Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2013.791766

51 (2013) 6882–6891
October

Taylor & Francis
Taylor & Francis Group

Derivatised L-methionine: a new amino polycarboxylate functionality for trace level speciation of chromium by solid-phase extraction

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Received 4 April 2012; Accepted 30 January 2013

ABSTRACT

Chemical speciation and separation of inorganic chromium species in environmental samples were performed using a newly synthesised chelating ligand, N,N-(Bis-acetato) L-methionine. The ligand can bind very efficiently with Cr(III) and Cr(VI) at two different pH. The ligand loaded on alumina can be reused several times without any significant loss of the ligating group. The maximum adsorption capacity for Cr(III) at any pH above 4.0 is 0.5663 mmol g^{-1} and for Cr(VI) at pH 2.0 is 1.23 mmol g^{-1}. About 3.0 mol L^{-1} HCl can completely desorb both chromium species from the polymeric matrix. The detection limit (three times the standard deviation of the blank, as obtained from flame atomic absorption spectroscopic (FAAS) method) for Cr(III) and Cr(VI) were found to be 45 and 46 ng mL^{-1}, respectively. The sorption of both Cr(III) and Cr(VI) was found to follow a second-order rate law. The developed method is used for the chemical speciation and removal of chromium species from different environmental samples and validated by comparing with some standard samples as well as by comparing with results using previously developed method. The concentration of chromium was monitored using FAAS.

Keywords: Chromium; Speciation; Chelating resin; L-methionine; FAAS

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1. Introduction

Studies on trace level chemical speciation of some elements have found paramount importance as they are not only involved in different physical and biological functions but also impose toxicity to the environment depending on their chemical form. Chromium is one of them. Cr(VI) compounds are carcinogenic [1], whereas Cr(III) is considered to be an essential nutrient for the maintenance of normal glucose tolerance factor [2]. Hence, speciation of chromium in environmental samples is very vital and also a long-standing analytical challenge. Steel factories, tanning industries, electroplating industries, dying industries, chemical and pharmaceutical industries, artificial fertilisers, cooling water towers, combustion of fossil fuels and incineration of municipal wastes contribute to the emission and dispersion of chromium in the environment [3]. Low level (μg L^{-1}) of chromium in natural water and severe matrix interferences restrict its direct determination with sufficient sensitivity and accuracy.

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1944-3994/1944-3986

Very few instrumental techniques like electro-analytical method [4,5] can directly determine Cr(III) and Cr(VI) simultaneously in real samples. That is why researchers used solvent extraction [6], co-precipitation [7,8] and solid-phase extraction (SPE) [9–13] for prior separation and pre-concentration of the different chromium species. Among these, SPE has advantages over others as it can be reused for many cycles (so relatively cheaper), easy to handle and reasonably fast process. Costly and sophisticated instruments like ICP-MS or ICP-AES being unavailable in many laboratories, much cheaper instrument like AAS has been used for the determination of chromium species. US EPA and WHO has set the threshold value for total Cr as 0.1 mg L^{-1} for drinking water and 50 µg L^{-1} Cr(VI) as tolerance level, respectively [14]. Reports on pH-dependent Cr speciation, using a chelating sorbent, are still a few [15–18]. Herein, we report the pH-dependent Cr speciation in environmental samples using a new chelating resin containing N,N-(Bis-acetato) L-methionine.

2. Experimental

2.1. Reagents and solutions

All chemicals were analytical reagent (AR) grade, and all solutions were prepared in double-distilled water (DDW). Cr(III) and Cr(VI) stock solutions were prepared from $Cr(NO_3)_3{\cdot}9H_2O$ (Merck) and $K_2Cr_2O_7$ (Merck). Their solutions (50 mg L^{-1}) were prepared in 0.5 mol L^{-1} HNO_3 and DDW, respectively. These solutions were standardised against standard stock solutions of Cr(III) (50 mg L^{-1}) supplied by SOLUTIONS plus Inc. (Missouri, USA) which was tested vs. NIST SRM # 3108a using flame atomic absorption spectroscopic (FAAS). The solutions of metal ions were prepared from AR grade metal salts. Different buffer solutions were used for adjusting the pH and prepared as per the literature procedure [13], that is, HCl–KCl buffer (pH 1, 2), citrate buffer (pH 3, 4, 5, 6), phosphate buffer (pH 7, 8), boric acid–borax buffer (pH 9) and glycine/NaOH buffer (pH 10) solutions.

2.2. Instrumentation and apparatus

A VARIAN (Spectra AA 55) flame atomic absorption spectrophotometer (Australia) was used. All measurements were performed using integrated absorbance (peak area). Hollow cathode lamp for Cr was operated at 7.0 mA at wavelength 357.9 nm and at slit width 0.2 nm. Air and acetylene flow rates were 3.5 and 1.5 L min^{-1}, respectively. Fourier transform infra red (FTIR) spectra were recorded on a JASCO FTIR spectrophotometer (model: FTIR-H20). Thermogravimetric analysis was performed on a Perkin Elmer TG/DTA laboratory system l (Technology by SII). pH measurements were performed using Systronics digital pH meter (model 335). UV–vis spectra were obtained from a Shimadzu spectrophotometer (model: UV2101PC). A Kratos MALDI-TOF 1 mass spectrometer using the matrix α-ACHC and an extraction voltage of 4 kV was used for mass spectrometry. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a 200 and 50 MHz Varian Gemini 200. Glass apparatus were soaked with 9.0 mol L^{-1} HNO_3 overnight and cleaned with DDW. A short glass column with an inner diameter of 10 mm and a length of 100 mm, equipped with porous frits, was filled up to a height of 30 mm with a suspension of 1 g of the chelating resin in DDW.

2.3. Sampling [19]

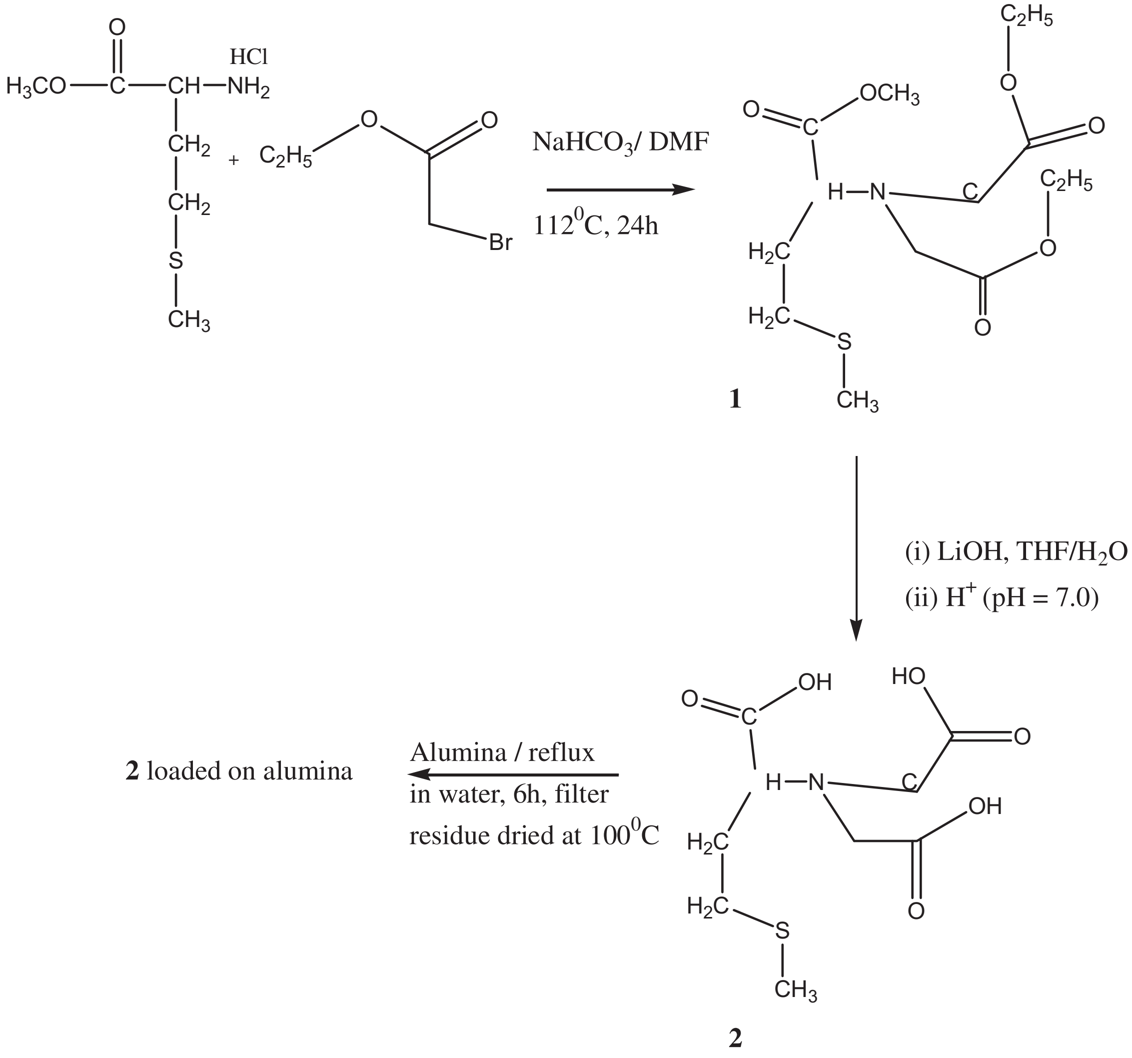
Wastewater samples from different sources like tannery industrial water at Kolkata, industrial waste water at Durgapur, West Bengal, India, were collected in well-cleaned polyethylene bottles. pH of the real samples was noted using a pen pH meter. Then, the samples were acidified with 0.05 mol L^{-1} H_2SO4 to prevent any unwanted precipitation of the metal hydroxide. The samples were filtered through a 0.45-µm Millipore membrane filter.

2.4. Preparation of the resin

2.4.1. Synthesis of N,N-(Bis-acetato) L-methionine methyl ester (BAMME, *1*) (Scheme 1)

Ethylbromoacetate (3.34 g, 20.04 mmol) was dissolved in 60 mL DMF. To this solution, L-methionine methyl ester hydrochloride (2 g, 10.02 mmol) was added followed by the addition of $NaHCO_3$ (13 g, 154.8 mmol). The resulting mixture was refluxed at 110–112˚C for 24 h. Upon evaporation of solvent, a solid remained which was dissolved in water–methylene chloride mixture. Organic layer was collected by solvent extraction method, dried over anhydrous K_2CO_3 and subjected to column chromatography (ethyl acetate/ methylene chloride = 1:1) to yield 4.25 g (55%) of N,N-(Bis-acetato) L-methionine methyl ester as a light-yellow oil .

^{1}H NMR ($CDCl_3$, 200 MHz): δ: 1.32 (6H, *t*, CH_3); 1.99 (3H, *s*, CH_3); 2.12 (2H, m, CH_2); 2.50 (2H, m, CH_2); 3.60 (1H, *t*, CH, $J_{CH\text{–}CH2} = 6.88$ Hz); 3.70 (3H, *s*, CH_3); 3.87 (4H, *s*, CH_2), 4.12 (4H, m, CH_2); ^{13}C-NMR ($CDCl_3$, 50 MHz): δ: 13.8, 15.45, 29.46, 31.11, 50.5, 54.71, 57.55, 61.81, 173.21. Maldi-Tof: $[M + H]^+ = 336.2$.



Scheme 1. Synthesis of the BAM-loaded alumina.

2.4.2. Synthesis of N,N-(Bis-acetato) L-methionine (BAM,2) loaded on alumina (Scheme 1)

To a solution of BAMME **(1)** (2.0 g, 5.96 mmol in 50 mL tetrahydrofuran), 0.5 N aqueous LiOH (20 mL) solution was added under stirring at room temperature and the stirring was continued for 4 h. The solvent was removed under reduced pressure. The residue was dissolved in minimum amount of water, and the pH was adjusted to 7.0. As the extraction of the chelating ligand, N,N-(Bis-acetato) L-methionine (**2**) from water to any non-polar solvent was unsuccessful, the aqueous solution of BAM (**2**) was refluxed with 2 g alumina for 6 h for its complete sorption on alumina. Excess solvent was slowly evaporated on a water bath. Finally, alumina-loaded BAM (**2**) (here after sorbent) was dried under vacuum and used for analytical studies. FTIR data of selected functional groups (cm^{-1}): *v* (CO) 1,636; *v* (OH) 3,448. The colour of the sorbent was white (same as alumina). The bead size of the resin is 80–120 mesh.

2.5. Stability of the resin

About 250 mg sorbent was shaken with 100 mL of acid or alkaline solutions of different ionic strengths for 7 days, then filtered and washed with de-ionised water to free from acid or alkali and dried under vacuum. The metal's ion-exchange capacity was measured. The thermal stability of the sorbent was studied by thermogravimetry.

2.6. Water regain

Air-dried sorbent in basic form was stirred in DDW for 48 h, then filtered off by suction, weighed, dried at 1,00˚C for 48 h and reweighed.

2.7. Hydrogen ion capacity

About 1.0 g sorbent was first converted into its acidic form by treating with 6 mol L^{-1} HCl. The sorbent was first filtered off, washed with water and then dried at 100°C for 6 h to remove free HCl. The acidic hydrogen content of the sorbent was then determined by back titration with a standard alkali solution. The acidic form of the sorbent was equilibrated with 20 mL of 0.1 mol L^{-1} sodium hydroxide solution for 6 h at room temperature under stirring condition. Then, the solution was filtered under suction, washed with de-ionised water, and the excess alkali was titrated with standard solution of 0.1 mol L^{-1} HCl acid.

2.8. Chromium ion uptake as a function of pH

A batch technique was used, taking metal ion in excess to the sorbent. Capacities were determined in the pH range 2.0–10.0. To a glass-stoppered centrifuge tube (diameter 2.0 cm) containing 100 mg of the dry sorbent in basic form, 10 mL of the desired pH solution was added. After equilibration of this mixture, 30 mL of 100 μg mL^{-1} metal ion solution was added, and the mixture was shaken for 24 h. The pH of the equilibrating solution was adjusted by appropriate buffer solution. After 24 h, the solutions were filtered under suction, washed with de-ionised water to remove adhering metal ions. Then, the adsorbed metal ion was eluted with suitable eluting agent. The concentration of the eluted metal ions was measured by FAAS using air/acetylene flame.

2.9. Desorption of metal ions

Sorbent thus obtained after uptake of chromium ion in the above-mentioned batch technique was shaken with 30 mL of different eluents (1–3 mol L^{-1} HNO_3, 1–3 mol L^{-1} CH_3COOH and 1–3 mol L^{-1} HCl) for 24 h and filtered. The concentrations of metal ions in the filtrate were determined.

2.10. Kinetic studies

The concentrations of Cr(III) and Cr(VI) sorbed by the sorbent at the pH where maximum adsorption took place were monitored at different time intervals. From that data, different kinetic parameters such as rate constant etc., were determined for the sorption of Cr(III) and Cr(VI) on the sorbent using batch technique.

2.11. Column preparation

Air-dried sorbent (3.0 g) was immersed in DDW for 24 h. A glass column (100 × 10 mm) was packed with the sorbent to a bed volume of 2 mL. Before starting the experiment, the sorbent bed was thoroughly washed with 0.1 mol L^{-1} HNO_3 followed by DDW, till the effluent was free from acid. Sorption and desorption characteristics for Cr(III) and Cr(VI) in the column were studied at the optimum flow rate. Any adhering metal ions (not adsorbed) were completely washed out by using solutions of appropriate pH. The sorbed Cr(III) and Cr(VI) were completely eluted by suitable eluting agent. Concentrations of each chromium species thus eluted were measured as described earlier. Exchange capacities for the BMA-unloaded sorbent was measured at the respective pH to ascertain that it has no absorption for Cr(III) and Cr(VI) at those pH's, respectively.

2.12. Effect of flow rate

The sample flow rate had a significant effect not only on the retention of chromium species on to the sorbent, but also on their desorption by suitable eluting agents The sample flow rate was varied in the range 0.5–15 mL min^{-1}. The recovery of chromium species from the sorbent was monitored using FAAS.

2.13. Effect of sample volume

Sample volume was one of the important analytical parameter to be studied to obtain the maximum pre-concentration factor. About 50–1000 mL of sample solutions containing 50 mg $L^{-1}$of Cr(VI) (as it had higher sorption over Cr(III)) was passed through the column containing 250 mg sorbent under the optimum conditions. The concentration of Cr(VI) in the effluent was monitored by FAAS.

2.14. Procedure for Cr speciation

About 50 mL solution containing 50 mg L^{-1} chromium species, made in appropriate buffer (pH range from 2 to 10), was passed through 1 g of the sorbent, preconditioned at the requisite pH, at a optimal flow rate. Then, the column was thoroughly washed with DDW to remove adhering species followed by elution with suitable eluting agents. The concentration of Cr species was measured using FAAS. The total Cr species in the solution was a sum total of those obtained at two different pH.

2.15. Applications

Wastewater samples from different sources viz. tannery water from Kolkata and industrial water from Durgapur, West Bengal, India were collected and filtered through a 0.45-μm Millipore membrane filter. pH of the filtrate was adjusted to the optimum value and allowed to flow through the preconditioned column. After elution with suitable eluant, the concentration of Cr species was measured by FAAS. BAM-loaded sorbent allowed to determine two individual Cr species at widely different pH and hence the total inorganic chromium present in the sample. The results have been compared with a reference method [20].

3. Results and discussion

3.1. Synthesis and characterisation of the resin

N,N-(Bis-acetato)-L-methionine (BAM, 2) was synthesised according to Scheme 1. Elemental analysis, NMR, mass spectral data, FTIR and UV–vis spectra confirm the structure of BAM ligand, whereas the FTIR spectra of the final BAM loaded on alumina (Fig. 1) showed all the characteristic stretching frequencies present in compound 2; *ν* (CO) 1,636 cm^{-1}; *ν* (OH) 3,448 cm^{-1}, indicated the loading of the BAM moiety to the alumina.

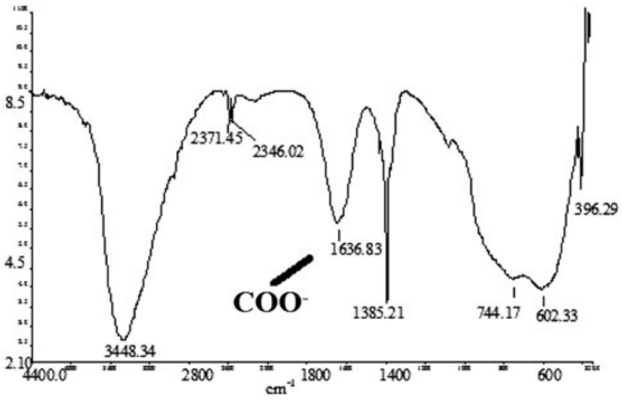


Fig. 1. FTIR spectra of BAM loaded alumina.

The chemical stability of the sorbent in 0.01–3 mol L^{-1} HNO_3 and 0.1 to 3 mol L^{-1} NaOH was examined. No significant change in the structure of the resin was observed (as evident from comparison of the FTIR spectra as well as metal ion and hydrogen ion exchange capacities). Thus, the resin was fairly stable in both acidic and alkaline conditions. Thermogravimetric analysis (Fig. 2) showed that the resin was fairly stable up to 237℃, although a initial weight loss (~6%) in between 28.55 and 78.23℃ might be attributed to the loss of adhering moisture. The water regain value for the resin was 12, which was satisfactory for column operation.

3.2. Effect of eluent type and volume

In order to elute sorbed Cr(III) and Cr(VI) from the sorbent, different eluting agents like hydrochloric acid, nitric acid and acetic acid were employed. The results were presented in Table 1. It was found that 4.5 mL of 3.0 mol L^{-1} HCl could be used to desorb both Cr(III) and Cr(VI) (50 mg L^{-1}, 1 g of the sorbent) from the sorbent.

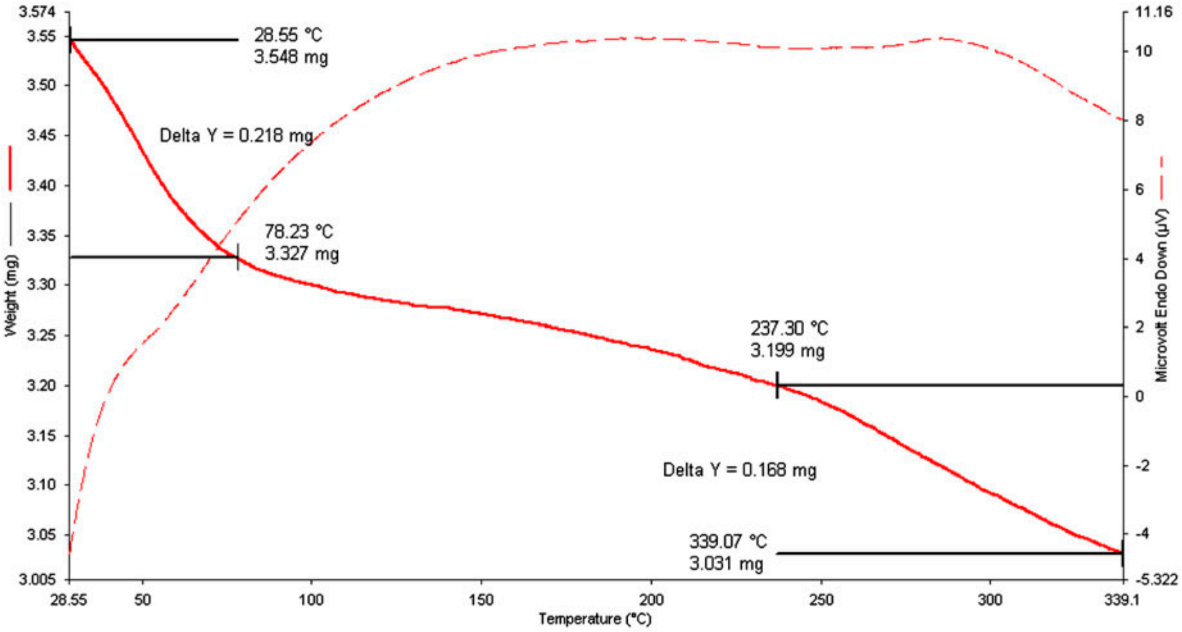


Fig. 2. Effect of temperature on the stability of BAM loaded alumina.

Table 1
Effect of different eluents on the desorption of chromium species from the resin

Eluent	Recovery (%) of Cr(III)	Recovery (%) of Cr(VI)
1.0 mol $L^{-1}$$HNO_3$	45 ± 2	10.9 ± 1
2.0 mol $L^{-1}$$HNO_3$	47.06 ± 5	10.37 ± 4
3.0 mol $L^{-1}$$HNO_3$	42.24 ± 4	7.96 ± 5
1.0 mol L^{-1}HCl	60.96 ± 2	28.0 ± 2
2.0 mol L^{-1} HCl	61.12 ± 3	32.7 ± 3
3.0 mol L^{-1} HCl	101.32 ± 4	100.7 ± 4
1.0 mol L^{-1}AcOH	17.9 ± 5	22.8 ± 5
2.0 mol L^{-1}AcOH	21.7 ± 5	18.05 ± 5
3.0 mol L^{-1}AcOH	21.6 ± 3	22.8 ± 5

3.3. Effect of sample volume

Sample breakthrough volume is an important parameter to study the volume of real sample that may be allowed to pass through the sorbent over which no sorption will occur. About 300 mL solution (concentration 50 mg L^{-1}) of Cr(VI) was allowed to pass through the column containing 1 g sorbent under optimum condition. Recovery of Cr(VI) was quantitative (96%) up to 81.0 mL of sample volume after which the recovery decreased quickly.

3.4. Sorption and desorption of Cr species as a function of pH

The hydrogen ion capacity of the sorbent was found to be 0.52 mmol g^{-1}. The effect of pH on the retention of Cr(III) and Cr(VI) on the sorbent had been investigated separately. pH of the solution was adjusted in the range of 1–10 for Cr(III) and 2.5–10 for Cr(VI), respectively, by using appropriate buffer solution. Effect of pH on the sorption of Cr(III) and Cr(VI) onto the sorbent was shown in Fig. 3. It was clear that the sorption of Cr(III) increased with pH to a maximum at pH 4.0 with no further change up to pH 10.0. Sorption of Cr(VI) was highest at pH 2.0 and then decreased with increasing pH. Thus, separation and simultaneous estimation of Cr(III) and Cr(VI) was possible by mere adjustment of pH using the same sorbent. The sorption of Cr(III) was established from the FTIR spectra of the Cr(III)-loaded sorbent (Fig. 4) [21].

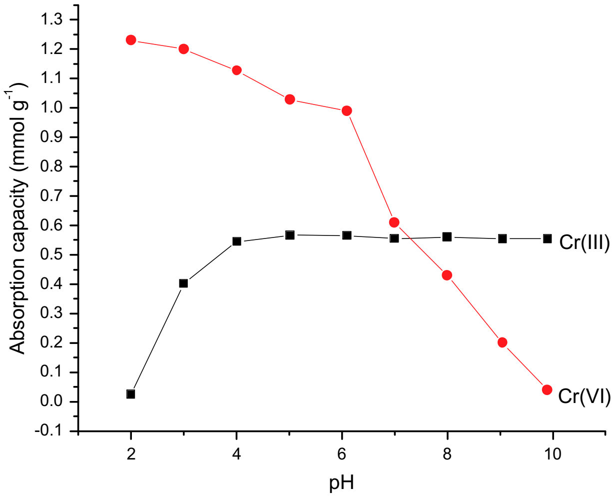


Fig. 3. Effect of pH on the sorption of Cr species by BAM loaded alumina.

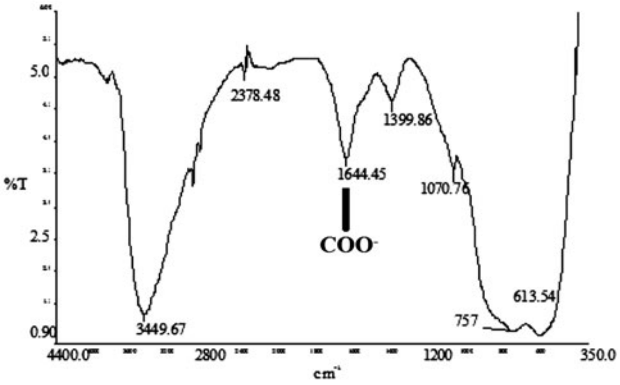


Fig. 4. FTIR spectra of BAM–Cr(III) complex loaded on alumina.

3.5. Effect of temperature

It has been found that with increasing temperature sorption capacity of the sorbent increases to a maximum value at 50°C (Fig. 5).

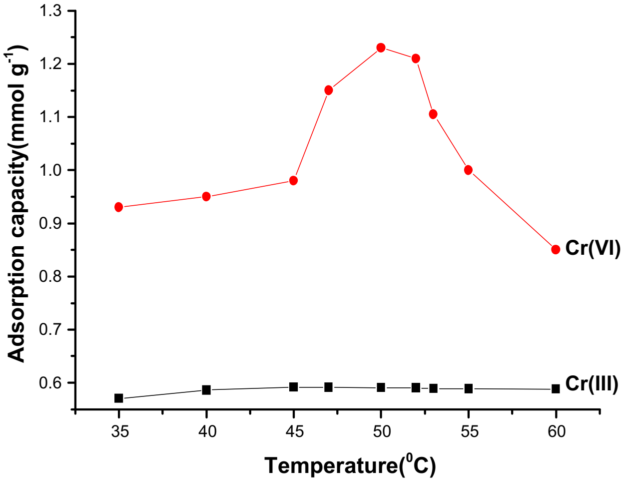


Fig. 5. Effect of temperature on sorption of Cr species by BAM loaded alumina.

3.6. Kinetic parameters

The rate of exchange of metal ion by a chelating resin was controlled by a second-order kinetic equation [22]. Using the equation $\ln Z = 2kQ_0(Q_0 - Q_\alpha)\,t/Q_\alpha$, where $Z = [Q_t(Q_0 - 2Q_\alpha) + Q_0Q_\alpha]/Q_0(Q_\alpha - Q_t)$ developed by Turse and Riemen [23]. The rate constant k was calculated from the slope S from the equation: $S = 2kQ_0(Q_0 - Q_\alpha)/Q_\alpha$, where Q_t was the amount of metal ion exchanged at time t, Q_α, was the maximum exchange capacity at equilibrium and Q_0 was the amount of chelating resin, in terms of milimoles of Na^+ exchanged after 24 h. A plot of $\ln Z$ vs. t (time) was presented in Fig. 6 and Fig. 7 for Cr(III) and Cr(VI), respectively. Different kinetic parameters were presented in Table 2.

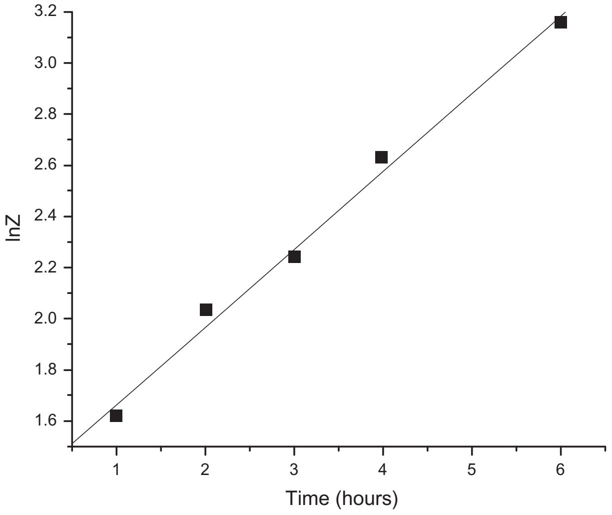


Fig. 6. Second order plot for the absorption of Cr(III) on BAM loaded alumina.

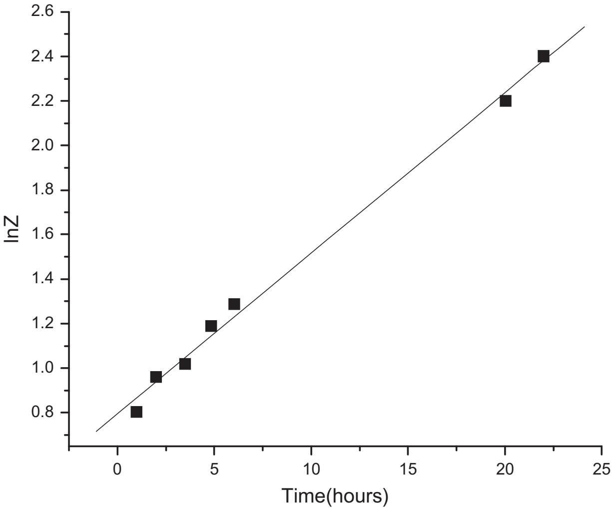


Fig. 7. Second order plot for the adsorption of Cr(VI) on BAM loaded alumina.

Table 2
Kinetics parameters of exchange rates of Cr(III) and Cr(VI) with the resin

Kinetic parameters	Cr(III)	Cr(VI)
pH	5.0	3.0
Q_0 (mmolg^{-1})	1.15	1.15
Q_α (mmolg^{-1})	0.597	1.02
S	0.32	0.99
K (mmol min^{-1})	0.20	0.23

3.7. Effect of diverse ions

In column operation, the presence of macro amounts (40-fold) of alkali, alkaline earth and transition metal ions (Cu(II), Hg(II), Cd(II), Pb(II), Al(III) and Fe(III) interfere to some extent) did not interfere. Effect of different anions has also been recorded. In each case of binary mixtures, 5 mg L^{-1} each of Cr(III) or Cr(VI) were taken along with other ions having concentration 200 mg L^{-1}. The results were summarised in Table 3.

Table 3
Effect of diverse ions on the sorption of Cr(III) and Cr(VI) on to the resin

Foreign ion[a]	% Recovery of Cr(III)	% Recovery of Cr(VI)
Al(III)	89.2	–
Fe(III)	93.1	–
Cu(II)	92.99	–
Hg(II)	91.5	–
Ni(II)	98.6	–
Cd(II)	94.07	–
Pb(II)	91.3	–
Li(I)	99.9	–
Zn(II)	98.6	–
Mn(II)	98.9	–
Mg(II)	99.25	–
Co(II)	99.8	–
AsO_4^{3-}	–	97.5
MoO_4^{2-}	–	98.3
VO_3^{-}	–	92.0
Cl^{-}	–	99.0
NO_3^{-}	–	99.5
PO_4^{3-}	–	98.7

[a] In each case the amount of foreign ion was added 40-fold excess with respect to Cr(III) and Cr(VI).

3.8. Influence of flow rate

The flow rate of the sample solution not only affected the retention of Cr species on the sorbent but also the duration of complete analysis. Therefore, the effect of the flow rate of sample solution was examined under the optimum conditions. The flow rate of the sample solution was adjusted in a range 0.5 to 15.0 mL min^{-1}. It was found that the retention of Cr species practically remains unaltered up to a flow rate of 7.0 mL min^{-1}. Above this value, the recoveries decreased gradually.

3.9. Evaluation of method performance

Calibration curve for quantitative analysis was linear up to 50 mg L^{-1} with a regression coefficient (R) of 0.997. Detection limit (3σ of the blank signal; $N = 20$) was found to be 4.5 μg mL^{-1} for Cr(III) and 4.6 μg mL^{-1} for Cr(VI). Precision of the method was evaluated by successive retention and elution cycle with 0.1 g of Cr(VI) in 100 mL of solution. Recovery was 97.4 ± 2.6% at 95% confidence level. An enrichment factor of 150 for Cr(III) and 130 for Cr(VI) was achieved.

4. Applications

4.1. Separation of Cr(III) and Cr(VI) from the binary synthetic mixtures

Several sets (each set in duplicate) of synthetic mixtures containing both Cr(III) and Cr(VI) have been prepared, where measured amounts of Cr(III) and Cr (VI) were mixed with a total volume of 100 mL. The pH of the solutions of one set was adjusted to 2.0, whereas the pH of the other set was maintained to 10.0 in order to enable their complete separation (as evident from Fig. 3). After elution with 3.0 mol L^{-1} HCl, the concentrations of Cr species were measured using FAAS. The results were summarised in Table 4.

4.2. Real samples analysis

The wastewater samples from different sources (three samples from tannery industrial area, Kolkata and three samples from Durgapur Industrial belt, West Bengal, India) were treated and analysed as described in Section 2.14. The results were presented in Table 5. The results were compared with a reference method [20], and a good agreement was found between the two (t-test, $p = 0.05$).

Table 4
Applications towards separation of Cr(III) and Cr(VI)) from synthetic mixtures (volume of the solution: 5 mL)

No. of observations	Amount taken (μg)	Amount found (μg)	Error (%)
1.	Cr(III) – 100	Cr(III) – 100.26 ± 0.02	0.026
	Cr(VI) – 100	Cr(VI) – 98.08 ± 0.01	1.92
2.	Cr(III) – 50	Cr(III) – 48.5 ± 0.03	1.5
	Cr(VI) – 100	Cr(VI) – 102.6 ± 0.2	2.6
3.	Cr(III) – 100	Cr(III) – 101.2 ± 0.01	1.2
	Cr(VI) – 50	Cr(VI) – 49.5 ± 0.03	0.05
4.	Cr(III) – 20	Cr(III) – 22.01 ± 0.02	2.01
	Cr(VI) – 300	C(VI) – 298.6 ± 0.01	1.4
5.	Cr(III) – 300	Cr(III) – 301.4 ± 0.4	1.4
	Cr(VI) – 20	Cr(VI) – 19.1 ± 0.5	1.0

Table 5
Level of chromium species in environmental samples as determined by the present method ($N = 4$)

	Present method (ng mL^{-1})		Reference method [20] (ng mL^{-1})	
Sample no.	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)
1[a]	681.2 ± 0.2	595 ± 2	684.2 ± 1	598 ± 3
2[a]	575 ± 3	512 ± 4	570 ± 4	509 ± 5
3[a]	467 ± 1	411 ± 3	472 ± 3	415 ± 2
4[b]	65.3 ± 3	54.3 ± 1	62.3 ± 3	51.3 ± 1
5[b]	43.1 ± 3	41.2 ± 4	41.1 ± 2	43.2 ± 4
6[b]	35.5 ± 4	37.5 ± 5	33.5 ± 0.8	36.0 ± 5

[a]Tannery water; [b]Industrial water.

Table 6
Comparison of the present method with some other existing methods

Matrix	LOD (μg mL^{-1})		Eluent	Pre-concentration factor		Sample analyzed
	Cr(III)	Cr(VI)		Cr(III)	Cr(VI)	
Acetyl acetone modified XAD-16 [24]	0.02	0.014	2 mol L^{-1} HNO_3 and 2 mol L^{-1} NaOH	100	140	Industrial samples
Cr(VI)- Dowex M 4195 chelating resin [25]	NA	1.94	4 mol L^{-1} NH_3	NA	95	Natural and waste water samples
2-naphthol-3,6-disulphonic acid [11]	NA	NA	4 mol L^{-1} HCl	97	97	Binary synthetic mixtures, natural water samples
Immobilized moss on a polysilicate matrix [26]	0.15	NA	10 mL of 2 mol L^{-1} HNO_3	20	NA	Water samples
Amberlite XAD-16/ 1,5-diphenylcarbazone [27]	NA	0.045	10 mL of 0.05 mol L^{-1} H_2SO_4 in methanol	NA	25	Water samples
Amberlite XAD-2/5-palmitoyl-8-hydroxyquinoline [28]	0.058	NA	20 mL of 2 mol L^{-1} HCl	50	NA	Water samples
Sepiolite/ Saccharomyces cerevisiae [14]	0.094	NA	10 mL of 1 mol L^{-1} HCl	75	NA	Water samples
BrPMAAm/AMPS/ DVB [29]	0.00158	NA	10 mL of 1 mol L^{-1} HCl	100	NA	Real water samples, spicked water sample
Pyridine-methionine modified merrifield polymer [30]	1.6	0.6	2 and 3 mol L^{-1} HNO_3	110	100	Environmental samples, industrial samples, binary mixtures
Present method	45×10^{-3}	46×10^{-3}	3.0 mol L^{-1} HCl	150	130	Binary synthetic mixtures, waste water samples

NA = Not available

5. Conclusions

It is found that BAM-loaded alumina can be used for selective removal and chemical speciation of inorganic chromium species as a function of pH from environmental samples. The developed method is reproducible and has a very competitive detection limit. The maximum sorption capacity for Cr(III) at pH 4.0 is $0.5663\,\mathrm{mmol\,g^{-1}}$ and for Cr(VI) at pH 2.0 is $1.23\,\mathrm{mmol\,g^{-1}}$. About $3.0\,\mathrm{mol\,L^{-1}}$ HCl can completely desorb both chromium species from the sorbent. The detection limit (three times the standard deviation of the blank, as obtained from FAAS method) for Cr(III) and Cr(VI) is found to be 45 and $46\,\mathrm{ng\,mL^{-1}}$, respectively. A comparison of the present method with the promising existing methods [11,14,24–30] has been presented as Table 6. We believe that three carboxylate anions [21] and one tertiary nitrogen moiety of the sorbent molecule are responsible for binding to Cr(III) at higher pH, whereas at lower pH (acidic) nitrogen centre gets protonated and act as an anion exchanger to bind with Cr(VI).

Acknowledgments

Financial assistance from UGC-DAE-Kolkata centre is gratefully acknowledged. Authors thank Sudipta Das, Subarna Guha, Animesh Sahana, Arnab Banerjee, Sisir Lohar and Debasis Karak for their assistance.

References

[1] J.O. Nrigae, E. Nieboer, Chromium in Natural and Human Environment, Wiley, New York, NY, 1988.
[2] V. Valcovic, Trace Elemental Analysis, Taylor and Francis, London, 1975.
[3] K. Stein, G. Schwedt, Fresenius' J. Anal. Chem. 350 (1994) 38–43.
[4] I. Turyan, D. Mandler, Anal. Chem. 69 (1997) 894–897.
[5] M. Korolczuk, M. Grabarczyk, Microchem. J. 62 (1999) 311–315.
[6] S. Abliz, J.D. Wang, H. Orshida, Spectrosc. Spect. Anal. 25 (2005) 2082–2085.
[7] J. Ueda, H. Satoh, S. Kagaya, Anal Sci. 13 (1997) 613–617.
[8] L. Wang, B. Hu, Z.C. Jiang, Z.Q. Li, Int. J. Environ. Anal. Chem. 82 (2002) 387–390.
[9] K. Kargosha, M. Noroozifar, Asian J. Spectrosc. 8 (2004) 101–109.
[10] M. Tüzen, M. Soyalk, J. Hazard. Mater. 129 (2006) 266–273; I. Narin, Y. Surme, M. Soylak and M. Dogan, J. Hazard. Mater. B. 136 (2006) 579–584.
[11] B.C. Mondal, D. Das, A.K. Das, Talanta 56 (2002) 145–152.
[12] D. Banerjee, A.K. Das, J. Ind. Chem. Soc. 83 (2006) 479–482.
[13] I. Narin, A. Kars, M. Soylak, J. Hazard. Mater. 150 (2008) 453–458.
[14] H. Bag, A.R. Turker, M. Lale, A. Tunceli, Talanta 51 (2000) 895–902.
[15] B.C. Mondal, A.K. Das, Bull. Chem. Soc. Jpn. 76(1) (2003) 111–114.
[16] V.N. Bulut, C. Duran, M. Tufekci, L. Elci, M. Soylak, J. Hazard. Mater. 143 (2007) 112–117.
[17] I. Kubrakova, T. Kudinova, A. Formanovsky, N. Kuzmin, G. Tsysin, Y. Zolotov, Analyst 119 (1994) 2477–2480.
[18] S.A. Steiner, M.D. Porter, J.S. Fritz, J. Chromatogr. A 1118 (2006) 62–67.
[19] M. de la Guardia, A. Morales-Rubiol, Sample preparation for chromium speciation, In: D. Barceló (Ed), Comprehensive Analytical Chemistry XLI, Elsevier Science, Amsterdam, pp. 1115–1171, 2003.
[20] L.C. Clesceri, A.E. Greenberg, A.D. Eaton, Standard Methods for the Examination of Water and Waste Water, APHA, American Water Works Association and Water Environment Federation, Washington, DC, 1998.
[21] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part B: Applications in Coordination, Organometallic, and Bioinorganic Chemistry, fifth ed., Wiley, New York, NY, 1997, p. 116.
[22] A.A. Frost, R.G. Pearson, Kinetics and Mechanism, Wiley, New York, NY, 174 1997.
[23] R. Turse, W.M. Rieman, III J. Phys. Chem. 65 (1961) 1821–1824.
[24] J. Memon, S.Q. Memon, M.I. Bhanger, M.Y. Khuhawar, J. Hazard. Mater. 163 (2009) 511–516.
[25] K.O. Saygi, M. Tuzen, M. Soylak, L. Elci, J. Hazard. Mater. 153 (2008) 1009–1014.
[26] M.V.B. Krishna, K. Chandrasekaran, S.V. Rao, D. Karunasagar, J. Arunachalam, Talanta 65 (2005) 135.
[27] A. Tunceli, A.R. Turker, Talanta 57 (2002) 1199–1204.
[28] H. Filik, Microchim. Acta. 140 (2002) 205.
[29] Ş. Tokalıoğlu, S. Arsav, A. Delibaş, C. Soykan, Anal. Chim. Acta 645 (2009) 36–41.
[30] A. Sahana, S. Das, A. Banerjee, S. Lohar, D. Karak, D. Das, J. Hazard. Mater. 185 (2011) 1448–1457.