution for the presentation of sorption kinetics. According to the literature (Dabrowski, 2001) sorption kinetics can be determined by the following main steps:

Internal diffusion: Diffusion of molecules inside the pores. External diffusion: Diffusion of molecules from the bulk phase toward the interface space.

Surface diffusion: Diffusion of molecules in the surface phase.

Adsorption/desorption elementary processes.

In this regard numbers of kinetic models have been used to evaluate the sorption efficiency of sorbents. In this study, the experimental data are subjected to different kinetic equations such as Lagergren (Lagergren, 1898), pseudo-second order rate expression (Aksu and İşoğlu, 2005), Morris–Weber (Weber and Morris, 1963) and Reichenberg (Reichenberg, 1953).

Lagergren/pseudo first order and pseudo second order kinetic equation are as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{7}$$

$$\frac{t}{q_t} = \left(\frac{t}{k_2 q_e^2}\right) + \left(\frac{1}{q_e}\right) \tag{8}$$

where q_t (mol/g) is the amount of sorbent adsorbed at time t, q_e (mol/g) is the amount of sorbent adsorbed at equilibrium and k_1 (min⁻¹) and k_2 (g/mol/min) are the sorption rate constants. The q_e and K_1 and K_2 were obtained from the slope and intercept of linear plots between ln ($q_e - q_t$) versus t and (t/q_e) versus t. Table 2 shows the values calculated from these plots. From the values of regression coefficient (R^2), it has been observed that experimental data follow pseudo second order kinetics.

Reichenberg equation (Eq. (9)) was used to test the sorption process, whether sorption is film diffusion or intra-particle.

$$Q = 1 - \frac{6e^{-B_t}}{\pi^2}$$
(9)

Rearranging the above equation in linear form we get

$$B_t = -0.4977 - \ln(1 - Q)$$

where $Q = q_t/q_m$, $B_t = \pi^2 D_i/r^2$ and q_t and q_m are adsorbed concentration at time *t* and the maximum sorption capacity and D_i is the effective diffusion coefficient of the sorbate species inside the sorbate particle.

It is clear from the linear plot of B_t versus time t (Fig. 7) that intra-particle diffusion is a rate controlling step with a small friction of sorption that occurs through film diffusion because the plot does not pass through the origin.

Morris–Weber equation was also used to explore the kinetic sorption process.



Figure 8 Morris–Weber plot at different temperatures for the sorption of Cr(VI) on MAX-4 resin.



Figure 9 Sorption of Cr(VI) onto MAX-4 resin as a function of time at different temperatures.



Figure 10 Arrhenius plot of the sorption of Cr(VI) on MAX-4 resin.

Table 3	Thermodynamic	parameters	for	sorption	of	Cr(VI)
on MAX-	4 resin.					

<i>∆H</i> (kJ/mol)	$\frac{\Delta S}{(kJ/mol/K)}$	ΔG (kJ mol)		
		298 K	308 K	318 K
43.655	0.161731	-4.608 ln $K_c = 1.861$	-6.006 ln $K_c = 2.346$	-7.851 ln $K_c = 2.971$



Figure 11 Effect of temperature on sorption of Cr(VI) on MAX-4 resin.



Figure 12 Sorption of Cr(VI) on MAX-4 resin in the presence of other anions.



Figure 13 Regeneration profile of resin with HCl.

$$q_t = R_d \sqrt{t} \tag{10}$$

where q_t is the adsorbed concentration at time t, and R_d is intra-particle diffusion rate constant. The linear plot (Fig. 8) of q_t versus \sqrt{t} shows that intra-particle diffusion occurs and line does not pass through the origin, which means the intra-particle diffusion is not the only rate limiting parameter controlling the process. The value of R_d from the slope was calculated as $0.9 \,\mu\text{mol/g}/\sqrt{t}$ (298 K), $0.2 \,\mu\text{mol/g}/\sqrt{t}$ (308 K) and $1.1 \,\mu\text{mol/g}/\sqrt{t}$ (318 K) with R^2 values 0.987, 0.991 and 0.987, respectively.

3.5. Thermodynamics of sorption

Sorption of Cr(VI) onto MAX-4 Resin was analyzed at different temperatures. It has been observed that as temperature increases the sorption capacity value increases (Fig. 9). The obtained values from the plot are 0.085 (298 K), 0.1017 (308 K) and 0.1188 mmol/g (318 K), respectively.

The temperature effect was analyzed by using Arrhenius equation (Solangi et al., 2011) at optimized conditions,

$$\ln k_1 = \ln A_o + \frac{E_a}{RT}$$

where A_o (1/min) is the "frequency factor" and independent of temperature, E_a (kj/mol) is the activation energy, R (8.314 J/mol/K) is the gas law constant and T is the absolute temperature. The value of E_a (94.32 kJ/mol) and A_o (0.757/min) is calculated from the plot of $\ln k_1$ versus 1/T (Fig. 10). The value of activation energy is in the range of 40–800 kJ/mol that suggests the sorption is chemical in nature (Nollet et al., 2003; Singh and Rawat, 1994).

From the plot of ln k_c versus 1/T (Fig. 11), numerical values of ΔH (kJ/mol), ΔS (kJ/mol /K) and ΔG (kJ/mol) were calculated using following equations.

$$\ln k_c = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \tag{11}$$

$$\Delta G = -RT\ln k_c \tag{12}$$

The evaluated thermodynamic parameters, change in enthalpy ΔH (kJ/mol), change in entropy ΔS (kJ/mol /K) and change in free energy ΔG (kJ/mol) are listed in Table 3. The negative value of ΔG shows the feasibility of the sorption process and the decrease in ΔG values with an increase in temperature indicates the spontaneity of the process at higher temperature. The positive value of ΔH confirms the endothermic process and ΔS reveals that there is good affinity of Cr(VI) toward MAX-4 Resin.

3.6. Interference study

Most industrial effluents are source of many contaminations. They may interfere with uptake of target species, for example existing of other anions such as F^- , Cl^- , Br^- , NO_3^- , etc. The

able 4 Comparison of Cr(VI) sorption capacity of MAX-4 resin with other sorbents.					
Resin	pH	Capacity mmol/g	Reference		
Azophenolcarboxylic acid resin	2.0	0.69	Pramanik, et al. (2007)		
6-Mercapto Purinylazo Resin	1.0.	1.06	Mondal (2003)		
Amberlite XAD-7 impregnated with Aliquat 336	6.0	0.97	Saha, et al. (2004)		
Amberlite XAD-16	1.0	0.40	Tunceli and Turker (2002)		
Lignocellulosic substrate	2.1	0.72	Dupont and Guillon (2003)		
Modified Amberlite XAD-4 (MAX-4)	6.9	1.08	Present study		

study was carried out with different concentration ratios of target and interfering anion, i.e. 1:1, 1:5 and 1:10. From the results it is concluded that there is no significant change in uptake of target species in the presence of other co-existing anions at optimized conditions (Fig. 12).

3.7. Desorption

Efficiency of resin can be justified with its reusability and comparative efficiency (Table 4). The used resin can be regenerated by washing with 5 M HCl (Fig. 13).

4. Conclusion

It has been concluded that modified Amberlite XAD-4 (MAX-4) resin is an efficient ion exchange material for the removal of Cr(VI) from aqueous media. The maximum sorption of Cr(VI) achieved at pH 6.9 means that the MAX-4 resin can work at neutral pH. The isotherm models, kinetics and thermodynamic study further confirm the experimental results. The interference study shows selectivity of resin for Cr(VI) at optimized conditions. Hopefully, this study will find applicability in analytical, environmental and industrial fields.

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