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Indirect speciation of Cr (VI) and Cr (III) in water and food samples using newly synthesized amberlite XAD-7 functionalized resin

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Key words: Preconcentration, Speciation, Chromium species, Amberlite XAD-7, Diphenylcarbazide

Abstract

The availability of good quality water is essential for avoiding diseases and improving the quality of life. The increase in both industrial activities and human population has adversely affected several aspects of the environment including the quality of water bodies. Because of the high solubility of heavy metal ions in the aquatic environment, the heavy metals can be adsorbed by living organisms and cause severe health disorders even at relatively low levels. The main aim of the present study was to develop a new solid phase sorbent for speciation and preconcentration of chromium species by functionalizing Amberlite XAD-7 with diphenylcarbazide. FTIR analysis was conducted in order to confirm the successful functionalization. Cr (VI) was preconcentrated using batch method. Hydroxylamine hydrochloride was used as reducing agent to reduce Cr (VI) to Cr (III) and total chromium was determined. Cr (III) was calculated by subtracting the concentration of Cr (VI) from total chromium. Effect of different parameters such as pH, time, and sample volume, shaking time, eluent type, volume and concentration was investigated for maximum sorption as well as recovery of Cr (VI). Quantitative recovery of Cr (VI) 95.8 ± 1.098 was achieved at pH 4 using 10 mL of 2 M HNO_3. Kinetic, and thermodynamic studies showed that the sorption of Cr (VI) is second order, endothermic and spontaneous. With good overall properties like good recovery, maximum selectivity and stable application capacity, this newly functionalized XAD-7 resin can be successfully used for the removal of chromium from different aqueous and food samples.

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Introduction

Among the heavy metals, chromium is one of the most common pollutants in the environment and exists in different oxidation states. The most common oxidation states of chromium are trivalent and hexavalent chromium. The toxicity of chromium depends upon the type of oxidation state in which it is present due to the difference in biological action, biochemical behavior and their adverse effects on the environment (Hassanien *et al.*, 2008) Trivalent chromium is one of the vital nutrients in the living organisms and controls the glucose level by sustaining the insulin functioning. It also transfers proteins and fats by combining with different hormones. Sources of trivalent chromium are many industrial processes exclusively in tanning leather (Memon *et al.*, 2009; Tokalıoglu *et al.*, 2009). Hexavalent chromium is cancer-causing and due to its strong oxidizing power, it can also harm lever, kidney and lungs. Hexavalent chromium is transported to the environment through the industrial effluents of textile, steel and electroplating industries (Mahmoud *et al.*, 2008). The US environmental protection agency has set 0.1 mg L^{-1} as the tolerable limit of total chromium in drinking water whereas according to World Health Organization, 50 µg L^{-1} is the recommendation value for Cr (VI) (Duran *et al.* 2007; Narin *et al.*, 2008).
As the reactivity and adverse effects of chromium depends on the type of oxidation state present in different environmental and biological systems, therefore speciation of chromium is of particular importance.

The selective determination of hexavalent chromium is very important due to its small size, strong oxidative property and its easy permeability through living cells membranes. Determination of Trivalent and hexavalent chromium using instrumental techniques like flame and graphite furnace atomic absorption spectrophotometry, inductively coupled plasma mass and atomic emission spectrometry and other spectroscopic techniques is less sensitive and difficult (Bulut *et al.*, 2007). Therefore, to overcome this problem usually some separation and enrichment steps like liquid liquid extraction (just like solid phase extraction, in liquid liquid extraction both phases are in liquid state), co-precipitation, solid phase extraction, off line and on line preconcentration become necessary (Mansur *et al.*, 2008; Uluozlu *et al.*, 2010; Lemos and Baliza, 2005). Speciation is usually done by separation and enrichment of one of the chromium species either Cr (VI) or Cr (III) and then total chromium is determined either by oxidation of Cr (III) to Cr (VI) or by reduction of Cr (VI) to Cr (III) using suitable procedures (Tuzen and Soylak, 2007).

Solid phase extraction plays a very significant role in chromium speciation due to its flexibility, simplicity, environment friendliness, reusability, high preconcentration factor, absence of liquid phase and from economic point of view (Narin *et al.*, 2008; Silva *et al.*, 2000). For speciation and solid phase extraction of chromium, different types of solid supports like activated alumina (Marques *et al.* 2001), activated carbon (Gil *et al.*, 2006), and functionalized resins (Pramanik *et al.*, 2007) are used.

Functionalized resins can be synthesized using a small sized ligand and a suitable cross-linked polymer depending upon different targeted properties either physically i.e. simple immobilization of ligand on polymer or chemically through an intermediate spacer like $-N=N-$ or $-CH_2-$ (Filik 2002; Kumar *et al.* 2000). Functionalized resins are superior in many respects such as when used as solid phase then, three types of phenomena take place i.e. physical adsorption, complex formation and ion exchange (Tokalıoglu *et al.* 2009).

Amberlite XAD-7 is an acrylic ester has high surface area, uniform pore size and is homogenous. Diphenylcarbazide is a specific ligand for chromium. The main objective of the present study is therefore to remove Cr (VI) from different water and food samples and then to determine Cr (III) by subtracting Cr (VI) concentration from total chromium using functionalized Amberlite XAD-7 with diphenylcarbazide.

Different parameters affecting the removal of Cr (VI) has been optimized using batch method. XAD-DPC was characterized by FTIR. The mechanism for the removal of Cr (VI) was evaluated by applying different types of isothermal and kinetic models. Thermodynamic studies were also carried out to investigate the feasibility of the adsorption of Cr (VI) onto newly functionalized XAD-DPC. Recovery studies were also conducted to find out the cost efficiency of the sorbent.

Materials and methods

Instruments

For characterization, FTIR spectrophotometer Pretige 21 Shimadzu Japan was used. For the analysis of chromium, a Perkin-Elmer Analyst 200 Atomic Absorption Spectrometer with air-acetylene flame was used.

Materials

All reagents used in this work were of analytical reagent grade purity purchased from Merck, Germany without any further purification. Amberlite XAD-7 was purchased from Alfa Aesar, N,N-Methylene bisacrylamide was purchased from Biom Laboratories USA and Potassium peroxydisulphate from BDH, England.

Solution preparation

Stock 1000 µgmL^{-1} chromium standard solution was purchased from Merck. Working standards were prepared from this solution by dilution. Stock 1000 µgmL^{-1} solutions of Cr (III) and Cr (VI) were prepared by dissolving appropriate amounts of $Cr(NO_3)_3$. $4H_2O$ and K_2CrO_4 in distilled water. Working solutions of desired concentration were prepared by proper dilution of this solution. Mellvain Buffer solutions of pH 2-8 were prepared by adjusting pH of stock solution of 0.2 M disodium phosphate with 0.1 M citric acid.

Synthesis of functionalized resin

Amberlite XAD-7 (25 g) was immersed in 300 mL solution in a 1000 mL beaker containing 1.5 g of potassium peroxydisulphate and 5g of N, N′-methylenebisacrylamide. To this reaction mixture 17.5 g acrylamide was added and it was stirred at 70 °C for 3 hr. The product was washed thoroughly with acetone and distilled water and was dried at room temperature. For modification with 1,5-diphenylcarbazide, 1,5-diphenylcarbazide (10 g) was dissolved in hot ethanol and refluxed with product at 70 °C for 6 hr. The modified Amberlite XAD-7 (XAD-DPC) was washed with ethanol and dried.

Batch preconcentration procedure for Cr (VI)

XAD-DPC (100 mg) was taken in separate beakers. To each beaker 50 mL of 2 µgmL^{-1} of Cr (VI) solution was added. The pH of each solution was adjusted to pH 4 by adding suitable volume of Mellvain buffer of pH 4 and was allowed to equilibrate for 60 min. It was then filtered and the filtrate was collected in a 100 mL volumetric flask and diluted upto the mark with distilled water. The unsorbed metal ions concentration in the filtrate was determined using flame atomic absorption spectrophotometer (FAAS). For desorption, the loaded XAD-DPC was equilibrated with 10 mL of 2 M HNO_3 in acetone. The mixture was then filtered and the filtrate was collected in a 100 mL volumetric flask and diluted upto the mark. The desorbed metal ions concentration in the filtrate was determined using FAAS.

Sorption capacity (q_e) and percent sorption was calculated according to the following general equations:

$$q_e = \left[\frac{C_i - C_f}{m}\right] V \qquad (1)$$

$$\%\,sorption = \left[\frac{C_i - C_f}{C_i}\right] X100 \qquad (2)$$

Where q_e is the amount of chromium sorbed on the sorbent (mgg^{-1}), C_i and C_f represent the initial and equilibrium concentrations in µgmL^{-1}, respectively; V is the volume of chromium solution (mL) and m is the amount of sorbent (g).

Total chromium determination

Total chromium was determined by reducing Cr (VI) to Cr (III). For this purpose, 2 mL of 2 M HCl and 1 mL of 5 % hydroxylamine hydrochloride were added to 80 mL solution containing 0.8 µgmL^{-1} of Cr (VI) and Cr (III) and was kept for 45 min at room temperature. After reduction of Cr (VI) to Cr (III), pH of the solution was adjusted to pH 4 and final volume was made up to 100 mL with distilled water. The batch preconcentration procedure was applied and total chromium was determined by FAAS. The concentration of Cr (III) was calculated by subtracting Cr (VI) concentration from total chromium concentration.

Preparation and analysis of real samples

Water samples from river Jhelum and tap water from our laboratory and from Baragali summer campus was collected in pre-washed polyethylene bottles and were analyzed without any pretreatment. Tomato, spinach and onion were collected from local vegetable market. They were washed with tap water and then with distilled water. These were sliced in uniform size and dried in an oven at 100 °C for 24 h. The vegetables were grounded to fine powder and 0.5 g of this powder was taken and wet digested in 10 mL mixture of HNO_3, $HCLO_4$ and H_2SO_4 acids (5:1:1) at 80 °C on a hot plate. The mixture was filtered, transferred to 50 mL flask and volume was made up to the mark. These samples were then used for chromium determination by the above described preconcentration method.

Results and discussion

Characterization of functionalized resin

FTIR spectra of simple and functionalzied Amberlite XAD-7 (XAD-DPC) were recorded in the range of 40-4000 cm^{-1} in order to confirm the successful functionalization of Amberlite XAD-7 with diphenylcarbazide. On comparing the spectra given in Figure 1 & 2, it was clear that in case of XAD-DPC, new IR bands have appeared. These bands are at 1630 cm^{-1} for (N-C=O), 3410 cm^{-1} for NH, 1590 cm^{-1} for N-N, 1600 cm^{-1} for C=C aromatic and at 3044 cm^{-1} for C-H aromatic. Thus FTIR analysis indicated the successful functionalization of Amberlite XAD-7.

Table 1. Effect of eluent volume on % recovery of Cr (VI) using 2 M HNO_3 in acetone as eluent.

Volume of Eluent (mL)	Recovery (%)
5	56.2±0.598
10	95.8±0.654
15	94.5±0.843
20	90.2±0.913
25	90.4±0.786

Effect of pH on Sorption and desorption of Cr (VI) and Cr (III)

The initial pH of the solution is the major factor that confines the sorption capacity of the sorbent as well as for desorption of the heavy metal ions from the sorbent to make the sorbent available for the next sorption/desorption cycle. The sorption/desorption of Cr (VI) and Cr (III) as a function of H^{+} concentration was investigated in the pH range of 2-8 using Mellvain buffer of pH 2-8. As Cr (VI) forms complex with diphenylcarbazide at a highly acidic pH therefore the quantitative recovery for Cr (VI) (95.5 %) was observed at relatively high pH i.e. at pH 4 whereas for Cr (III), no quantitative recovery was achieved at this pH. For Cr (III), the maximum recovery was 12 % at pH 2. So, the two chromium species can be separated easily at pH 4. To carry out further experiments for Cr (VI), pH 4 was selected as optimal pH in the Mellvain buffer system.

Effect of shaking time, type, concentration and volume of eluent

The maximum recovery of Cr (VI) was achieved by optimizing the shaking time, volume and concentration of eluent and their type. The shaking time was varied from 10-70 min and 20 min was found to be optimum shaking time (Fig. 4). The eluent volume was varied from 5-25 mL and 10 mL was found to be optimum eluent volume (Table 1). To get the maximum recovery, hydrochloric and nitric acid were investigated in different molar concentrations. The results are shown in Fig. 5. The maximum recovery was achieved with 2 M HNO_3.

Effect of sample volume and preconcentration factor

For finding out the effect of sample volume, the total metal ion concentration (500 µg) and the amount of sorbent (100 mg) were kept constant and the sample volume was varied from 50 mL to 1000 mL. The results are shown in Fig. 6. It can be seen from the figure that sorption of Cr (VI) decreases from 100.0 % to 71.4 % with increasing sample volume from 50 to 1000 mL.

Table 2. Preconcentration factor for sorption of Cr (VI) from XAD-DPC.

Initial Sample volume (mL)	Final eluent volume (mL)	Preconcentration factor	Desorption (%)
50	10	5	95.8
100	10	10	100
150	10	15	100
200	10	20	100
300	10	30	100
400	10	40	100
500	10	50	100
1000	10	100	100

Table 3. Kinetic parameters for sorption of Cr (VI) using XAD-DPC.

q_e (mgg^{-1}) (exp.)	Pseudo first order kinetic model			Pseudo second order kinetic mode			Intra particle diffusion model			Elovich model		
	K_1 (min^{-1})	q_e (mgg^{-1})	R^2	K_2 (gmg^{-1} min^{-1})	q_e (mgg^{-1})	R^2	K_{int} (mgg^{-1} min$^{1/2}$)	C	R^2	α (mgg^{-1} min^{-1})	β (g mg^{-1})	R^2
2.00	0.038	0.135	0.4417	0.498	2.009	1.000	1.8293	0.460	0.5712	1.875E+10	14.92	0.5712

Recovery of Cr (VI) for different sample volumes (50 to 1000 mL) was also carried out under optimum condition for Cr (VI). The results are shown in Fig. 7. It was observed that sorption of Cr (VI) decreases with increase in sample volume therefore maximum desorption was achieved with increase in sample volume.

Preconcentration factor was calculated and is given in Table 2. It can be seen from the table that a maximum preconcentration factor of 100 was obtained for functionalized resin.

Kinetics of Sorption

The results of contact time were used to study the kinetic mechanism that controls the sorption process. Four kinetic models i.e. pseudo first order, pseudo second order, intraparticle diffusion and Elovich were employed for the interpretation of the experimental data. These four models are given in Eqs. 3-6.

Table 4. Freundlich and Langmuir parameters for sorption of Cr (VI) using XAD-DPC.

Freundlich model				Langmuir model		
K_F (mgg^{-1})	n	1/n	R^2	a_L (Lmg^{-1})	q_{max} (mgg^{-1})	R^2
2.47	1.5260	0.6553	0.9274	2.12E+2	14.97	0.9567

Table 5. Thermodynamic parameters for sorption of Cr (VI) from aqueous solution using XAD-DPC.

T (K)	ΔG° (KJmol^{-1})	ΔH° (KJmol^{-1})	ΔS° (JK^{-1}mol^{-1})
303	-3.50	26.6	98.7
313	-4.08		
323	-5.12		
333	-6.45		
343	-6.87		
353	8.10		

$$log(q_e - q_t) = logq_e - \frac{K_1 t}{2.303} \quad (3)$$

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{K_2 q_e^2} \quad (4)$$

$$q_t = K_{int} t^{1/2} + C \quad (5)$$

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t) \quad (6)$$

Where q_e and q_t is the amount of metal ion sorbed (mgg^{-1}) at equilibrium and at any given time and K_1 and K_2 are the pseudo first order and pseudo second order reaction rate constant for sorption (min^{-1}). C is the intercept and related to the thickness of the boundary layer and K_{int} ($mgg^{-1}min^{-1/2}$) is the intraparticle diffusion rate constant. α and β are known as the Elovich coefficients, α represents the initial adsorption rate ($mgg^{-1}min^{-1}$) and β is related to the extent of surface coverage and activation energy for chemisorption ($gmin^{-1}$) respectively.

Table 6. Effect of interfering ions on sorption of Cr (VI) using XAD-DPC.

Interfering Ion	Conc. of interfering ions (μgmL^{-1})	% Sorption of Cr(VI)	Interfering ion	Conc. of interfering ions (μgmL^{-1})	% Sorption of Cr(VI)
Cr(III)	0	100±0.608	Pb(II)	0	100±0.569
	1	100±0.321		1	100±0.160
	2	100±0.230		2	100±0.069
	4	100±0.199		4	100±0.193
	8	100±0.413		8	100±0.576
	10	100±0.190		10	100±0.240
	12	80±0.090		12	67±0.467
	15	65±0.157		15	56±0.132
Mn(II)	0	100±0.453	Fe(III)	0	100±0.290
	1	100±0.139		1	100±0.109
	2	100±0.276		2	100±0.161
	4	100±0.189		4	100±0.189
	8	100±0.169		8	100±0.156
	10	100±0.540		10	76±0.127
	12	65±0.170	Cu(II)	0	100±0.256
	15	56±0.690		1	100±0.323
Cd(II)	0	100±0.274		2	100±0.860
	1	100±0.540		4	100±0.324
	2	100±0.860		8	100±0.171
	4	100±0.534		10	100±0.109
	8	100±0.320		12	67±0.176
	10	100±0.100		15	45±0.456
	12	75±0.189	Ni(II)	0	100±0.130
	15	50±0.320		1	100±0.768
Co(II)	0	100±0.189		2	100±0.476
	1	97±0.115		4	100±0.189
	2	80±0.070		8	100±0.167
	4	56±0.221		10	100±0.453
	8	40±0.089		12	76±0.567
	10	37±0.342		15	57±0.176

The kinetic parameters calculated from Eqs. 3-6 are given in table 3. The maximum value of correlation coefficient (1.000) and the close resemblance of experimental theoretical values of sorption capacity show that the sorption data can be best described by second order model.

This proposes that the rate controlling step for the sorption of Cr (VI) onto XAD-DPC is chemisorption, where valency forces are involved via electrons sharing or exchange between the functionalized resin and Cr (VI).

Effect of initial metal ion concentration/ Sorption isotherm Study

The relationship between the concentrations of metal ions in the solution and the amount of metal ions sorbed onto the resin is best described by different types of isotherms at constant temperature and pressure. Two sorption isotherms Freundlich and Langmuir were applied in the present study and these isotherms showed a good linear correlation for a wide metal ion concentration range (0.01-25 µgmL^{-1}). The Freundlich isotherm is used to describe the sorption onto the heterogenous surfaces. Freundlich isotherm is expressed by the following equation:

$$q_e = K_F C_e^{\frac{1}{n}} \qquad (7)$$

The linear form of Freundlich equation is given below

$$log q_e = log K_F + \frac{1}{n} log C_e \qquad (8)$$

Where K_F is the Freundlich sorption isotherm constant (mgg^{-1}), 1/n (gL^{-1}) is a measure of the sorption intensity or the heterogeneity factor. While q_e is the amount sorbed (mgg^{-1}) and C_e is the equilibrium concentration (µgmL^{-1}).

Table 7. Preconcentration and determination of Cr (VI) and Cr (III) in spiked aqueous samples using XAD-DPC.

Sample	Added (µgmL^{-1})		Found (µgmL^{-1})		Total (µgmL^{-1})	Recovery (%)	
	Cr (VI)	Cr (III)	Cr (VI)	Cr (III)		Cr (VI)	Cr (III)
Tap water from Laboratory	0.5	0	0.497±0.606	----	0.497±0.605	100±0.209	----
	1	0.5	1.120±0.274	0.512±0.354	1.632±0.174	95.0±0.126	97.0±0.112
	2	1	1.998±0.142	1.009±0.128	3.007±0.043	91.6±0.233	95.0±0.141
Tap water from Baragali campus	0.5	0	0.501±0.569	----	0.501±0.367	100±0.141	----
	1	0.5	0.897±0.109	0.512±0.324	1.409±0.209	96.0±0.043	100±0.032
	2	1	2.098±0.815	1.109±0.071	3.207±0.070	90.8±0.098	97.9±0.225
River water	0.5	0	0.489±0.290	----	0.489±0.200	100±0.035	----
	1	0.5	1.005±0.713	0.510±0.253	1.515±0.213	95.4±0.176	100±0.234
	2	1	1.986±0.130	0.990±0.462	2.976±0.123	91.7±0.098	98.7±0.165

Table 8. Preconcentration and determination of Cr (VI) in food samples using XAD-DPC.

Vegetable samples	Cr (VI) found (µgmL^{-1})	Sorption (%)	Desorption (%)
Onion-I	0.50±0.009	100±0.354	100±0.022
Onion-II	0.56±0.010	100±0.128	102±0.116
Spinach	0.49±0.124	100±0.071	101±0.087
Tomato	0.60±0.210	100±0.124	100±0.114

The Langmuir isotherm model is used to describe sorption for sorbents that have homogenous and flat surfaces.

This model assumes that only monolayer sorption can take place in a one-on-one manner. The Langmuir isotherm is expressed by the following equation:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{q_{max}} \qquad (9)$$

Where C_e is the equilibrium concentration (µgmL^{-1}), q_e is the amount of solute sorbed per gram of sorbent, q_{max} is the maximum sorption capacity in mgg^{-1} and b is the Langmuir isotherm constant which represents the sorption energy in Lmg^{-1}.

The values of different constants calculated from the slope and intercept of linear forms of Freundlich and Langmuir isotherm are given in Table 4.

The sorption capacity calculated from the Langmuir isotherm is higher as compared to Freundlich isotherm indicating that the sorption of Cr (VI) onto XAD-DPC is following Langmuir isotherm. The bonding strength (a_L) calculated from intercept of linear line of Langmuir is 212.6 which is due to the strong chelation of Cr (VI) with XAD-DPC.

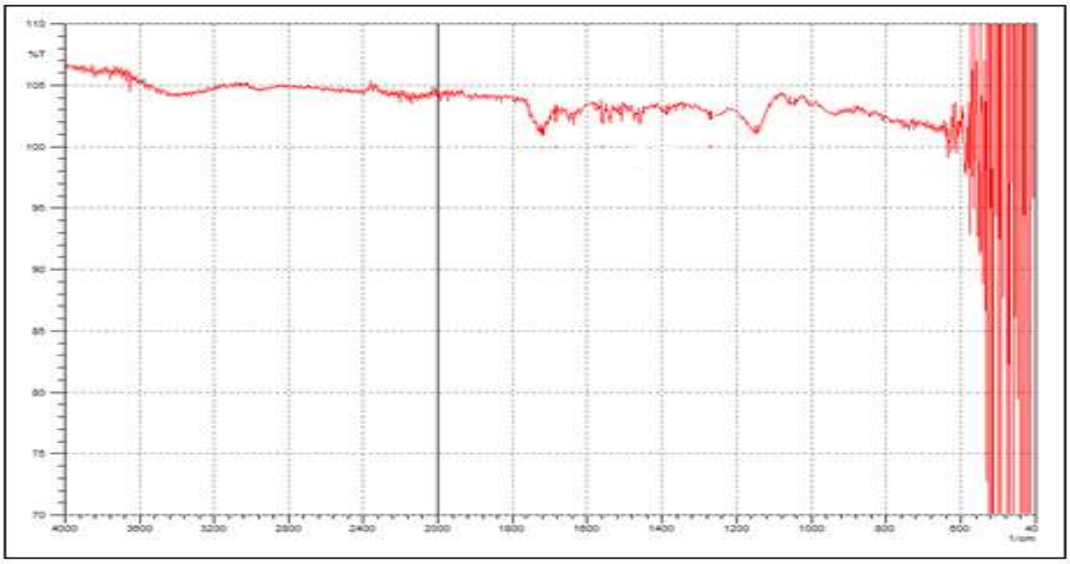

Fig. 1. FTIR spectrum of simple Amberlite XAD-7.

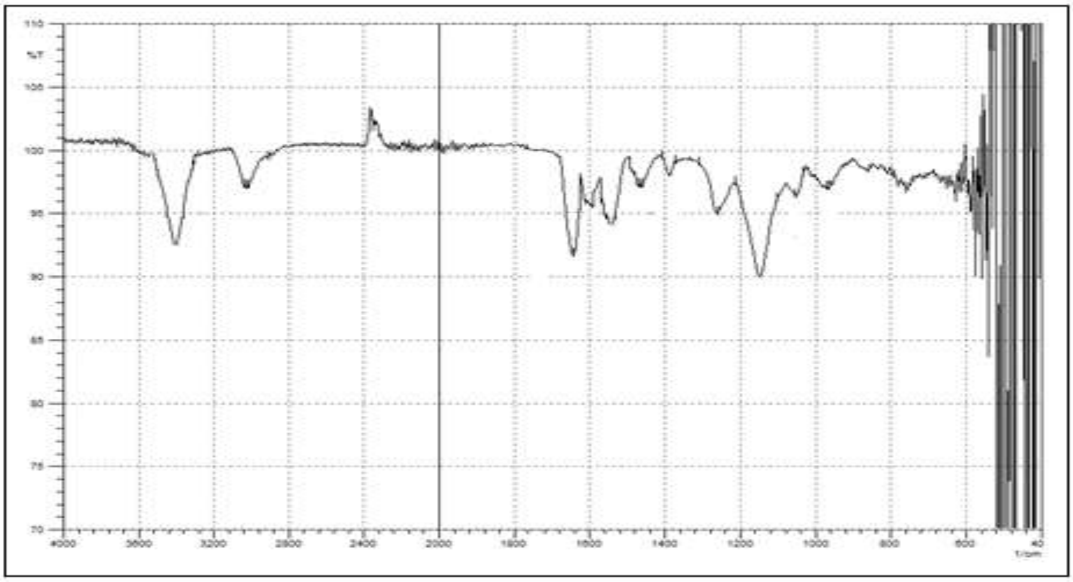

Fig. 2. FTIR spectrum of XAD-DPC.

The basic characteristics of Langmuir isotherm can be described by R_L. R_L is a separation and dimensionless parameter which indicates whether the sorption of metal ions is favorable or not onto the sorbent. R_L is represented by eq. 10.

$$R_L = \frac{1}{1+bC_o} \qquad (10)$$

where C_o is the initial metal ion concentration in μgmL^{-1}. The values of R_L indicate the type of Langmuir isotherm as $R_L = 0$, for irreversible, $0 < R_L < 1$, for favorable, $R_L = 1$ for linear and $R_L > 1$ for unfavorable (Memon *et al.* 2007; Sharma *et al.* 2009).

The values of R_L have been found between 0 and 1 showing favorable sorption of Cr (VI) onto functionalized resin.

Equilibrium and thermodynamic studies

The effect of temperature on the sorption characteristics of Cr (VI) onto XAD-DPC was investigated by determining the sorption isotherms in 303-353 K temperature range.

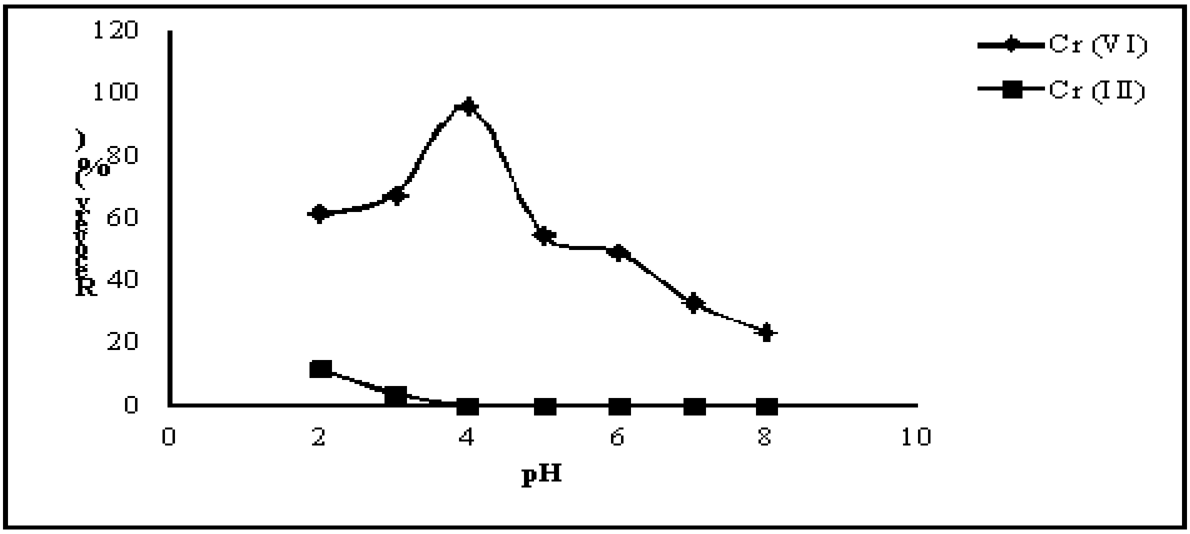

Fig. 3. Effect of pH on % recoveries of Cr (VI) and Cr (III).

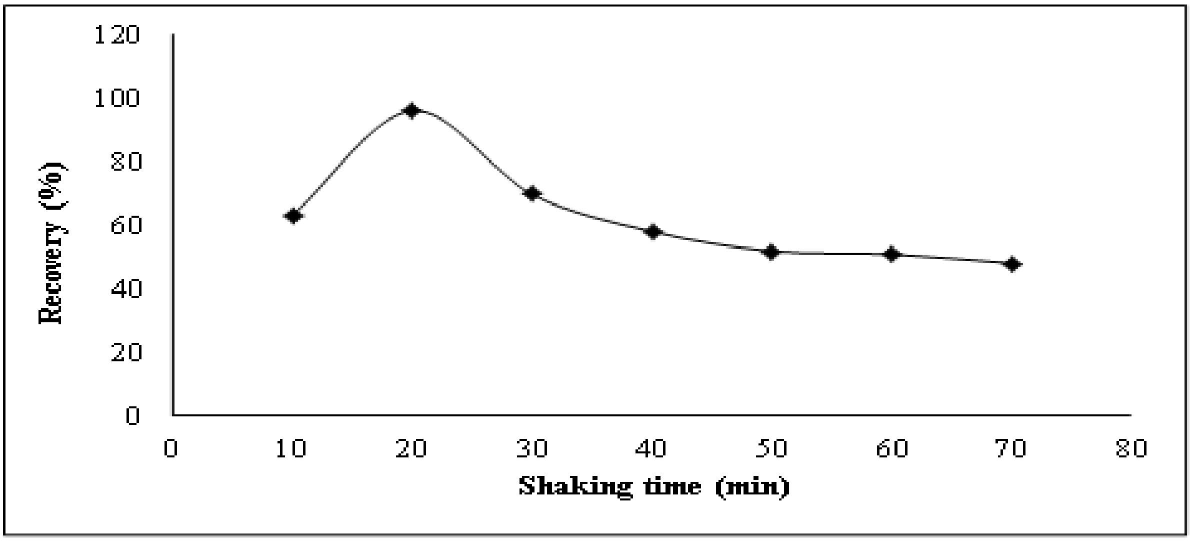

Fig. 4. Effect of shaking time on % recovery of Cr (VI) using 10 mL of 2 M HNO_3 in acetone.

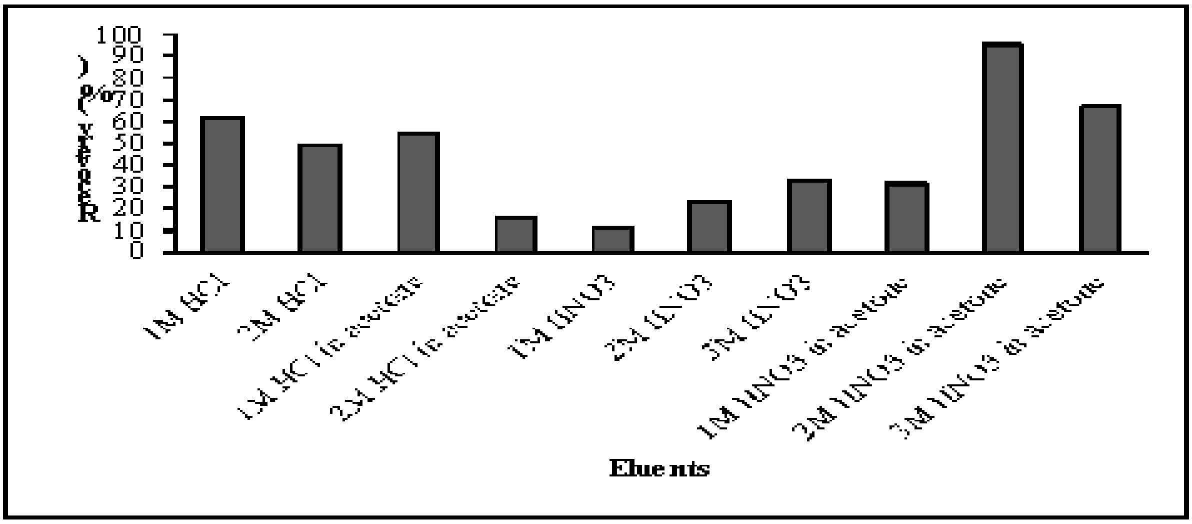

Fig. 5. Effect of type and concentration of eluent on % recovery of Cr (VI).

Thermodynamic parameters like change in Gibbs free energy (ΔGº), change in enthalpy (ΔHº) and change in entropy (ΔSº) were calculated by using the classical thermodynamic equations given below.

$$\Delta G^{\circ} = -RT\ln K_D \quad (11)$$

$$K_D = \frac{q_e}{C_e} \quad (12)$$

$$\ln K_D = -\frac{\Delta G^{\circ}}{RT} = -\frac{\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R} \quad (13)$$

Where K_D is the distribution constant, q_e and C_e are already described above.

The values of ΔGº, ΔHº and ΔSº were calculated using above Eqs. and are given in table 5. The positive value of ΔHº shows that the sorption of Cr (VI) is an endothermic process.

The values of ΔGº confirmed that the sorption is spontaneous and feasible in nature. The positive value of ΔSº shows strong affinity of XAD-DPC for sorption of Cr (VI) as it leads to increase in randomness at the interface between solid and solution.

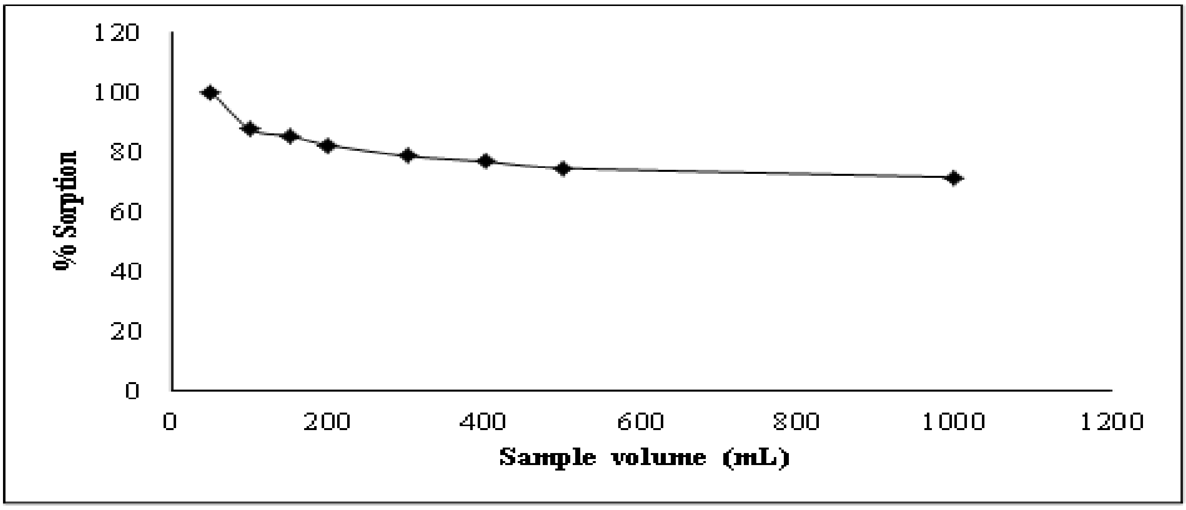

Fig. 6. Effect of sample volume on % sorption of Cr (VI).

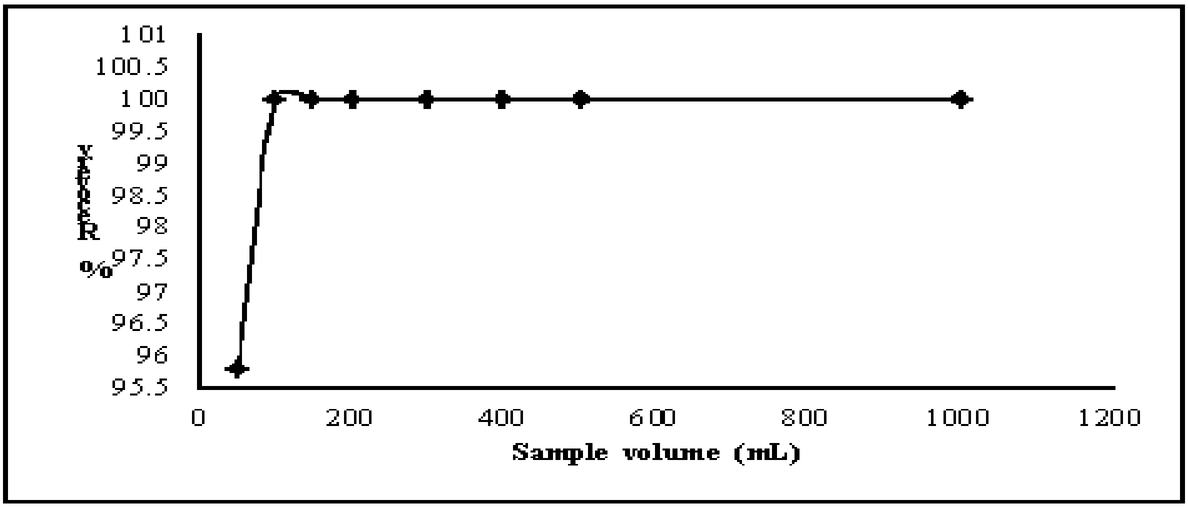

Fig. 7. Effect of sample volume on % desorption of Cr (VI) from XAD-DPC.

Effect of interfering ions

The selective sorption behavior of XAD-DPC for Cr (VI) sorption was investigated in the mixed solutions containing selected foreign ions like Co (II), Fe (III), Cu (II), Pb (II), Cr (III), Mn (II), Ni (II) and Cd (II) in the range of 0.1 µgmL^{-1} to 15 µgmL^{-1} under optimum conditions. The results are given in Table 6. It can be seen from the table that in the presence of other metal ions even at concentration higher than the equimolar concentration, XAD-DPC showed greater sorption for Cr (VI) indicating that XAD-DPC is very selective for Cr (VI). Since in daily life the removal of toxic metals is carried in mixed metal ions system, therefore the high selectivity of XAD-DPC is a matter of practical importance and Cr (VI) can be removed from matrices which contain interfering ions.

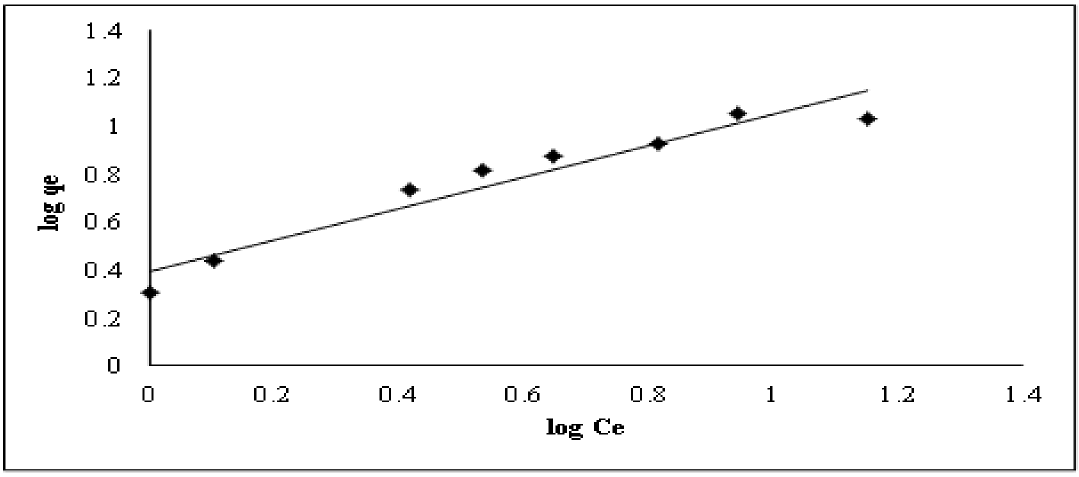

Fig. 8. Freundlich sorption isotherm for sorption of Cr (VI).

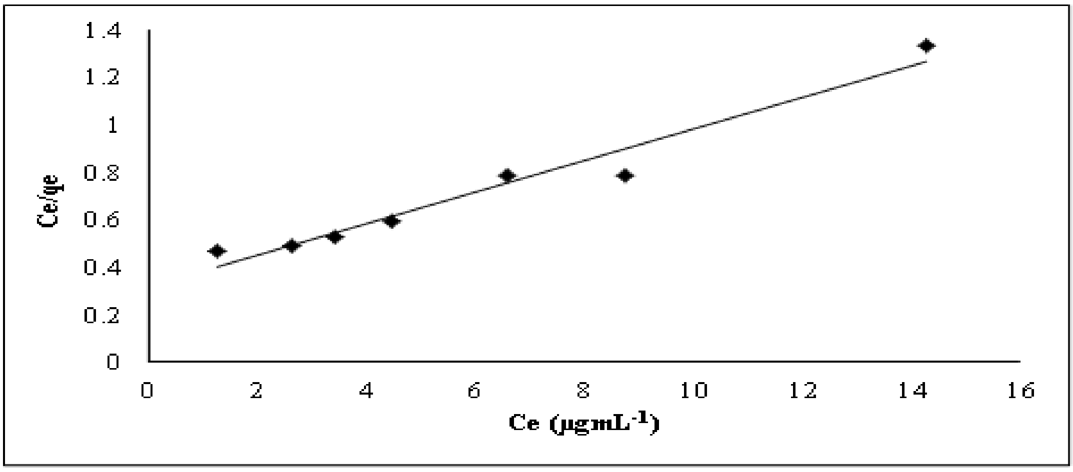

Fig. 9. Langmuir sorption isotherm for sorption of Cr (VI).

Application of the method

The preconcentration procedure using XAD-DPC was applied for the speciation of chromium species in different water samples collected from tap of laboratory and Baragali summer campus and river Jhelum. As there was no chromium in these samples, therefore samples were spiked by standard addition method and their sorption and desorption was studied. The results are given in Table 7. The water samples were spiked with different concentrations (0.5 to 2.0 µgmL^{-1}) of chromium species and their concentration were determined by FAAS. Cr (VI) was determined using batch preconcentration method and Cr (III) was determined by subtracting Cr (VI) from total chromium. It can be seen from the table that % recovery for Cr (VI) and Cr (III) is in the range of 91-100 % and 95-100 % respectively.

Cr (VI) was also determined in food samples. The results are given in Table 8. From these results it can be concluded that XAD-DPC can be effectively used for preconcentration and determination of Cr (VI) in real samples at trace level.

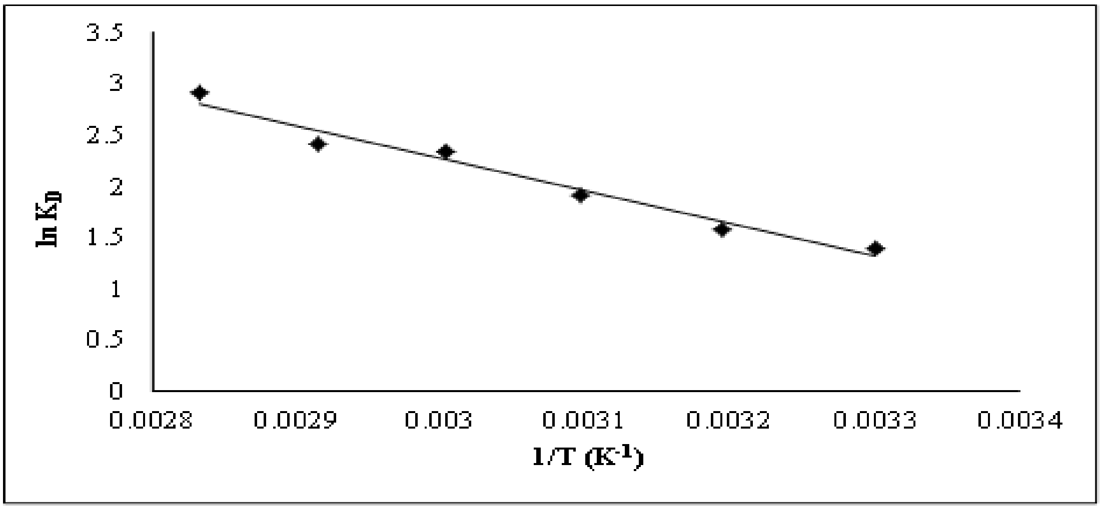

Fig. 10. Thermodynamic studies for sorption of Cr (VI).

Conclusion

A new chelating resin XAD-DPC is successfully synthesized by grafting diphenylcarbazide on the surface of Amberlite XAD-7. The batch preconconcentration method indicated an excellent selective behavior of the resin for Cr (VI) in the mixed metal solutions containing different interfering ions. FTIR confirmed the successful functionalization of XAD with diphenylcarbazide.

The sorption process follows second order and Langmuir isotherm best fits the sorption data indicating that the sorption of Cr (VI) is chemisorption in nature and monolayer is formed onto the sorbent. Thermodynamic studies shows that the sorption is endothermic and spontaneous. 96 % desorption was achieved with 2 M HNO_3 in acetone for Cr (VI) whereas the recovery of Cr (III) was only 12 %. Therefore, the newly synthesized resin cannot be only used in the speciation of Cr (III) and Cr (VI) but can also be used for the selective removal of Cr (VI) from different samples of environmental importance.

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