

Solid phase extraction of chromium(VI) from aqueous solutions by adsorption of its ion-association complex with cetyltrimethylammoniumbromide on an alumina column

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Received 30 August 2006; received in revised form 16 October 2006; accepted 17 October 2006

Available online 26 October 2006

Abstract

A simple approach has been developed for the solid phase extraction of chromium(VI) based on the adsorption of its ion-association complex with cetyltrimethylammoniumbromide (CTABr) on an alumina column. The effect of various parameters such as acidity, stability of the column, sample volume, effect of diverse ions, etc. have been studied in detail. The adsorbed complex could be eluted using sodium hydroxide and the concentration of chromium has been established using visible spectrophotometry after complexation with diphenyl carbazide. The calibration graph was linear in the range 0–0.5 $\mu\text{g mL}^{-1}$ chromium(VI) with a detection limit of 5 $\mu\text{g L}^{-1}$. A highest preconcentration factor of 25 could be obtained for 250 mL sample volume. The data from the column studies were also studied using the Thomas model of adsorption. The experimental results obtained were correlated with the proposed model of adsorption. The Thomas rate constant k was found to be 0.0025 L/min mg and the maximum adsorption capacity q_0 was found to be 0.36 mg Cr/g alumina at an initial chromium(VI) concentration of 1 mg L^{-1} . The validity of the method has been checked by applying it to study the recovery of chromium in spiked water samples and electroplating wastewater.

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Keywords: Chromium(VI); Cetyltrimethylammoniumbromide; Alumina; Solid phase extraction; Thomas model

1. Introduction

The considerable emphasis on the removal of toxic metal ions led to the development of a variety of analytical methodologies. Hence, there has been considerable growth in the analytical chemistry of various metal ions. Chromium is not an exception to this. Among the stable oxidation states of chromium, Cr(III) is an essential dietary mineral in low doses, whereas Cr(VI) is carcinogenic [1].

In view of the toxic nature of chromium(VI), development of methods in order to establish their levels in the environment and industrial quality control are quite significant. Solid phase extraction has been explored for the preconcentration of many metal ions [2–5]. A variety of adsorbents have been used for the preconcentration of chromium [6–13].

A survey of the literature for the preconcentration of chromium(VI) reveals that solid phase extraction is one of the versatile methods. The major advantage of solid phase extraction is the high selectivity and enrichment factor that could be achieved in this method. Among the various adsorbents, silica and alumina have been extensively studied for the adsorption of chromium.

In this paper, a simple methodology is proposed for the solid phase extraction of chromium based on the adsorption of its ion-association complex with cetyltrimethylammoniumbromide on a basic alumina column. The adsorbed complex could be easily eluted using sodium hydroxide and the recovery of chromium was established using visible spectrophotometry after complexation with diphenyl carbazide. The effects of various experimental parameters such as sample volume, volume of eluent, flow rate, effect of diverse ions, etc. were studied in detail. The data from the column studies were fitted with the Thomas model of adsorption. The validity of the proposed method was checked by applying it to the determination of chromium in spiked water samples and electroplating wastewater.

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2. Experimental

2.1. Reagents

Analytical grade reagents were used in the preparation of all solutions. Triple distilled water was used for the preparation of solutions. 0.374 g of potassium chromate (Qualigens, India) was weighed and made to 100 mL by addition of water in a standard volumetric flask. This solution corresponds to $1000 \mu\text{g mL}^{-1}$. A working solution of $10 \mu\text{g mL}^{-1}$ was prepared by appropriate dilution.

Basic alumina (Himedia, India) of pore diameter 20–50 mesh was used for adsorption. A 2% solution of cetyltrimethylammoniumbromide was prepared by dissolving 2 g of the surfactant in 100 mL of triple distilled water. Acetone (E. Merck) was used as such without further purification.

0.25 g of 1,5-diphenyl carbazide (CDH, India) was taken in a volumetric flask and diluted to 100 mL using acetone.

Sulfuric acid of the required concentrations was prepared from concentrated sulfuric acid by appropriate dilution.

2.2. Instrumentation

A Jasco model UV–vis spectrophotometer was used for absorbance measurements. One centimeter matched quartz cells were used to record the absorbances.

The pH of the solutions was measured using an Elico pH meter.

2.3. Column preparation

A glass column 1.5 cm in diameter and 15 cm in length was used for preconcentration. Slurry of 2 g of basic alumina in 50 mL triple distilled water was prepared and the column was packed to a height of 5 cm.

The column was washed using triple distilled water followed by conditioning it using 0.1 mol L^{-1} sulfuric acid. Cotton was placed at the bottom and at the top of the column for allowing the adsorbent to settle properly.

2.4. Procedure for solid phase extraction

A 1 mL volume of $10 \mu\text{g mL}^{-1}$ solution of Cr(VI) was mixed with 5 mL of 0.5 mol L^{-1} sulfuric acid followed by the addition of 5 mL of 2% cetyltrimethylammoniumbromide and the resulting volume was maintained at 100 mL. The sample solution was loaded on to the column containing basic alumina maintaining a flow rate of 2 mL min^{-1} . The ion-association complex was adsorbed on to the column, which was evident from the absorbance of the resulting solution (measured after complexation with diphenyl carbazide) that emerged out of the column. The adsorbed complex was then eluted using 10 mL of 5 mol L^{-1} sodium hydroxide. The eluate was acidified with sulfuric acid and the concentration of chromium(VI) was analyzed after complexation with diphenyl carbazide by visible spectrophotometry at 540 nm.

2.5. Thomas model of adsorption

Thomas model is one of the widely used mathematical modeling methods for fixed bed column studies [14]. In the present method, the Thomas model was used to correlate the experimental data for two representative initial concentrations of chromium(VI). The Thomas model can be expressed mathematically as:

$$\frac{C}{C_0} = \frac{1}{1 + \exp[k/Q(q_0M - C_0V)]}$$

where C_0 is the initial chromium concentration, mg L^{-1} ; C the eluent chromium concentration, mg L^{-1} ; k the Thomas rate constant, L/min mg ; M the mass of the adsorbent, g ; q_0 the maximum adsorption capacity, mg Cr/g alumina ; Q the flow rate, mL min^{-1} ; V is the sample volume, mL .

From the plot of $\ln[(C_0/C) - 1]$ against the varying sample volume V , the intercept kq_0M/Q and the slope kC_0/Q were calculated, and using these values, the Thomas rate constant k and the adsorption capacity q_0 were calculated accordingly.

3. Results and discussion

3.1. Effect of pH

The effect of pH was studied for the recovery of $10 \mu\text{g}$ chromium(VI) in a sample volume of 100 mL. The adsorbed chromium(VI) was eluted using 10 mL of 5 mol L^{-1} sodium hydroxide solution. The results are presented in Fig. 1. As can be seen from the figure, it is evident that the recovery of chromium is quantitative (>95%) in the pH range 1.15–1.39. Beyond this range, there was considerable decrease in the percentage recovery of chromium.

3.2. Effect of eluting agents

Different eluting agents were tried to desorb the chromium (VI) from the column. Some of the eluting agents tried were

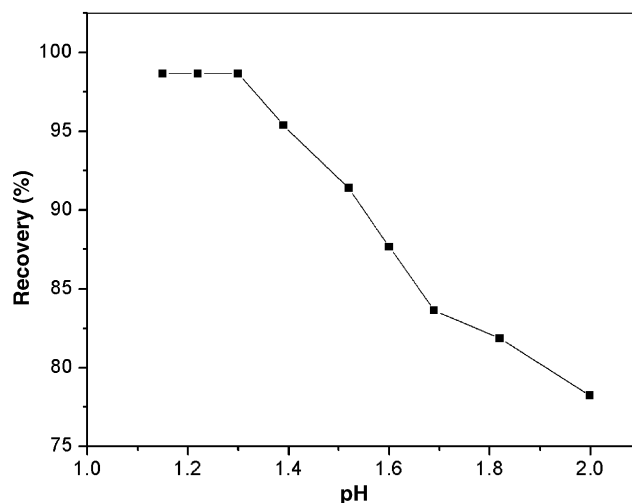


Fig. 1. Effect of pH on the recovery of chromium(VI).

Table 1
Effect of various eluting agents on the recovery of chromium

Eluent	Recovery of chromium (%)
Sulfuric acid	46.7
Sodium hydroxide	98.9
Nitric acid	20
Ammonia	26.7
Hydrochloric acid	50
Ascorbic acid	0

sulfuric acid, sodium hydroxide, nitric acid, ammonium hydroxide, hydrochloric acid and ascorbic acid. The elution studies were carried out maintaining an overall Cr(VI) concentration of $10\ \mu\text{g}$ in 100 mL sample volume. The results are presented in Table 1. The elution was quantitative with $5\ \text{mol L}^{-1}$ sodium hydroxide solution as the eluting agent.

3.3. Effect of concentration of sodium hydroxide

The concentration of sodium hydroxide solution as the eluting agent was varied from 0.5 to $7\ \text{mol L}^{-1}$, respectively. The results are presented in Fig. 2. It was observed that maximum quantitative recovery of chromium(VI) was observed with $5\ \text{mol L}^{-1}$ of sodium hydroxide solution. Beyond $5\ \text{mol L}^{-1}$ there was no change in the percentage recovery of chromium(VI).

3.4. Effect of volume of the eluent

The volume of $5\ \text{mol L}^{-1}$ sodium hydroxide solution as the eluting agent was varied from 5 to 15 mL. It was observed that maximum quantitative recovery of chromium(VI) was observed with 10 mL of sodium hydroxide solution. A lower volume of sodium hydroxide was not effective in the complete elution of the complex.

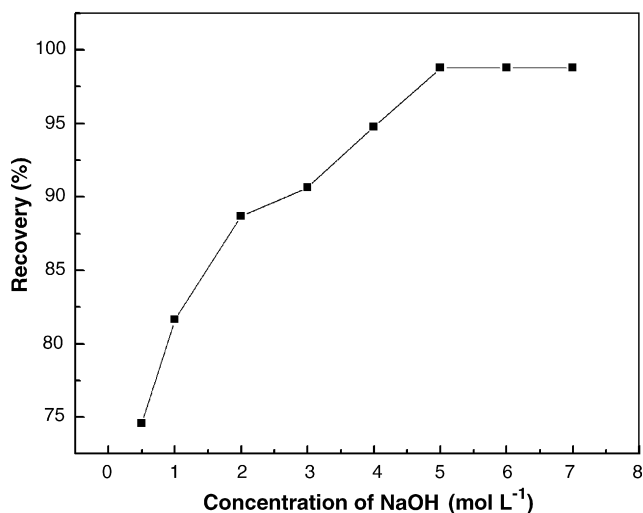


Fig. 2. Effect of concentration of NaOH on the recovery of chromium(VI).

3.5. Effect of the amount of basic alumina loaded on the column

The amount of basic alumina loaded on the column was varied from 1.0 to 5.0 g. The concentration of chromium(VI) was maintained at $10\ \mu\text{g}$ in a 100 mL sample volume. Quantitative recovery of chromium(VI) could be attained in the range 1.5–5.0 g of basic alumina. For amounts less than 1.5 g there was a significant reduction in the recovery of chromium beyond a sample volume of 75 mL.

3.6. Effect of sample volume

A 1 mL volume of $10\ \mu\text{g mL}^{-1}$ solution of Cr(VI) was mixed with 5 mL of $0.5\ \text{mol L}^{-1}$ sulfuric acid followed by the addition of 5 mL of 2% cetyltrimethylammoniumbromide and the sample volume was varied from 50 to 500 mL. The resulting complex was eluted using 10 mL of $5\ \text{mol L}^{-1}$ sodium hydroxide solution. The effect of the sample volume and the corresponding preconcentration factors are given in Fig. 3. As can be seen from the figure, it is evident that the recovery of chromium is quantitative (>95%) up to 250 mL sample volume. A preconcentration factor of 25 could be attained for quantitative recovery (>95%) of Cr(VI) when the sample volume was 250 mL.

3.7. Effect of flow rate

The flow rate of $1\text{--}5\ \text{mL min}^{-1}$ was found to be suitable for optimum loading of the ion-association complex on the basic alumina column. At higher flow rates, there was a reduction in the percentage adsorption of chromium. This could be probably due to the insufficient contact time between the sample solution and the basic alumina column. A flow rate of $1\ \text{mL min}^{-1}$ was maintained for the elution of the complex.

3.8. Stability of the column

The stability of the column was tested using $10\ \mu\text{g}$ Cr(VI) maintaining a sample volume of 100 mL. The adsorbed Cr(VI)

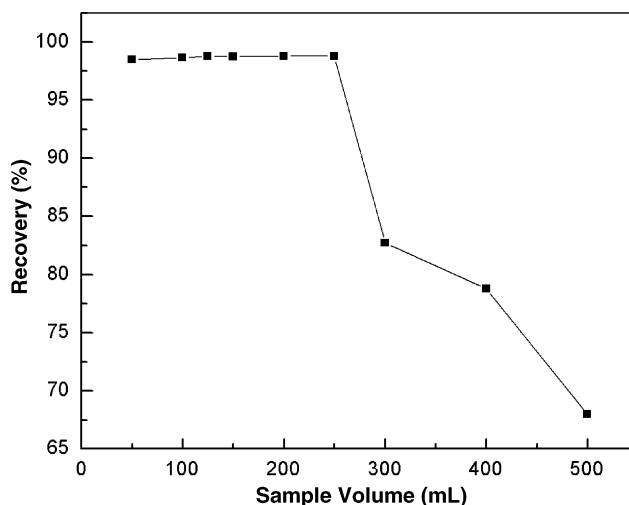


Fig. 3. Effect of sample volume on the recovery of chromium(VI).

was desorbed using 10 mL of 5 mol L⁻¹ sodium hydroxide solution. The column was stable for 13 cycles and could be used with good precision and quantitative recovery (>95%) for 13 cycles. Beyond 13 cycles, there was a reduction in the recovery of chromium.

3.9. Precision and detection limit

The precision studies were carried out at 0.1 µg mL⁻¹ level of chromium by carrying out ten separate determinations using the above-mentioned procedure. The sample volume was maintained at 100 mL. The relative standard deviation of the method was found to be 5.0%. The sensitivity of the developed method is reflected by the limit of detection (LOD) studies, defined as the lowest concentration of chromium(VI) below which quantitative sorption of the metal ion by basic alumina is not perceptibly seen. The LOD for Cr(VI) was found to be 5 µg L⁻¹.

3.10. Effect of diverse ions

The effect of diverse ions was studied at varying concentrations. The solid phase extraction studies were carried out as mentioned above using 10 µg Cr(VI) maintaining a sample volume of 100 mL. The studies indicated that Ca²⁺, Mg²⁺, Ni²⁺, Cu²⁺, SO₄²⁻, Fe³⁺, Zn²⁺, Co²⁺, Cl⁻, NO₃⁻ did not cause any significant reduction in the recovery of chromium. The results

Table 2
Effect of diverse ions on the recovery of chromium

Ions	Amount (µg)	Recovery of chromium* (%)
Mg ²⁺	500	98.66
	1000	98.75
	250	98.66
Ca ²⁺	500	98.46
	1000	98.85
	250	98.75
Ni ²⁺	1000	98.64
	500	98.76
	250	98.75
Cl ⁻	1000	98.28
	500	98.74
	250	98.54
NO ₃ ⁻	1000	98.54
	500	98.63
	250	98.82
SO ₄ ²⁻	1000	98.72
	500	98.66
	250	98.43
Co ²⁺	1000	98.68
	500	98.62
	250	98.76
Cu ²⁺	500	98.75
	250	98.85
	1000	98.64
Fe ²⁺	150	98.82
	500	64.55
	1000	63.0

* Average of three determinations.

Table 3
Thomas model parameters

Initial chromium concentration, C ₀ (mg L ⁻¹)	Thomas rate constant, k (L/min mg)	Maximum adsorption capacity, q ₀ (mg Cr/g alumina)	Regression coefficient, R
1	0.0024389	0.366	0.96
0.67	0.0025087	0.357	0.96

are presented in Table 2 showing the recovery of chromium with varying concentrations of metal ions. Except Fe²⁺, the recovery was found to be quantitative in the concentration range of the metal ions that was investigated. Since, the ions that are commonly present in water samples did not affect significantly the recovery of chromium the method was applied to study the recovery of chromium in tap water and well water samples.

3.11. Correlation of experimental results with Thomas model of adsorption

A number of mathematic models have been proposed for the design of fixed-bed adsorption studies. Among these, Thomas model is simple to use and the data obtained from the column studies was examined using the kinetic model developed by Thomas. In the proposed method, taking an initial concentration of 1 and 0.67 mg L⁻¹ of chromium(VI), and varying the sample volume from 100 to 1000 mL, the Thomas rate constant *k* and the maximum adsorption capacity *q*₀ was calculated. The results are presented in Table 3. The data obtained from the column studies fitted well with the Thomas model of adsorption.

3.12. Recovery study in spiked water samples

The proposed method was applied to tap water and well water samples by spiking known concentrations of chromium in varying sample volumes. The recovery of chromium was found to be quantitative with an average relative standard deviation of 4.2% on triplicate measurements and the results are shown in Table 4.

3.13. Analysis of chromium(VI) in electroplating wastewater

The proposed method was applied to study the recovery of chromium(VI) in electroplating wastewater sample. The elec-

Table 4
Recovery studies in tap water and well water samples

Sample	Cr(VI) added (µg)	Cr(VI) found (µg)	Sample volume (mL)	Recovery of chromium (%)
Tap water	5.0	4.92	100	98.4
	2.0	1.97	250	98.5
	10	9.87	200	98.7
	10	9.83	250	98.3
	10	9.87	100	98.7
	10	9.87	250	98.7
Well water	5.0	4.91	250	98.2
	4.0	3.93	200	98.3
	2.0	1.96	250	98.0

Table 5
Analysis of chromium(VI) in electroplating wastewater

Sample	Concentration of chromium(VI) added (mg L^{-1})	Concentration of chromium(VI) found (mg L^{-1})	Relative standard deviation (%)	Recovery (%)
Electroplating wastewater	0	123.0	3.8	–
	5.0	127.8	3.6	99.8
	10.0	132.7	4.1	99.7

Table 6
Comparison of the proposed method with some of the methods reported in literature

SPE support/chelating agent	Method	Preconcentration factor	Detection limit ($\mu\text{g L}^{-1}$)	Reference
Amberlite XAD-16/1,5-diphenyl carbazone	FAAS	25	45	[7]
Naphthalene/potassiumethylxanthate	FAAS	100	0.5	[12]
Chitin/1,5-diphenyl carbazide	Spectrophotometry	–	50	[15]
C-18 bonded silica/CTABr	FAAS	45	20	[16]
Amborsorb-563/1,5-diphenyl carbazide	Spectrophotometry	30	3.4	[17]
Sacchromyces cervisiae/sepiolite	FAAS	75	94	[18]
Funaria/polysilicate	FAAS	20	145	[19]
Chromosorb-108/dithizone	FAAS	71	0.75	[20]
Amborsorb-563/APDC	FAAS	125	2.7	[21]

FAAS, flame atomic absorption spectrometry.

troplating wastewater sample had the following characteristics: pH 3.2; calcium, 52 mg L^{-1} ; magnesium, 10.5 mg L^{-1} ; chloride, 820 mg L^{-1} ; sulfate, 570 mg L^{-1} . The wastewater sample was diluted to the required concentration and the preconcentration procedure was applied as mentioned above. The recovery of chromium was found to be quantitative and the results are presented in Table 5.

4. Conclusions

The proposed method for chromium is simple, and could be effectively used for the solid phase extraction of chromium. The preconcentration factor was 25 for a 250 mL sample volume. The calibration graph was linear in the range $0\text{--}0.5 \mu\text{g mL}^{-1}$. The method showed minimum interferences with commonly found ions in real samples and the recovery of chromium was quantitative. The quantitative recovery of chromium(VI) in spiked water samples and electroplating wastewater sample with a relative standard deviation of 4% reflects the validity and accuracy of the method when applied to real samples. Basic alumina exhibits comparable capacity values in comparison to most of the metal matrix combinations reported in the literature as shown in Table 6. The column exhibited good stability under the experimental conditions. The important features of the proposed method are its high sorption capacity with good enrichment factor. The experimental results fitted well into the Thomas model of adsorption. The developed method is sensitive in detecting chromium(VI) at ppb levels. The column exhibited good stability and reproducibility of data up to 13 cycles of continuous usage.

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