



## Use of modified sorbent for the separation and preconcentration of chromium species from industrial waste water

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### ABSTRACT

A simple and sensitive method based on solid phase extraction (SPE) on acetyl acetone modified XAD-16 has been established for separation of Cr (III) and Cr (VI) from industrial water samples. Two forms of chromium showed different exchange capacities at different pH values, viz. Cr (III) selectively retained at pH 5–7 whereas Cr (VI) retained at pH 1. Hence complete separation of the two forms of chromium is possible. Retained species were eluted with 5 mL of 2 mol L<sup>-1</sup> HNO<sub>3</sub> and 2 mol L<sup>-1</sup> NaOH. The detection limit of 0.02 and 0.014 μg mL<sup>-1</sup> was achieved for Cr (III) and Cr (VI), respectively, with an enrichment factor of 100 and 140. Various kinetic and thermodynamic parameters were also determined. The metal ion concentration was measured by atomic Absorption Spectroscopy. The possible retention mechanism is also discussed. The method was successfully applied for the speciation of chromium in industrial water samples.

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### 1. Introduction

Industrial activities discharge waste is often contaminated by variety of toxic metals, which also includes chromium [1]. The chromium metal and its compound are widely used in anodizing operation in the surface industry, in making alloys, chrome plating, leather tanning, batteries, refractory, mordant dyeing, paints, welding, catalysis, corrosion control, oxidation, wood preservative and various other industrial applications [2,3]. The physiological effects of chromium on the biological system depend upon its oxidation state, i.e.: Cr (III) and Cr (VI). Cr (III) may be considered as an essential trace element for the proper functioning of living organisms (mammals), e.g.: for the maintenance of “glucose tolerance factor”; it is thought to be a cofactor for the insulin action and to have a role in the peripheral activity of this hormone. On the contrary Cr (VI) can be toxic and has an adverse impact on the liver, lung and kidney [4]. Chromium compound causes cancer by oxi-

dizing the biological species such as DNA and some proteins [5]. The threshold limit for chromium uptake in air is 0.1 mg m<sup>-3</sup> and in water is 0.05 mg dm<sup>-3</sup> [2].

Owing to these two contrasting effects, precise and accurate determination of both species in environmental samples is essential [6]. Chromium content in natural waters is normally at μg L<sup>-1</sup> level and there are also severe matrix interferences which can not be minimized. Therefore, the direct determination may not be possible with sufficient sensitivity and selectivity even by methods such as inductively coupled plasma AES. Several speciation studies of chromium have been conducted with solid and liquid samples [7,8] including liquid–liquid extraction [9,10], cloud point extraction [7], co-precipitation [11,12], ion-exchange [13,14] and adsorption [15–18]. Among these methods chelating resin or ion-exchange type sorbents used in the speciation pretreatment are more promising. The major drawback of most of these ion-exchange or chelating sorbents is that they show a preferential affinity for a single oxidation state and the other could be determined by oxidizing and reducing with a suitable oxidizing and reducing agent. Herein, we report the synthesis of a new resin having acetylacetone anchored by the reduction of amino group (–NH<sub>2</sub>) to the polymeric Amberlite XAD-16 and its application to the separation and speciation of chromium without any prior oxidation or reduction in industrial water samples.

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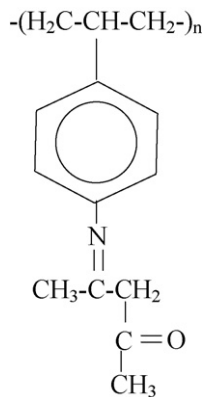


Fig. 1. A single repeat unit of XAD-16 modified with acetylacetone.

## 2. Experimental

### 2.1. Apparatus and reagent

All chemicals used were of analytical or equivalent grade. Stock standard solutions of Cr (III) and Cr (VI) were prepared by dissolving appropriate amount of  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  in  $0.5 \text{ mol L}^{-1}$  HCl and  $\text{K}_2\text{Cr}_2\text{O}_7$  in de-ionized water (conductivity  $0.5 \mu\text{S cm}^{-1}$ , pH 6).

Buffer solutions of pH 1–3, 4–6, and 7–9 were prepared by mixing appropriate ratios of 0.1 M HCl and KCl, 0.5 M acetic acid and sodium acetate and 0.5 M ammonia and  $\text{NH}_4\text{Cl}$  solutions, respectively. Amberlite XAD-16 (surface area of  $825 \text{ m}^2 \text{ g}^{-1}$ , pore diameter 14.4 nm and bead size 20–50 mesh) was procured from Fluka, Germany.

A Varian atomic Absorption Spectrometer was used for the determination of chromium.

All pH measurements were made with digital inoLab level 1 pH meter. A Gallenkamp automatic shaker model BKS 305-010, U.K. was used for the batch experiments. The flow of the sample through the column was adjusted using three-channel peristaltic pump.

### 2.2. Synthesis of Amberlite XAD-16 loaded with acetyl acetone

The styrene–divinylbenzene copolymer was prepared according to the procedure reported [19] with slight modification. The synthesis involves nitration of XAD-16, followed by the reduction to form an aromatic amine. The reduced Resin was then treated with  $100 \text{ cm}^3$  of acetylacetone at  $4^\circ\text{C}$  for 24 h. The resulting brown-colored beads were filtered and washed with water and then dried at room temperature.

CHN analysis of XAD-16 modified with acetylacetone (Fig. 1) found the values of C 76.0%, H 7.4% and N 6.0% which are in good agreement with the theoretical values calculated for  $(\text{C}_{14}\text{H}_{17}\text{NO}) \cdot \text{H}_2\text{O}$ , %C 72.1, %H 7.725, %N 6.0.

### 2.3. General separation and preconcentration procedure

For the optimization of column separation and preconcentration method two columns ( $10 \text{ mm} \times 50 \text{ mm}$ ) were prepared and connected to three channel peristaltic pump that ensured the flow rate of  $1 \text{ mL min}^{-1}$ . Sorption was performed from 10 to 250 mL solutions containing known amount of both Cr (III) and Cr (VI). Solutions were adjusted to a pH 5 in the case of preconcentration of Cr (III) on the column 1 and to pH 1 in the case of preconcentration of Cr (VI) on the column 2. The preconcentration of investigated species was then performed simultaneously. Sorbed Cr (III) and Cr (VI) ions were desorbed with  $5 \text{ mL}$  of  $2 \text{ mol L}^{-1}$  HCl and  $2 \text{ mol L}^{-1}$  NaOH, respec-

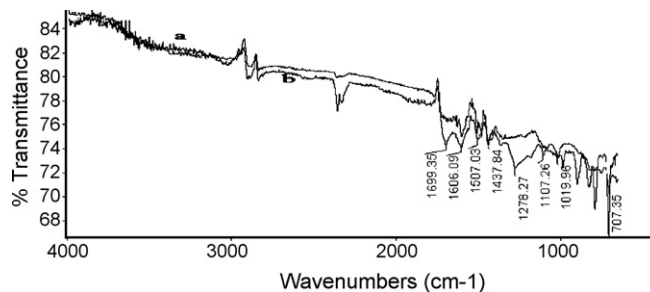


Fig. 2. FT-IR spectra of unmodified XAD-16 (a) and acetylacetone modified XAD-16 (b).

tively, at a flow rate of  $0.5 \text{ mL min}^{-1}$ . Eluted samples were analyzed with atomic absorption spectrometry.

Batch experiments were performed to determine thermodynamic and kinetic parameters. Acetylacetone modified resin was mixed with 25 mL aliquot of Cr (III) and Cr (VI) separately in a shaker thermostatted to the desired temperature and adjusted to the desired shaking speed. After certain time the concentration of metal ions was determined.

The following equations were used to calculate the percentage uptake (% Sorption).

$$\% \text{ Sorption} = \frac{C_0 - C}{C_0} \times 100 \quad (1)$$

where  $C_0$  and  $C$  are the initial and final concentrations, respectively, of metal ions in solution.

## 3. Results and discussion

### 3.1. Characterization of the resin

The FT-IR spectrum of acetylacetone-loaded Amberlite XAD-16 in comparison with FT-IR spectrum of pure Amberlite XAD-16 (Fig. 2) depicted three additional bands at 1699.35, 1278 and  $1107.26 \text{ cm}^{-1}$ . These appear to originate from the ligand molecule and are characteristic of  $-\text{C}=\text{N}$  ( $1690\text{--}1650 \text{ cm}^{-1}$ ),  $\text{Ar}-\text{N}-\text{C}-$  ( $1360\text{--}1250 \text{ cm}^{-1}$ ) and  $-\text{C}-\text{C}$  stretching vibrations for ketone, respectively [20]. This shows the successful conversion of XAD-16 into modified resin. The TGA (Fig. 3) of the modified resin showed two-step mass losses up to  $644^\circ\text{C}$ . The first step mass loss of about 9% up to  $106^\circ\text{C}$  may have been due to sorbed water molecule. The second step mass loss starts above  $106^\circ\text{C}$  and can be attributed to the loss of coupled unit. Mass loss of 42.8% corresponds to the molecular mass of  $92.4 \text{ g mol}^{-1}$  and as can be seen from Fig. 1 the

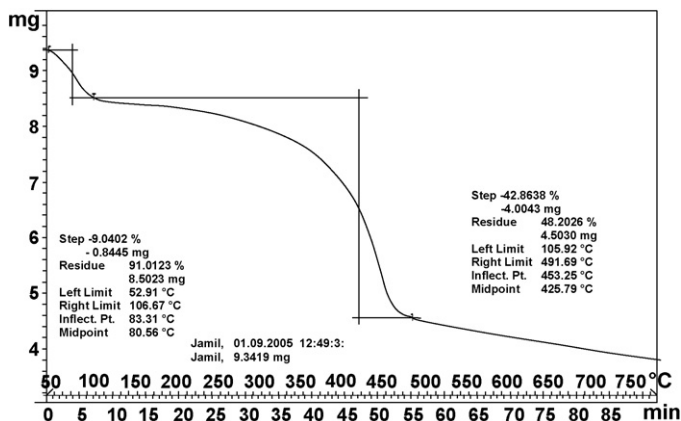


Fig. 3. TGA curve of acetylacetone modified XAD-16.

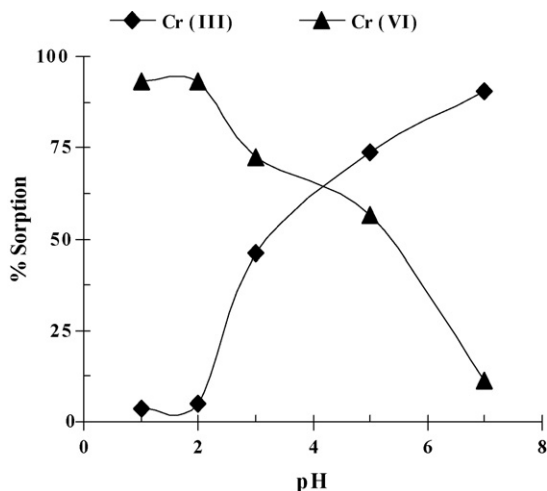


Fig. 4. The effect of pH on the separation of Cr (III) and Cr (VI) ions.

molecular mass of coupled unit is  $98 \text{ g mol}^{-1}$  which makes approximately the 45% mass of resin. Therefore, it is more likely that the second step mass loss is due to the loss of coupled unit on XAD-16.

According to the FT-IR, TGA and CHN interpretation the possible single repeat unit of acetyl acetone modified XAD-16 is presented in Fig. 1.

### 3.2. Influence of pH on separation of Cr (III) and Cr (VI)

Differences between sorption energies of Cr (III) and Cr (VI) on the acetylacetone modified XAD-16 surface provide the main reason for their selective preconcentration on the surface. Results concerning the effect of pH on the solid phase extraction are presented in Fig. 4, and it is apparent that  $\text{pH} > 4$  is appropriate for the preconcentration of Cr (III) on modified resin. The quantitative recovery of Cr (VI) is obtained at pH values  $< 3$ . Depending on the pH, XAD-16 modified with acetyl acetone can then selectively adsorb Cr (III) or Cr (VI), this makes modified XAD-16 a very promising solid phase extractant in the chromium speciation analysis.

### 3.3. Elution

Elution of Cr (III) and Cr (VI) from XAD-16-acetylacetone surface, by  $\text{HNO}_3$  and NaOH, respectively, at different concentrations and volumes was investigated. Recovery was quantitative ( $\sim 99\%$ ) with  $5 \text{ mL } 2 \text{ mol L}^{-1}$  NaOH and  $5 \text{ mL } 2 \text{ mol L}^{-1}$   $\text{HNO}_3$  for Cr (VI) and Cr (III), respectively.

### 3.4. Limit of detection and preconcentration factor

In order to explore the possibility of enriching low concentrations of analyte from large volumes, the maximum applicable sample volume must be determined. For this purpose sample solutions of different volumes containing  $10 \mu\text{g}$  of both Cr (III) and Cr (VI) were passed through columns under optimum conditions. The recovery was quantitative using  $500 \text{ mL}$  sample volume for Cr (III) and  $700 \text{ mL}$  for Cr (VI). These adsorbed species can be eluted with  $5 \text{ mL}$  of  $\text{HNO}_3$  and NaOH. So an enrichment factor of 100 ( $500/5$ ) and 140 ( $700/5$ ) was achieved for Cr (III) and Cr (VI), respectively, with the detection limit of  $0.02$  and  $0.014 \mu\text{g mL}^{-1}$ , respectively.

### 3.5. Kinetic study

Kinetic measurement were made under the optimum conditions, i.e. pH, a stirring speed ( $60$  and  $100 \text{ rpm}$  for Cr (III) and Cr (VI), respectively), and an amount of resin ( $0.1 \text{ g}$  for both species) by batch extraction at different times from  $1$  to  $30 \text{ min}$ . Sorption of Cr (III) and Cr (VI) were  $95.24\%$  and  $91.89\%$ , respectively, after  $10 \text{ min}$  agitation time. This rapid sorption is indicative of diffusion of solute through a hypothetical film or hydrodynamic boundary [21]. To study the mechanism of the particle diffusion the Morris-Weber equation [22]

$$(q_t = K_{\text{ird}}\sqrt{t}) \quad (2)$$

was applied, where  $q_t$  is the amount of metal ion sorbed at time  $t$  and  $K_{\text{ird}}$  is the rate constant for inter-particle transport ( $\mu\text{mol g}^{-1} \text{ min}^{-1/2}$ ). The data obtained are indicative of rapid diffusion of both species. The curves were linear up to  $12 \text{ min}$  with regression coefficients of  $0.9811$  and  $0.9504$  for Cr (III) and Cr (VI), respectively; these deviated as the agitation time was increased. From the initial slope of the plot values of  $K_{\text{ird}}$  were estimated to be  $17.6 \pm 0.82$  and  $34.6 \pm 3.54 \mu\text{mol g}^{-1} \text{ min}^{-1/2}$  for Cr (III) and Cr (VI), respectively. Kinetic data for the sorption of both Cr (III) and Cr (VI) on XAD-16-acetylacetone according to a first-order reaction and a time-dependent process are given by the Lagergren equation [23],

$$\log(q_e - q_t) = \log q_e - \frac{K_t}{2.303} \quad (3)$$

where  $q_e$  is the amount of metal ions adsorbed on modified adsorbent ( $\text{mol g}^{-1}$ ) at equilibrium.

A straight-line plot of  $\log(q_e - q_t)$  against  $t$  (Fig. 5) indicates the process is first-order in both cases. The rate constants for sorption, calculated from the slope, are  $0.41 \pm 0.02$  and  $0.95 \pm 0.10 \text{ min}^{-1}$  for Cr (III) and Cr (VI) ions, respectively.

### 3.6. Effect of metal ion concentration

Uptake of both species on the XAD-16-acetylacetone was determined as a function of metal ion concentration in the aqueous solution. The resulting isotherms show the good linear relationship over the relatively wide range of ion concentration tested ( $1.92 \times 10^{-5}$  to  $1.35 \times 10^{-3} \text{ M}$ ). The effects of tested metal ion concentrations on XAD-16-acetylacetone were analyzed in terms of the Freundlich

$$\log C_{\text{ads}} = \log A + \frac{1}{n} \log C_e \quad (4)$$

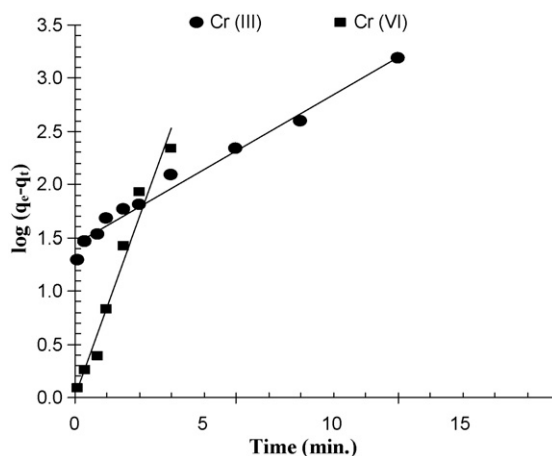


Fig. 5. Lagergren plot for the sorption of Cr (III) and Cr (VI) ions on XAD-16-acetylacetone.

**Table 1**  
Langmuir, Freundlich and D–R data for the sorption of Cr (III) and Cr (VI) on XAD-16-acetylacetone

Chromium species	Langmuir		Freundlich			Dubinin–Radushkevich					
	$Q$ ( $\mu\text{mol g}^{-1}$ )	$b$ ( $\text{L g}^{-1}$ )	$R_L$	$r$	$A$ ( $\text{mmol g}^{-1}$ )	$1/n$	$r$	$X_m$ ( $\text{mmol g}^{-1}$ )	$\beta \times 10^{-3}$ ( $\text{kJ}^2 \text{mol}^{-2}$ )	$E$ ( $\text{kJ mol}^{-1}$ )	$r$
Cr (III)	971 ± 110	$(1.27 \pm 0.7) \times 10^4$	0.6–0.1	0.95	15 ± 10	0.4 ± 0.1	0.896	1.99 ± 0.38	−2.42 ± 0.32	14.37 ± 0.95	0.96
Cr (VI)	723 ± 108	$(32.698 \pm 8.5) \times 10^{-3}$	0.99–0.99	0.96	18.8 ± 2.5	0.86 ± 0.11	0.97	1.12 ± 12.95	−6.38 ± 0.68	8.85 ± 0.47	0.96

$r$  is correlation coefficient,  $R_L$  dimensionless constant.

$$\text{Langmuir} \left( \frac{C_e}{C_{\text{ads}}} = \frac{1}{Qb} + \frac{C_e}{Q} \right) \quad (5)$$

$$\text{Dubinin – Radushkevich} (\ln C_{\text{ads}} = \ln X_m - \beta \varepsilon^2) \quad (6)$$

and

$$\varepsilon = RT \ln[1 + 1/C_e] \text{ equations,} \quad (7)$$

where  $C_{\text{ads}}$  is the amount of metal ions sorbed per mass unit ( $\text{mg g}^{-1}$ ) of the XAD-16-acetylacetone and  $C_e$  is the amount of metal ions in the liquid phase at equilibrium ( $\text{mol L}^{-1}$ ).  $A$  ( $\text{mmol g}^{-1}$ ),  $n$ ,  $Q$  ( $\mu\text{mol g}^{-1}$ ),  $b$  ( $\text{L g}^{-1}$ ),  $X_m$  ( $\text{mmol g}^{-1}$ ), and  $\beta$  ( $\text{kJ}^2 \text{mol}^{-2}$ ) are the Freundlich, Langmuir, and D–R constants, respectively [24]. The Freundlich, Langmuir, and D–R constants were evaluated from the slopes and intercepts of linear plots for both species studied. The results are listed in Table 1. The numerical value of the Freundlich constant  $1/n$ ,  $<1$ , shows that the sorption capacity is only slightly suppressed at lower equilibrium concentrations. The essential characteristic of the Langmuir isotherm can be explained in terms of a dimensionless constant, separation factor ( $R_L$ ), calculated by using the equation  $R_L = 1/(1 + bC_i)$  where  $C_i$  is the initial concentration of metal ions.  $R_L$  describes the type of Langmuir isotherm to be irreversible ( $R_L = 0$ ), favorable ( $0 < R_L < 1$ ), linear ( $R_L = 1$ ) or unfavorable ( $R_L > 1$ ) [24]. The values of  $R_L$  calculated, falls in the range 0.1–0.99 for both Cr (III) and Cr (VI) species indicating highly favorable sorption of chromium species on XAD-16-acetylacetone (Table 1).

The value of  $E$  evaluated from the slope ( $\beta$ ) of the D–R curve using the equation  $E = 1/\sqrt{-2\beta}$  is  $14.37 \pm 0.95$  for Cr (III), which is in the range of 9–16  $\text{kJ mol}^{-1}$  and are expected for chemisorp-

tion or ion exchange [25]. Hence, it is very likely that Cr (III) ions are sorbed on functionalized resin predominantly by ion-exchange mechanism. The value of  $E$  for Cr (VI) species is  $8.85 \pm 0.47 \text{ kJ mol}^{-1}$  and indicates the physical nature of sorption on modified XAD-16.

The sorption capacity is different for all three sorption isotherms. This difference can be interpreted in terms of the assumption made when deriving these sorption models. For example the Langmuir model considers that the adsorption process takes place on a surface composed of a fixed number of adsorption sites of equal energy one molecule being adsorbed per adsorption site until monolayer coverage is achieved. Whereas, Freundlich model consider the multilayer formation which leads to greater sorption capacities [26].

### 3.7. Thermodynamics investigations

The dependence on temperature of sorption of the chromium species on XAD-16-acetylacetone was evaluated using the equations

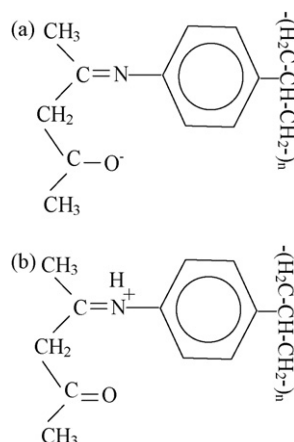
$$\ln K_c = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \quad (8)$$

**Table 3**  
Effect of concomitant cations on chromium sorption

Cations	Tolerance Level (1:10)	
	Cr (VI)	Cr (III)
Nil	100	99.24
Ag (I)	100	97.40
Al (III)	80.36	83.81
Ba (II)	100	98.57
Be (II)	90	88.73
Bi (III)	76.92	88.24
Ca (II)	97	86.27
Cd (II)	89	87.23
Ce (IV)	100	95
Co (II)	100	95.89
Cu (II)	97.53	100
Fe (II)	96.92	86.79
Fe (III)	80	75
Ga	94.59	95.89
Hg (I)	100	96.72
K	100	94.23
La	100	100
Mg	100	99.48
Mn (II)	100	86.79
Mn (VII)	83.46	81.67
Mo (V)	73.33	70.37
Na	100	99.11
Ni (II)	57.14	85.71
Pb (II)	100	97.78
Pt	98.50	100
Ru	99.87	98.11
Sn (II)	82.11	96.30
Tl (I)	98.62	100
V (V)	95.03	88
Zn	98.60	98.59
Zr	85.42	85.11

**Table 2**  
Thermodynamic data for the sorption of chromium species on XAD-16-acetylacetone

Metal ions	$\Delta H$ ( $\text{kJ mol}^{-1}$ )	$\Delta S$ ( $\text{kJ mol}^{-1} \text{K}^{-1}$ )	$\Delta G_{298 \text{ K}}$ ( $\text{kJ mol}^{-1}$ )	$R^2$
Cr (III)	−(54.70 ± 4.79)	0.20 ± 0.02	−5.73	0.9775
Cr (VI)	−(83.86 ± 5.80)	0.301 ± 0.019	−6.46	0.9767



**Fig. 6.** (a) Negatively charged surface of XAD-16-acetylacetone in the presence of base. (b). Positively charged surface of XAD-16-acetylacetone in the presence of acid.

**Table 4**  
Effect of concomitant anions on chromium sorption

Tolerance Level (1:50) Anions	%Sorption	
	Cr (III)	Cr (VI)
Br <sup>-</sup>	74.47	80
Citrate	82	65.28
CO <sub>3</sub> <sup>2-</sup>	78	89.19
F <sup>-</sup>	82.76	79.22
HCO <sub>3</sub> <sup>-</sup>	98	88.57
HPO <sub>4</sub> <sup>2-</sup>	100	86.84
HSO <sub>4</sub> <sup>-</sup>	80	78
NO <sub>3</sub> <sup>-</sup>	98	91
Oxalate	85	83
PO <sub>4</sub> <sup>3-</sup>	92	88
SCN <sup>-</sup>	73.24	77.27
SO <sub>3</sub> <sup>2-</sup>	74.42	80
SO <sub>4</sub> <sup>2-</sup>	76.83	78.26
Tartrate	89	96

and

$$\Delta G = -RT \ln K_c \quad (9)$$

where  $\Delta H$  (kJ mol<sup>-1</sup>),  $\Delta S$  (kJ mol<sup>-1</sup> K<sup>-1</sup>),  $\Delta G$  (kJ mol<sup>-1</sup>) and  $T$  are the enthalpy, entropy, Gibbs free energy and absolute temperature, respectively,  $R$  is the gas constant and  $K_c$  is the equilibrium constant.

Plot of  $\log K_c$  against  $1/T$  gives the numerical values of  $\Delta H$  and  $\Delta S$  from the slopes and intercepts, respectively. Values are given in Table 2. The negative values of  $\Delta H$  show the exothermic and the negative values of  $\Delta G$  show the spontaneous nature of reaction.

### 3.8. Retention mechanism of chromium species on acetylacetone modified XAD-16

#### 3.8.1. Sorption mechanism of Cr (III)

Sorption of Cr (III) on modified sorbent can be explained on the basis of a well-known reaction between Cr (III) and acetylacetone [27]. In the presence of base, acetylacetone (2,4 pentadione) forms the acetylacetonate anions (Fig. 6a) and then acetylacetonate ligand interacts with the metal through negatively charged oxygen.

#### 3.8.2. Sorption mechanism of Cr (VI)

Sorption of Cr (VI) ions can be explained in term of species of Cr (VI) formed in aqueous solutions, at different pH values. The main species of Cr (VI) formed at pH values 1–7 are HCrO<sub>4</sub><sup>-</sup>, CrO<sub>4</sub><sup>2-</sup> and CrO<sub>7</sub><sup>2-</sup> [28] and as the surface of the modified sorbent becomes negatively charged (Fig. 6a) at pH value above 3 the negatively charged chromate ions do not adsorbed on the surface at pH values above 3. The surface of XAD-16-acetyl acetone becomes positively charged due to protonation of nitrogen (Fig. 6b) in acidic medium hence, attracts the negatively charged chromate ions. The value of sorption energy obtained from D–R isotherm ( $8.85 \pm 0.47$  kJ mol<sup>-1</sup>) also confirms the physical nature of sorption.

**Table 5**  
Determination of chromium species from industrial water samples

Sample	Name of industry	Cr (III) found (μg/mL)	Cr (III) SA <sup>a</sup>	% Recovery	Cr (VI) (μg/mL)	Cr (VI) SA <sup>a</sup>	% Recovery
01	M. M. S. Leather Tanning	5.72	15.7	99.8	7.54	17.5	99.7
02	Fasto Leather Workers	ND	9.82	98.2	ND	10	100
03	Alma Leathers	4.06	13.8	98.1	5.39	15.28	99.2
04	Leather Tanning	4.33	13.99	97.6	5.75	15.74	99.9
05	National Oil Refinery	ND	9.85	98.5	ND	9.9	99

ND: not detected.

<sup>a</sup> SA standard addition 10 μg.

**Table 6**  
Comparison of sorption capacities of Cr (III) and Cr (VI) on different sorbents

Surface	Sorption capacity (mmol g <sup>-1</sup> )		Reference
	Cr (III)	Cr (VI)	
Modified Silica MCM-41	0.00904	–	[29]
Xanthine functionalized XAD	0.6718	1.132	[30]
Shellac modified XAD	0.00577	0.0173	[31]
Maleic acid functionalized XAD	0.1446	–	[32]
Imidazole-4,5-dicarboxylic acid modified XAD	0.41	1.12	[33]
6-Mercaptopurinylo functionalized XAD	0.44	1.06	[34]
Acetylacetone modified XAD	15.0	18.8	This work (based on Freundlich isotherm)

### 3.9. Reusability of XAD-16-acetylacetone

In order to check the longevity of the sorbent, XAD-16-acetylacetone was subjected to several loading and elution experiments. The capacity of the sorbent was found to be practically constant (variation of 1–3%) after repeated use of more than eight times, thus the multiple use of sorbent was seen to be feasible.

### 3.10. Effect of concomitant ions

The validity and accuracy of the technique for selective extraction of chromium species in water was measured under optimized conditions selected for the sorption of both species. The concentration ratios of 1:100 and 1:50 were used for anions and 1:10 for cations. The cations were added as their nitrates or chlorides and anions were incorporated as sodium and potassium salts. The results of sorption of chromium species in presence of cations are presented in Table 3. All the metal ions showed lower sorption than Cr (III) and Cr (VI), especially Ag, As, Co, Hg, Pb and Zn in the case of Cr (III) whereas for Cr (VI) the method is much more selective. It is deduced from the results that these metal ions can be easily separated from chromium species, using acetylacetone modified XAD-16 as sorbent. The results for the % sorption of chromium species in presence of anions (1:100) are presented in Table 4. Both Cr (III) and Cr (VI) species observe a little decrease in % sorption (~2–25%) in case of Cr (III) and (~3–34%) in case of Cr (VI) at the concentration ratios 1:100. The effect became negligible at the concentration ratios of 1:50 for both species.

### 3.11. Analytical applications

The analytical applicability of XAD-16 modified with acetylacetone was tested for separation and preconcentration of chromium species from environmental and industrial water samples obtained from Karachi, Pakistan. A 100 mL aliquot of water sample was filtered and adjusted to required pH. Another 100 mL aliquot of water sample was spiked by standard addition at the adjusted pH. The solutions were then passed through the column at a flow rate

of 1 mL min<sup>-1</sup>. The metal ions were eluted and determined. The results are given in Table 5. % RSD. was within 2% in all cases, which shows the suitability of modified sorbent for preconcentration and removal of chromium species separately from industrial water samples.

### 3.12. Comparison of sorption capacities

Comparison of sorption capacities of functionalized XAD resins with different modified sorbents (Table 6) showed that acetylacetone modified XAD-16 has 22–1659 and 16–1086 times higher capacity values for Cr (III) and Cr (VI), respectively.

## 4. Conclusion

Present work explores a new sensitive and selective sorbent for the preconcentration and separation of essential Cr (III) and toxic Cr (VI). The main advantages of procedure are (a) both species can be adsorbed without the need for oxidation or reduction, (b) sensitivity and (c) rapid attainment of phase equilibration and good enrichment values.

The kinetics of sorption of both species follows a first-order rate equation. The negative value of  $\Delta G$  is indicative of the spontaneous nature of sorption which shows the feasibility of sorbent for chromium removal. Study shows that the Amberlite XAD-16-acetylacetone has the ability to extract Cr (III) and Cr (VI) from environmental and industrial waste.

## References

- [1] L. Moner, N. Ashoum, Modified activated carbon for the removal of copper, zinc, chromium and cyanide, *Sep. Purif. Technol.* 26 (2002) 137–146.
- [2] E.R. Plunkett, *Handbook of Industrial Toxicology*, third ed., Edward Arnold Chemical Publishing Co., Inc., USA, 1987.
- [3] H.G. Seiler, H. Sigel, A. Sigel, *Handbook on Toxicity of Inorganic Compound*, Marcel Dekker Inc., New York, USA, 1988.
- [4] C.D. Klaassen, *Toxicology the Basic Science of Poisons*, McGraw-Hill, New York, 2001.
- [5] S. Langard, T. Norseth, *Handbook on Toxicology of Metals*, Elsevier Sciences, Amsterdam, 1986.
- [6] F.S. Shemirani, D. Abkenar, A.A. Mirroshandel, M.S. Niasari, R.R. Kozania, Preconcentration and speciation of chromium in water samples by atomic absorption spectrometry after cloud-point extraction, *Anal. Sci.* 19 (2003) 1453–1456.
- [7] A. Salvado, A.E. Morales-Rubio, M. Guardia, Analytical methodologies for chromium speciation in solid matrices: a survey of literature, *Fresenius J. Anal. Chem.* 362 (1998) 239–248.
- [8] M.J. Marques, A. Salvador, A.E. Morales-Rubio, M. Guardia, Chromium speciation in liquid matrices: a survey of the literature, *Fresenius J. Anal. Chem.* 367 (2000) 601–613.
- [9] K.S. Subramanian, Determination of chromium (III) and chromium (VI) by ammonium pyrrolidinedithioate methyl isobutyl ketone-furnace atomic absorption spectrometry, *Anal. Chem.* 60 (1988) 11–15.
- [10] M. Sugiyaura, O. Fujino, S. Kihara, M. Matsui, Preconcentration by dithiocarbamate extraction for determination of trace elements in natural waters by inductively-coupled plasma atomic emission spectrometry, *Anal. Chim. Acta* 181 (1986) 159–168.
- [11] C.R. Lan, C.L. Tseng, M.H. Yang, Two-step coprecipitation method for differentiating chromium species in water followed by determination of chromium by neutron activation analysis, *Analyst* 116 (1991) 35–38.
- [12] A. Boughrief, L. Duran, M. Wartel, Determination of dissolved chromium (III) and chromium (VI) in sea-water by electrothermal atomic absorption spectrometry, *J. Anal. At. Spectrom.* 9 (1994) 1135–1142.
- [13] R. Milacic, J. Stupar, N. Kozuh, J. Korosin, Critical evaluation of three analytical techniques for the determination of chromium (VI) in soil extracts, *Analyst* 117 (1992) 125–130.
- [14] K. Yoshimura, Application of ion-exchanger phase absorptiometry to flow analysis. Determination of trace amount of chromium (VI) in water, *Analyst* 113 (1988) 471–474.
- [15] E. Vassileva, Use of high surface area TiO<sub>2</sub> for preconcentration and following determination of Cr species by on-line flow injection inductively coupled plasma atomic emission spectrometry, *Analyst* 28 (2000) 878–884.
- [16] A. Xue, S. Qian, G. Huang, L. Chen, Separation and preconcentration of chromium speciation on chitosan and determination by graphite furnace atomic absorption spectrometry, *J. Anal. Spectrom.* 15 (2000) 1513–1515.
- [17] M.T.S. Cordero, E.I.V. Alonso, A.G. Torres, J.M.C. Pavon, Development of a new system for the speciation of the chromium in natural waters and human urine samples by combining ion exchange and ETA-AAS, *J. Anal. At. Spectrom.* 19 (2004) 398–403.
- [18] F. Shemirani, M. Rajabi, Preconcentration of chromium (III) and speciation of chromium by electrothermal atomic absorption spectrometry using cellulose adsorbent, *Fresenius J. Anal. Chem.* 371 (2001) 1037–1040.
- [19] S.Q. Memon, M.I. Bhangar, M.Y. Khuhawer, Sorption profile and thermodynamic characteristics of nitrosonaphthol functionalized sorbent for metal ion enrichment, *Collect. Czech. Chem. Commun.* 70 (2005) 1341–1356.
- [20] G. Socrates, *Infrared Characteristic Group Frequencies*, Wiley-Interscience Publication, 1980.
- [21] W.J. Weber, Adsorption theory, concepts, models, in: F.L. Slejko (Ed.), *Adsorption Technology, A Step-by-Step Approach to Process Evaluation, Application*, Marcel Dekker Inc., New York, 1985.
- [22] W.J. Morris, C. Weber, Kinetics of adsorption on carbon from solution, *J. Sanita Eng. Division ASCE* 89 (1963) 31–59.
- [23] S. Lagergren, K. Sevens, *Theorie der sogennanten adsorption geloster stoffe*, *Vetenskapska Handl.* 24 (1898) 1–39.
- [24] D.M. Ruthven, *Principles of Adsorption and Adsorption Processes*, Wiley, New York, 1984.
- [25] M.M. Saeed, Adsorption profile and thermodynamic parameters of the preconcentration of Eu (III) on 2-thenoyltrifluoroacetone loaded polyurethane (PUR) foam, *J. Radioanal. Nucl. Chem.* 256 (2003) 73–80.
- [26] I. Quinones, G. Guiochon, Extension of a Jovanovic–Freundlich isotherm model to multicomponent adsorption on heterogeneous surfaces, *J. Chromatogr. A* 796 (1998) 15–40.
- [27] Z. Szafran, R.M. Pike, M.M. Singh, *Microscale Inorganic Chemistry*, Wiley, New York, 1991.
- [28] C.F. Baes Jr., R.E. Mesmer, *The Hydrolysis of Cations*, Wiley-Interscience, New York, 1976.
- [29] M.R. Ganjali, L.H. Babaei, A. Badii, K. Saberian, S.B. Abureihan, G.M. Ziarani, M. Salavati-Niasari, A novel method for fast enrichment and monitoring of hexavalent and trivalent chromium at the ppt level with modified silica mcm-41 and its determination by inductively coupled plasma optical emission spectrometry, *Quim. Nova* 29 (3) (2006) 440–443.
- [30] D.D. Banerjee, A.K. Das, Application of xanthine functionalized resin in speciation of chromium in natural water, *J. Indian Chem. Soc.* 83 (5) (2006) 479–484.
- [31] Y. Sibel, A. Resat, Chromium speciation analysis by separation of Cr(III) from Cr(VI) on a XAD sorbent derivatized with shellac: a natural polymer, *Int. J. Environ. Anal. Chem.* 86 (2006) 915–929.
- [32] Y. Sibel, A. Resat, Chromium (III, VI) speciation analysis with preconcentration on a maleic acid-functionalized XAD sorbent, *Anal. Chim. Acta* 505 (2004) 25–35.
- [33] D. Banerjee, B.C. Mondal, A.K. Das, Application of a chelating resin containing imidazole-4,5-dicarboxylic acid in chromium speciation, *J. Indian Chem. Soc.* 80 (8) (2003) 769–772.
- [34] B.C. Mondal, A.K. Das, Use of 6-mercapto purinylazo resin in chromium speciation, *Bull. Chem. Soc. Jpn.* 76 (2003) 111–114.