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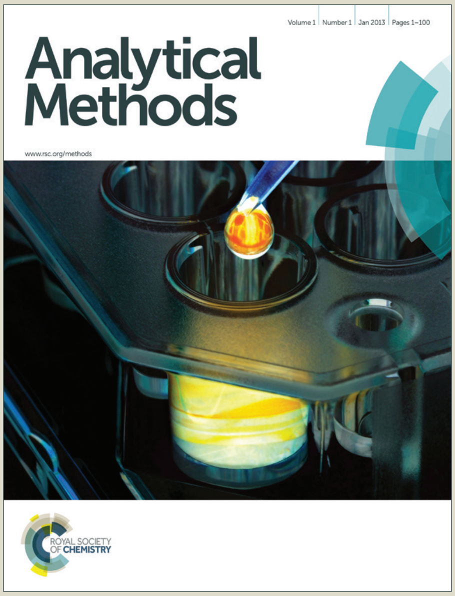

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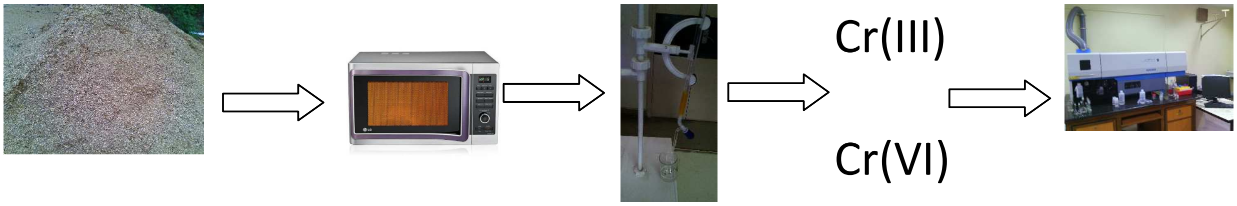
Cr(III)
Cr(VI)

Microwave assisted extraction of Cr(III) and Cr(VI) from soil/sediment combined with ion exchange separation and Inductively Coupled Plasma Optical Emission Spectrometry detection

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Abstract

An analytical methodology has been developed for the speciation of Cr(III) and Cr(VI) in soil/ sediments. The species of interest were extracted from samples using a solution containing 0.1 M EDTA, 1% tetrabutyl ammonium bromide (TBAB) and little HF in a domestic microwave oven. Conditions for quantitative extraction of Cr species from sediments were optimized. The separation of anionic Cr(VI) from the sediment extract has been carried out using sulfate form of Dowex-1 at pH 4.5. Though the extract contained anionic EDTA complex of Cr(III), it was eluted out quantitatively. The adsorbed Cr(VI) was eluted with 2M HNO_3. The determination of separated Cr(VI), Cr(III) in the effluent and total Cr in the extract has been carried out using ICP-OES. The recovery of total Cr from original samples was 96- 99% and that of Cr(III) and Cr(VI) spiked was 97- 102% with RSD in the range 5-6 %. The developed methodology has been applied for the speciation of Cr in a certified reference material stream sediment (GBW-07312) and also four real world samples two sediments collected from Hussain Sagar lake, Hyderabad, India and two soils collected near Uranium Corporation of India Limited (UCIL), Tummalapalli, Kadapa, India. The total concentration of Cr in the extract was in good agreement with the certified value of stream sediment and with complete dissolution method in case of real world samples. The limit of detection of Cr(VI) was 0.02 mg/L corresponding to a method detection limit of 5.0 mg/kg.

Key words: Speciation, Cr(III), Cr(VI), sediment, soil, microwave

Introduction

Monitoring of trace elements in the environmental samples is extremely important as it helps in controlling exposure of humans and animals to toxic substances present there in.[1,2] In recent years, it is recognized that trace element determinations must involve true metal speciation in addition to total metal determination as toxicity and bio availability depends on individual species of an element. Chromium is one such element, whose species namely Cr(III) and Cr(VI) have opposing toxicities.[3] The importance of chromium speciation is governed by the fact that the toxicity and reactivity depend on the chemical form or oxidation state of chromium. Cr(III) is relatively non-toxic and is an essential nutrient for humans, and trace amount of Cr(III) is considered as essential to mammals for their maintenance of normal glucose tolerance factor, lipid and protein metabolism, and are therefore essential for human health.[4] Cr(VI) is mobile, bio-available and toxic.[5] Elevated concentrations of Cr(VI) in soil/sediments are most likely to be arising due to waste from industries such as tanning, metal plating, pigment and anticorrosion coatings.[6] In soils, although not readily adsorbed to most mineral surfaces, Cr(VI) is adsorbed by clay minerals that possess exposed inorganic hydroxyl groups of iron and aluminum oxides.[7] It is classified by both the International Agency for Research on cancer and US Environmental Protection Agency (USEPA) as known human carcinogen and hexavalent Cr compounds are also known to have mutagenic potential.[8,9] Toxicity arising from Cr(VI) may occur via inhalation, ingestion or dermal exposure. It has an irritating and corrosive effect on skin and mucous membranes resulting in ulceration and dermatitis.[10] Hence speciation analysis of sediments and soils, is often necessary to assess the content, origin, mobility and bioavailability of a species of interest, as well as to evaluate the possible risk posed by the disposal of dredged materials. Sediments not only play an important role in influencing the pollution of various water bodies, but also used to record the history of their pollution. Determinations by inductively coupled plasma optical emission spectrometry (ICP- OES), inductively coupled plasma- mass spectrometry (ICP-MS) and electrothermal atomic absorption spectrometry (ET-AAS) can only yield the total amount of chromium as they contain element specific detectors. Hence, preliminary separation and pre-concentration of species are required prior to the determination of analytes by any of the techniques mentioned above. Online separation methods based on HPLC-ICP-MS, HPLC-ICP-OES and CE-ICP-MS have been reported for the speciation of Cr.[11-14] Offline separation methods have also been reported in which individual species are separated and analysed by element specific detectors.[15-17] However, a simple method without any complicated set up is desirable for the routine monitoring of Cr(VI) in solid environmental samples such as soil, sediment etc.

The present paper describes a simple leaching procedure for the extraction of Cr(III) and Cr(VI) using a domestic microwave oven followed by their separation using sulfate form of Dowex-1 and determination by ICP-OES. The procedure has been applied for the speciation of Cr(III) and

Cr(VI) in stream sediment (GBW- 07312) a certified reference material and also four real world samples two each collected from banks of Hussain Sagar lake and near UCIL, Kadapa. Optimization of conditions for quantitative leaching and also separation of Cr(III) and Cr(VI) from the extracts have been discussed for their determination by Inductively coupled plasma optical emission spectrometry (ICP-OES).

Experimental

Instrumentation

An inductively coupled plasma optical emission spectrometer (ICP-OES), Model ULTIMA 2, Horiba Jobin Yvon, France has been used for studies and quantifications. A domestic microwave oven (Videocon, India, Maximum output 700 W) was used for the extraction of Cr(III) and Cr(VI) from the soil and sediment samples. The operating conditions of ICP-OES are given in Table 1.

Reagents

Analytical reagents grade chemicals were used throughout the study. Pure water of 18MΩcm resistivity was prepared by passing potable water through a mixed bed ion exchanger and then through a Milli-Q^{TM} water purification system (Millipore Corporation, Bedford, MA, USA). Dowex-1 (chloride form) was obtained from Sigma, St. Louis, MO, USA. Standards of Cr(III) and Cr(VI) were prepared using Cr(III) chloride and potassium dichromate respectively. HF and EDTA were from Merck and tetra butyl ammonium bromide is procured from SISCO, Mumbai, India. Polypropylene centrifuge tubes used for sample preparation were soaked in 20% HNO_3 overnight and cleaned free of acid and then rinsed with de-ionized water. The reagents namely 0.1 M EDTA and 1% tetra butyl ammonium bromide were prepared 100 mL each by dissolving appropriate amounts in de-ionised water.

Preparation of sulfate form of Dowex-1

Sulfate form of Dowex-1 was prepared from chloride form of the resin. Commercial Dowex-1 (10g, chloride form, 50- 100 mesh) resin was placed in a 50-mm i.d. column, equilibrated with 2M HNO_3, washed with Milli-Q water, and equilibrated with HCl. The resin thus obtained was loaded with 100 mL of 10% potassium sulfate to convert it into the sulfate form, air dried and used for the subsequent studies. The flow rate used for resin preparation, studies and analysis was 1 mL min^{-1}.

Sample preparation

Extraction of Cr(III) and Cr(VI)

The applicability of method developed has been demonstrated by analyzing stream sediment (GBW- 07312) a certified reference material and four real world sediment/soil samples collected two each from Hussain sagar lake, Hyderabad and near UCIL, Pulivendula, Kadapa. The samples have been collected into precleaned polythene bags, air dried, ground and sieved to -80 mesh and used for analysis. A simple and rapid microwave-assisted extraction procedure was used for the extraction of Cr(III), Cr(VI) from soil and sediment samples. A domestic microwave oven was used as the extracting device. Approximately 0.1 g each of samples was weighed accurately into 15 mL polyethylene centrifuge tubes and 3 mL of 0.1 M EDTA, 0.5 mL of 1% tetra butyl ammonium bromide and 0.5 mL of HF were added. The microwave oven was operated for 1 min at maximum power (700 W). The tubes were cooled to room temperature and centrifuged (Remi, India) at around 1500 rpm and supernatants were transferred into 10 mL volumetric flasks and diluted to the mark with de-ionised water. The parameters required for quantitative extraction i.e., amounts of EDTA and tetra butyl ammonium bromide and time of exposure to microwaves have been optimized. The extracts were used for ion exchange separation without any further treatment.

Separation of Cr(III) and Cr(VI)

Preliminary experiments were carried out on sediment extract spiked with Cr(III) and Cr(VI) separately. The species of interest have been separated from the sediment extracts involving adsorption of Cr(VI) on anion exchanger followed by elution using HNO_3. The effluent was analyzed for Cr(III) after suitable dilution. Conditions for quantitative adsorption of Cr(VI) and elution of Cr(III) such as pH of loading solution, volume of HNO_3 for elution of Cr(VI), volume of eluting agent have been optimized.

Adsorption

A 10 mm i.d. column was prepared using 2 g of the sulfate form of Dowex-1 resin. Sediment extract containing Cr(III) and Cr(VI) both natural and spiked was passed through the resin at a flow rate of 1 mL min^{-1}. The above experiment was repeated at different pH levels (1.5-7.5) of the loading solution to select suitable pH. The effluent was analysed for Cr(III) by ICP-OES.

Elution

After adsorption, the resin was washed with 10 mL de-ionized water with pH adjusted to that of the loading solution and added to the effluent. The adsorbed Cr(VI) was eluted from the column of resin using 25 mL of different concentrations of HNO_3 (0.5- 3.0M) at a flow rate of 1mL min^{-1}. The volume of the eluate was made up to 25 mL and analyzed for Cr(VI) by ICP-OES.

Validation

The accuracy of the method developed was verified by comparing the sum of the concentrations of individual species obtained by the present method with the certified values for total Cr and/or those obtained from the total dissolution method (fusion method). Since there is no reference value for the real-world samples, the extraction efficiency of chromium has been verified by comparing the total chromium in the extracts using the present procedure with those obtained from the complete dissolution method. For total dissolution, samples were fused with NaOH and the fusion mixture was dissolved in HNO_3 and total Cr was determined by ICP-OES after suitable dilution.

Fusion method for total chromium

Sediment sample (0.1g) and 1g of sodium hydroxide was taken in a zirconium crucible and heated on Bunsen burner to red hot and fused for 30 min. The fusion mixture was cooled, dissolved in 10% HNO_3 and made up to 100 mL .The solution was analyzed for total chromium by ICP-OES.

Results and Discussion

Extraction of Cr(III) and Cr(VI) from sediment/ soil

The speciation of Cr(III) and Cr(VI) in solid samples is difficult mainly because of the possibility of inter conversion of the species during sample preparation. A sample dissolution procedure which maintains species integrity is required. To avoid excess of salts, leaching of the species is a better alternative compared to complete dissolution. However, the species need to be extracted from the sediments quantitatively without any change in its oxidation state. Hintsa Gitet et.al., reported selective leaching of Cr(VI) from soils using USEPA 3060A method.[18] Other procedures are also reported for selective leaching of Cr(VI) using Na_3PO_4 or tetrabutyl ammonium bromide (TBAB) from sediments.[15,19] Chia-Yi Kuo et.al., reported a microwave assisted extraction procedure in which, combination of a complexing agent and an ion pairing reagent is used as extractant in presence of little HF, EDTA being the complexing agent and tetra butyl ammonium phosphate (TBAP) being ion pairing agent.[20] In the present study leaching of Cr species from soil/ sediments using EDTA and TBAB in presence of little HF has been attempted. Conditions required for quantitative extraction have been optimized. Based on our earlier experience HF was found to be necessary for quantitative leaching of Cr species.[20] Hence 0.5 mL HF has been added to 0.1 g of sample. The optimization of other parameters is given below.

Amount of EDTA

The volume of 0.1 M EDTA required for processing 0.1 g of sample has been optimized by varying the volume of EDTA in the range 1 mL to 5 mL keeping the volume of 1% TBAB at 0.5 mL. Percentage of extraction has been calculated by comparing the concentration of total Cr in the extract with that of concentration of total Cr obtained in sample solution dissolved by fusion method. Results are shown in Table 2. As can be seen the recovery of Cr increased with volume of EDTA till it was 3 mL and reached saturation on further increase.

Amount of tetra butyl ammonium bromide

The amount of ion pairing reagent is also crucial in order to extract species of interest. The volume of 1% TBAB, required for the quantitative leaching, is optimized by varying volume 0.1 mL to 1.0 mL keeping volume of 0.1 M EDTA constant at 3 mL. The results indicated that there is increase of extraction of total Cr with increase in the volume of the reagent. The results are shown in Table 3.

Recovery of Cr species from soil/ sediment

The recovery of total Cr in the extract was compared with total Cr obtained by fusion method or certified value. At optimized conditions, near quantitative recovery of total Cr was obtained for the reference material and real world samples (Table 4). The recovery of individual species was determined by spiking Cr(III) and Cr(VI) to 0.1 g of sediment/ soil, dried and then extracted by the extraction solution. The recoveries were found to be in the range 97- 102% and 98- 101% for Cr(III) and Cr(VI) respectively.

Separation of Cr(III) and Cr(VI) in the extract

In the sediment extract Cr(VI) is expected to be in the form of ion pair $[HCrO_4]^- \cdot [TBAB]^+$ and Cr(III) in the form $Cr[EDTA]^-$. Dowex-1, a strong anion exchanger, is reported to be one of the best suited resin for the anion exchange separation of Cr(VI) in presence of Cr(III).[21] Hence, Dowex-1 in chloride form was used for the separation/ preconcentration of Cr(VI). However, the recovery was rather poor 56% which could be due to the interference of other anions present in the sediment extract on Cr(VI). The sulfate form of Dowex-1 resin was used for the separation of Cr(VI) in sea water, in which the effect of associated anions on the adsorption of Cr(VI) has been alleviated.[22] Even though the possible mechanism for the adsorption of Cr(VI) is through anion exchange, the tolerance to high salt content/associated anions is possibly due to the presence of SO_4^{2-} as the counter ion which is doubly charged. It therefore has preference over singly charged ions such as Cl^-, NO_3^-, and HCO_3^- that are usually present in sediment. The anion of Cr(III) i.e., $Cr[EDTA]^-$ also present in the extract did not adsorb on to the resin. Hence the effluent was analysed for Cr(III). The tolerance of the resin for associated anions with respect to adsorption of Cr(VI), was found to be 20 mg mL $^{-1}$for Cl^-, 3mg mL^{-1} for SO_4^{2-}, and 150 µg mL^{-1}each for NO_3^- and HCO_3^- as reported earlier.[22] Hence, in the present work sulfate form of Dowex-1 was used for the separation of Cr(III) and Cr(VI). Conditions have been optimized for quantitative adsorption and rejection of Cr(III) and also elution of Cr(VI).

Optimization of Conditions

Adsorption

The effect of the pH of the loading solution on the adsorption of Cr(III) and Cr(VI) was studied by changing the pH of the loading solution from 1.5-7.5 for both Cr(III) and Cr(VI) separately. Preliminary experiments were carried out on deionized water spiked with 250 ng/mL each of Cr(III) and Cr(VI). The results are shown in Fig. 1. As shown for the adsorption of Cr(VI) and the rejection of Cr(III) a pH of 4.5 was found to be suitable.

Elution

After near quantitative adsorption, Cr(VI) was eluted with HNO_3. The concentration required has been optimized by elution with 25 mL of different concentrations of HNO_3 (0.5-2.5M). As shown in Table 5, elution with 2.0M HNO_3 yielded highest recovery and hence considered optimum. The volume of 2M HNO_3 required for near quantitative elution was also found to be 25 mL (Table 6).

Sample analysis

As the recovery of Cr(III) and Cr(VI) were near quantitative the developed methodology has been applied for the speciation of Cr in a certified reference material, stream sediment (GBW-07312) and was also applied to real world sediment and soil samples as mentioned above. The results are shown in Table 7. As can be seen the concentration of Cr in the extract is in good agreement with the certified value of stream sediment and with total Cr in case of real world samples. In all samples analysed the concentration of toxic Cr(VI) is much less compared to Cr(III) which is the major species accounting to around 85% of the total Cr. The limit of detection estimated based on the concentration necessary to yield a signal equal to three times the standard deviation of the blank measurements (n=6) was 0.02 mg/L corresponding to 5.0 mg/kg for Cr(VI).

CONCLUSIONS

The ion exchange method by using sulfate from of Dowex-1 was found to be suitable for the speciation of Cr(III) and Cr(VI) in sediment and soil samples. The interference due to anions present in the samples has been alleviated using doubly charged sulfate as counter ion. The recovery of Cr(VI) was found to be 98- 101% with an RSD of 5-6 %. The accuracy has been checked with a certified reference material, stream sediment (GBW- 07312). The method is simple, easy, low consumption of reagents, reuse of the resin and also enables the determination of Cr(VI) in real world samples make it suitable for the routine monitoring of Cr(VI) in sediment or soil samples.

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References

1. E. d. S. Silva, L. O. Correia, L. O. d. Santos, E. V. d. Santos Vieira and V. Z. Lemos, *Microchim. Acta*, 178 (2012) 269–275.
2. J. Scancar and R. Milacic, *J. Anal. Atom. Spectrom.* 29 (2014) 427- 443.
3. M. Jabłońska-Czapla, S. Szopa, K. Grygoyć, A. Łyko and R. Michalski, *Talanta* 120 (2014) 475–483.
4. A. Duran, M. Tuzen and M. Soylak, *Food and Chemical Toxicology* 49 (2011) 1633–1637.
5. J. Kotaś and Z. Stasicka, *Environmental Pollution,* 107 (2000) 263- 283.
6. K. O. Saygi, M. Tuzen, M. Soylak and L. Elci, *J. Hazard. Mat.* 153 (2008) 1009–1014.
7. M. Chrysochoou, D. R. Ferreira and C. P. Johnston, *J. Hazard. Mat.* 179 (2010) 650–657.
8. N. Panichev, K. Mandiwana, M. Kataeva and S. Siebert, *Spectrochim. Acta B* 60 (2005) 699– 703.
9. A. H. Stern, *Environmental Research* 110 (2010) 798–807.
10. M. Goldoni, A. Caglieri, D. Poli, M. V. Vettori, M. Corradi, P. Apostoli and A. Mutti, *Anal. Chim. Acta,* 562 (2006) 229- 235.
11. D. J. Burbridge, I. Koch, J. Zhang and K. J. Reimer, *Chemosphere* 89 (2012) 838–843.
12. L. -L. Wang, J. -Q. Wang, Z. -X. Zheng and P. Xiao, *J. Hazard. Mat.* 177 (2010) 114-118.

13. F. A. Byrdy, L. K. Olson, N. P. Vela and J. A. Caruso, *J. Chromatogr. A*, 1995, **712**, 311- 320.
14. C. -F. Yeh and S. -J. Jiang, *J. Chromatogr. A*, 2004, **1029**, 255- 261.
15. K. L. Mandiwana, *Talanta* 2008, **74**, 736–740.
16. A. Duran, M. Tuzen and M. Soylak, *Food and Chemical Toxicology* 2011, **49**, 1633–1637.
17. I. Narin, A. Kars and M. Soylak, *J. Hazard. Mat.* 2008, **150**, 453–458.
18. H. Gitet, P. A. Subramanian, D. Minilu, T. Kiros, M. Hilawie, G. Gebremariam and K. Taye, *Talanta* 2013, **116**, 626–629.
19. Y. Akama and A. Sali, *Talanta* 2002, **57**, 681–686.
20. C. -Y. Kuo, S. -J. Jiang and A.C.Sahayam, *J. Anal. At. Spectrom.* 2007, **22**, 636-641.
21. A.C. Sahayam, G. Venkateswarlu, S.C. Chaurasia, *Anal. Chim. Acta*, 2005, **537**, 267-270.
22. A. Aparna, M. Sumitra, G. Venkateswarlu, A. C. Sahayam, S. C. Chaurasia, and T. Mukherjee, *Atom. Spectrosc.* 2006, **27**, 123- 127.

Table 1
Operating conditions of ICP-OES

Power	1.1 kW
Wavelength	283.563 nm
Plasma gas flow rate	12.1 l min^{-1}
Nebulizer Type	concentric nebulizer
Spray Chamber	cyclonic
Nebulizer gas flow rate	0.83 l min^{-1}
Auxiliary gas flow rate	0.52 l min^{-1}
Solution uptake rate	2.0 ml min^{-1}

Table 2

Percentage recovery of total Cr with volume of 0.1 M EDTA

S.No.	Volume of 0.1 M EDTA (mL)	Recovery of Cr (%)
1	1	85.6 ± 3.2
2	2	93.1 ± 2.7
3	3	99.2 ± 2.1
4	4	99.1 ± 2.2
5	5	99.1 ± 2.0

Sample: 0.1 g; HF:0.5 mL; TBAB: 1% 0.5 mL

Table 3

Percentage recovery of total Cr with volume of 1% TBAB

S.No.	Volume of 1% TBAB (mL)	Recovery of Cr (%)
1	0.10	70.5 ± 4.5
2	0.25	91.6 ± 3.2
3	0.50	99.0 ± 2.1
4	0.75	98.9 ± 2.0
5	1.00	98.8 ± 2.2

Sample: 0.1 g; HF:0.5 mL; EDTA: 0.1 M 3 mL

Table 4

At optimum conditions (Sample: 0.1 g; HF:0.5 mL; 0.1M EDTA: 3 mL; 1% TBAB: 0.5 mL) recovery of total Cr from soil/ sediment

Sample	Total Cr by fusion (mg/kg)	Total Cr by extraction	Extraction of total Cr (%)
Stream sediment	33.0 ± 2.2	32.1 ± 2.4	97.2
Sediment 1	126 ± 4	130 ± 5	103.1
Sediment 2	41.5 ± 2.5	39.8 ± 2.6	95.9
Soil 1	113 ± 6	110 ± 7	97.3
Soil 2	26.5 ± 2.4	25.9 ± 2.5	99.7

Table 5

Elution of Cr(VI) with concentration of HNO_3.

S.No.	Concentration of HNO_3 (M)	% Recovery of Cr(VI)
1	0.5	25.8 ± 2.0
2	1.0	54.0 ± 1.9
3	1.5	95.2 ± 2.4
4	2.0	99.9 ± 1.0
5	2.5	98.9 ± 0.8

Table 6

Elution of Cr(VI) with volume of 2M HNO_3

S.No.	Volume of HNO_3 (mL)	Elution of Cr(VI) [%]
1	10	80.4 ± 6.0
2	15	86.1 ± 3.9
3	20	92.3 ± 3.2
4	25	98.9 ± 1.6

Table 7

Speciation of Cr in stream sediment and real world samples using present procedure

Sample	Total Cr [mg/kg]	Concentration Cr(III) [mg/kg]		Concentration Cr(VI) [mg/kg]	
		Present	Spike Recovery (%)	Present	Spike Recovery (%)
Stream Sediment (GBW07312)	33.0 ± 2.2	27.3 ± 1.1	98.1 ± 3.9	5.0 ± 0.4	92.5 ± 4.8
SED1	126 ± 4	111 ± 7	96.4 ± 3.1	19.7 ± 1.8	98.6 ± 4.1
SED2	41.5 ± 2.5	36.6 ± 3.8	98.2 ± 2.8	<5	97.8 ± 3.0
SOIL1	113 ± 6	99 ± 3	97.1 ± 2.3	10.6 ± 1.5	96.5 ± 2.7
SOIL2	26.5 ± 2.4	25.7 ± 1.3	98.0 ± 1.9	<5	94.9 ± 2.4

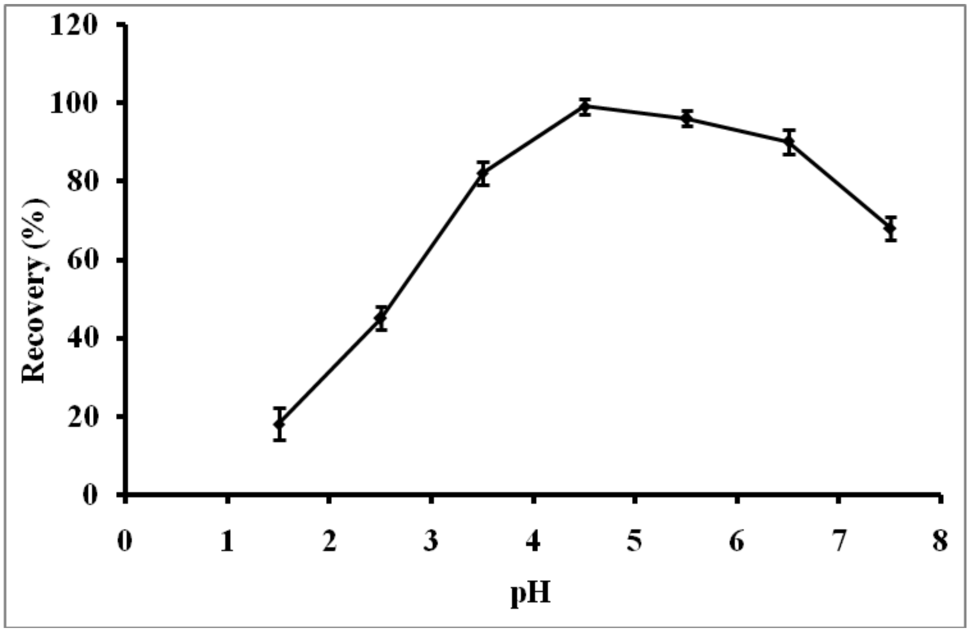

Fig. 1.

Figure Caption: Recovery of Cr(VI) from soil/ sediment extract with pH on sulfate form of Dowex-1