Removal and Preconcentration of Pb(II), V(V), Cr(VI) from the Aqueous Solution and Selective Separation of V(V)-Cr(VI) by Using Functionalized Amberlite XAD-16 Resin with Dithioethylenediamine

Ibrahim Dolak†, Ibrahim Tegin, Remziye Guzel† and Recep Ziyadanogullari*
Department of Chemistry, Faculty of Science and Art, Siirt University, 56100 Siirt, Turkey
Fax: (90)(484)2231998; Tel: (90)(484)2242623/1001; E-mail: recepz@dicle.edu.tr

Amberlit XAD-16 was functionalized using dithioethylenediamine as a ligand and characterized by elemental analysis and FTIR spectroscopy. The effects of contact time, pH, electrolyte and the concentration of eluents on separation and preconcentration of Pb(II), Cr(VI) and V(V) were studied. In addition, the batch capacity for each ion was determined under the optimum conditions. The preconcentration yields of Pb(II), Cr(VI) and V(V) were found to be 96.60 ± 3.02, 100.64 ± 2.24 and 98.20 ± 3.00 %, respectively, with 500 times preconcentration factor under the optimum conditions. The selective separation of Cr(VI)-V(V) was studied in terms of pH. It was determined that V(V) separated in 98.24 ± 1.21 % yield from the solution containing Cr(VI)-V(V) and Cr(VI) remained in the solution at pH 2.5, while Cr(VI) separated in 101.43 ± 3.09 % yield from the solution containing Cr(VI)-V(V) and V(V) remained in the solution at pH 8.5 by using Amberlit XAD-16-dithioethylenediamine -Pb(II).

Key Words: Removal, Preconcentration, Selective separation, Amberlite XAD-16, Dithioethylenediamine.

INTRODUCTION

The use of instrumental methods for trace metal quantification frequently requires preconcentration procedures to lower the detection limits. Methods widely used for preconcentration usually involve an ion exchange or liquid-liquid extraction separation. Chelating ion exchange resins are cabaple of preconcentrating metal ions selectively from a large aqueous volume and may easily be coupled with flame atomic absorption spectrometry (FAAS) to enhance its sensitivity. A chelating resin-based on-line preconcentration and matrix separation of metal ions followed by their determination with FAAS and ICP have also been employed[1-3].

Recently, several chelating matrices have been developed using resins of amberlite XAD series as a support to have very high capacity. This can be made possible by increasing the number of chelating sites and to make them accessible.

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†Department of Chemistry, Faculty of Science and Art, Dicle University, 21280 Diyarbakir, Turkey.

This can be achieved by selecting a ligand of small size and a polymeric support of moderate cross-linking. The synthesis of insoluble functionalized polymers having good stability, high sorption capacity for metal ions and flexibility in working conditions has attracted the attention of researchers. A number of ligands such as pyrocatechol[4] thiosalicylic acid[5], poly dithiocarbamate[6], *o*-aminophenol[7], 1-(2-pyridylazo-2-naphthol[8], dithizone[9], *o*-vanillinthiosemicarbazone[10] have been used to develop resins of XAD series as a support.

Vanadium has been noticed as the index element in urban environmental pollution and speciation analysis of trace amounts of V(V) and V(IV) ions has become important, because V(V) more toxic than V(IV). Recently many kinds of conventional analytical methods in conjuction with various preconcentration and separation methods have been developed for the determination of vanadium in natural waters. Generally, preconcentration techniques using chelating resins were combined with atomic spectroscopic and flow injection techniques *e.g.*, AAS using sulphoxine cellulose[11] or strong anionic exchange column loaded with EDTA[12], FI analysis using sephadex G-25 gel with catalytic photometric detection[13,14], ICP-AES associated with FI using macroporous type resins after complexation[15], air segmented continuous FA (ASCFA) using two kinds of chelating resins[16].

Chromium is not 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[17]. In view of the toxic nature of Cr(VI), developments of methods in order to establish their levels in the environment and industrial quality control are quite significant. A variety of adsorbents have been used for the preconcentration of Cr(VI)[17-20]. In this study, removal of Pb(II), V(V) and Cr(VI) from solution, their preconcentration and selective separation of V(V) and Cr(VI) were investigated systematically by Amberlite XAD-16 functionalized using dithioethylenediamine.

EXPERIMENTAL

Perkin-Elmer Analyst 200 PC/400 model atomic absorption spectrometer was used to determine Cr(VI) and Pb(II), Perkin Elmer Optima 2100 DV model ICP spectrometer was used to determine V(V) and pH measurements were made Mettler Toledo digital pH meter equipped with a glass electrode. FTIR spectra of functionalized resins were recorded with Mattson 1000 IR spectrometer using KBr dises in the range 4000-700 cm^{-1}. Fisons E-1108 model element analysis instruments was used to determine N and S in functionalized Amberlite XAD-16 resin with dithioethylenediamine by using in terms of sulfanilamide standard.

All chemicals were of analytical reagent grade from Merck or Fluka unless otherwise stated. Standard and stock solutions were prepared using double distilled water: Pb(NO$_3$)$_2$ (1000 mg L^{-1} Pb(II) in 0.1 mol L^{-1} HNO$_3$), K$_2$CrO$_4$ (1000 mg L^{-1} Cr(VI) in double bidistiled water), V$_2$O$_5$ (1000 mg L^{-1} V(V) in 0.1 mol L^{-1} NaOH), (Amberlit XAD-16 (styrene-divinylbenzene copolymer, surface area 588 m^2 g^{-1}, pore diamater: 4.2 nm and bead size 20-60 mesh) was supplied by sigma. For the pH adjustment 0.01-1.00 mol L^{-1} HNO$_3$ and NaOH solutions.

Synthesis process of Amberlite XAD-16-dithioethylenediamine

Chloromethylation: The chloromethylation of Amberlite XAD-16 resin was performed as follows. Electrophilic substitution of the Amberlite XAD-16 resin with CH_2Cl_2 was carried out by a Friedel-Craft reaction. 10 g of Amberlite XAD-16 resin in 20 mL of 1-octanol was reacted with 40 mL of CH_2Cl_2 in the presence of 5 g $AlCl_3$ as catalyst at room temperature. The temperature was increased to 70 ºC and the mixture was stirred for 24 h at 70 ºC. The mixture was cooled; the chlorinated resin filtered and washed 6 mol L^{-1} HCl abundantly. Then, chlorinated resin washed with $CHCl_3$ and acetone, successively.

Bonding of rubeanic acid to Amberlite XAD-16-CH₂Cl: The chloromethylated resin of Amberlite XAD-16 in 50 mL of nitrobenzene was reacted with 0.25 g rubeanic acid in the presence of 5 g $AlCl_3$. This mixture was shaken at 70 ºC for 72 h. Then, the product was filtered, washed with 1 mol L^{-1} HCl abundantly and washed with ethanol, chloroform and acetone successively. The product was heated reflux in 20 mL ethanol for 2 h.

Reduction of Amberlite XAD-16-CH₂-rubeanic acid with NaBH₄: Amberlite XAD-16-CH₂-rubeanic acid in 50 mL methanol was reacted with 0.5 g NaBH₄. This mixture was shaken at room temperature for 24 h. The product was filtered, washed with 1 mol L^{-1} NaOH and 1 mol L^{-1} HCl abundantly.

The reaction sequence for various stages of the preparation of the functionalized Amberlite XAD-16 resin with dithioethylenediamine resin is shown in Fig. 1[21].
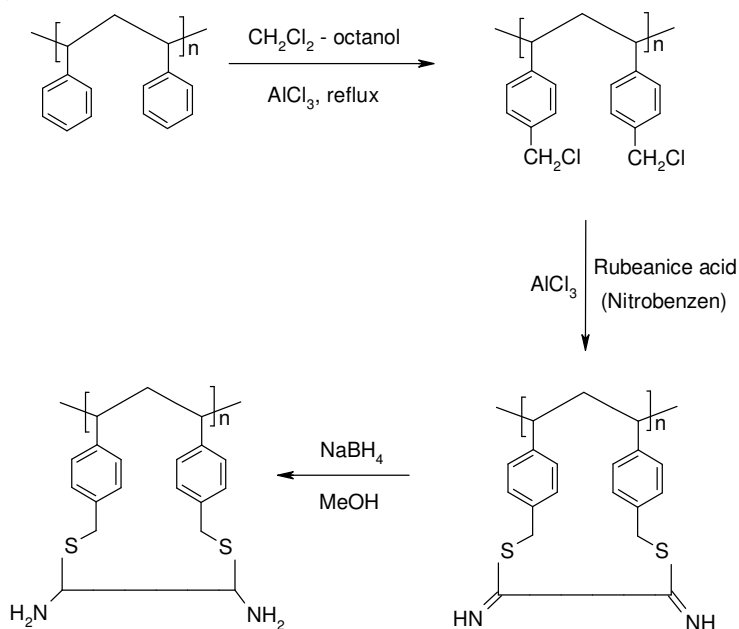

Fig. 1.   Reaction sequence for various stages of the preparation of the Amberlite XAD-16 resin functionalized with dithioethylenediamine

Characterization studies: The FTIR spectra of Amberlit XAD-16 and dithio-ethylenediamine functionalized Amberlit XAD-16 have been recorded (Figs. 2-4). S and N in functionalized Amberlite XAD-16 resin with dithioethylenediamine were measured three times by element analyses instrument. Amounts of S and N were found to be 1.36 and 0.60 %, respectively.
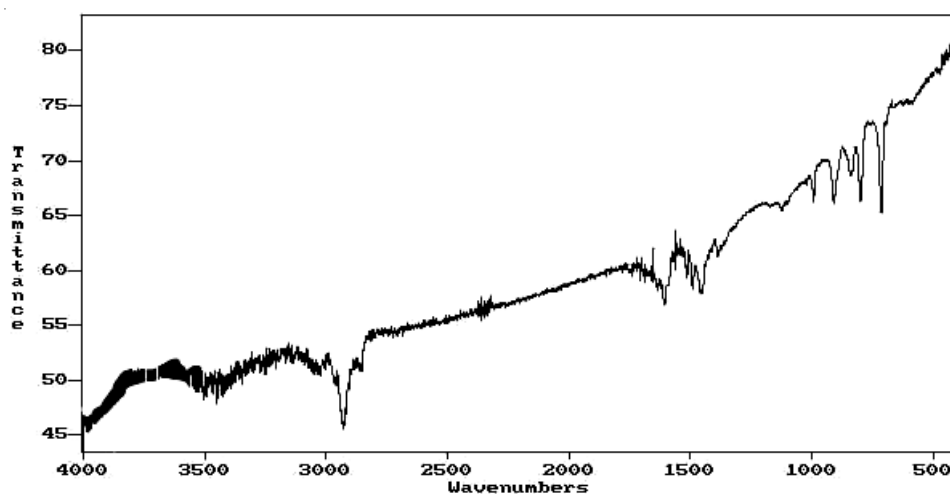

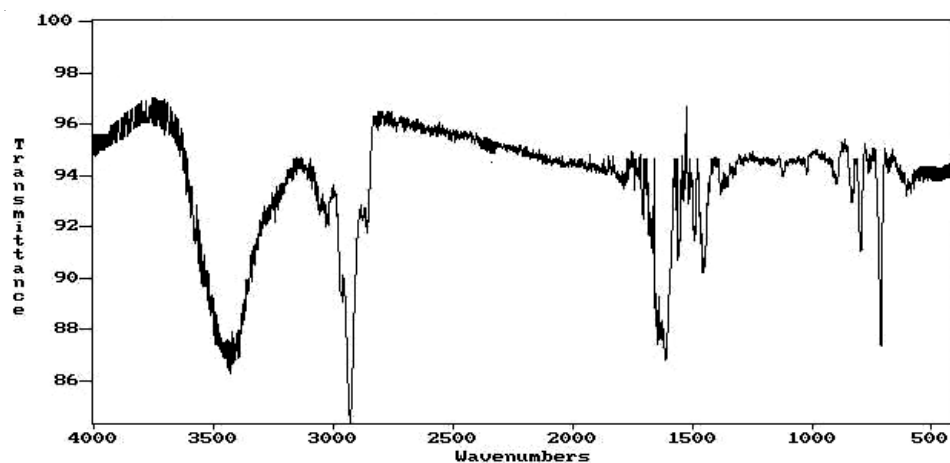Fig. 2. IR spectrum of Amberlit XAD-16

Fig. 3. IR spectrum of Amberlit XAD-16-rubeanic acid

Column preparation: A glass column (30 cm length and 10 mm i.d.) containing 0.10 g of functionalized Amberlite XAD-16 resin using dithioethylenediamine (*ca.* 7.5 cm bed height) has been used for preconcentration of Pb(II), Cr(VI) and [V(V)] and removal from solution. A glass-wool plug was rested on stopcock of the column

and another plug of glass wool placed on top of the resin to avoid the distribution of the resin during sample passage. HNO_3, $H_2C_2O_4$ and deionized water were passed through the column in order to condition and clean it.
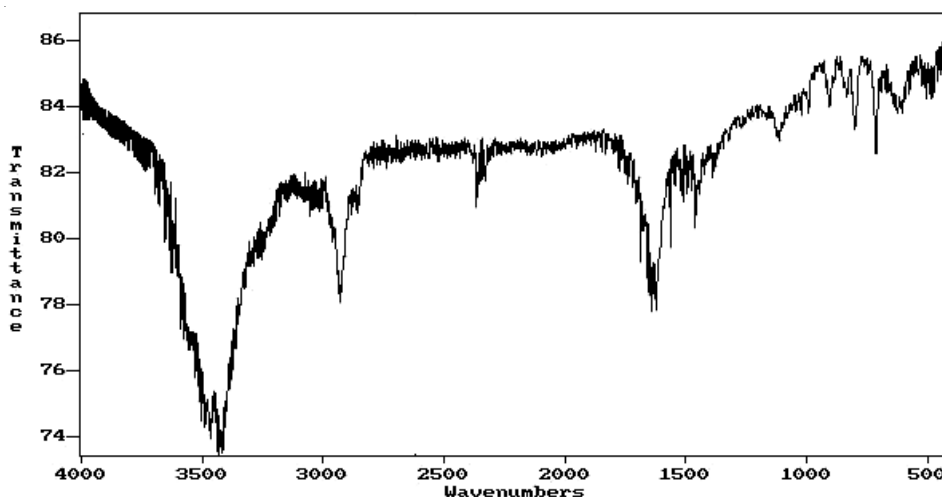

Fig. 4. IR spectrum of Amberlit XAD-16-dithioethylenediamine

Investigation of optimum pH for preconcentration: The solutions were adjusted to various pH in the range 2-9. the retained Pb(II) were eluted with 10 mL 1.2 mol L^{-1} HNO_3, V(V) were eluted with 0.1 mol L^{-1} $H_2C_2O_4$ and Cr(VI) were eluted 0.3 mol L^{-1} $H_2C_2O_4$ and determined in eluted by AAS and ICP.

Investigation of the preconcentration factor of the resin for metal ions: To find preconcentration factor of the resin for varying volumes of the analyte, 10 µg L^{-1} of metal ions 5000 mL volumes were passed through the resin bed, the retained metals were eluted with 10 mL eluent and determined by AAS and ICP.

Investigation of the effect of concentration of eluent on metal eluation efficiency: The effect of concentration of eluent on metal eluation efficiency was investigated in the range 0.4-2.0 mol L^{-1} HNO_3 and 0.1-0.5 mol L^{-1} $H_2C_2O_4$.

Effect of inert electrolytes: The possible effect of inert electrolytes (ionic strength in fluence) was investigated by repeating metal retention experiments in 100-fold greater concentrations of electrolyte solutions containing (NaCl, Na_2SO_4, $NaNO_3$, Na_2HPO_4, NaH_2PO_4), prepared in optimum pH range.

Batch capacity: 50 mL of 50 mg mL^{-1} working solutions of metals were brought to optimum pH and transferred to 250 mL stoppered flasks. To each was added 0.1 g of Amberlit XAD-16-dithioethylenediamine, each was stoppered and agitated for 5, 10, 15, 20, 25 and 30 min at room temperature. At the end of each batch contact, the metal loaded sorbent was filtered off and the metal remaining in the filtrate was measured by AAS and ICP.

RESULTS AND DISCUSSION

Effect of contact time on binding yield: It was established that optimum contact time was 30 min for Pb(II), 15 min for Cr(VI) and 20 min for V(V) were sufficient in the experiments performed to determine optimum contact time in removal of Pb(II), Cr(VI) and V(V) from the solutions and the results are shown in Figs. 5 and 6.
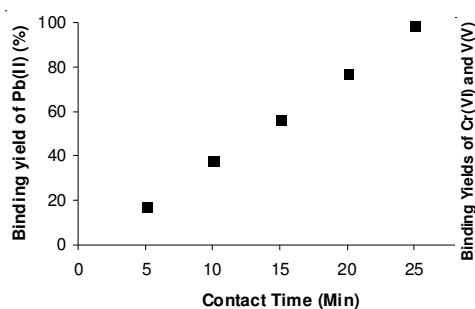

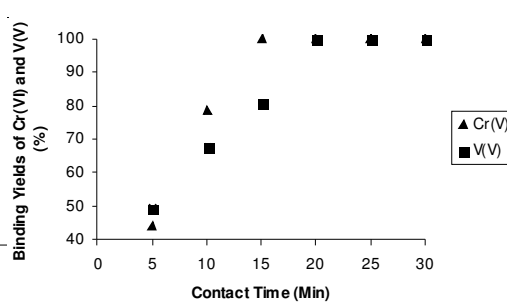Fig. 5.   Effect of contact time on binding yield of Pb(II)

Fig. 6.   Effect of contact time on binding yield of Cr(VI) and V(V)

Effect of pH on binding yield: It was established that optimum pH was 5-6 for Pb(II), 7-8 for Cr(VI) and 2-3 for V(V) were sufficient in the experiments performed to determine optimum pH in removal of Pb(II), Cr(VI) and V(V) from the solutions and the results are shown in Figs. 7 and 8.
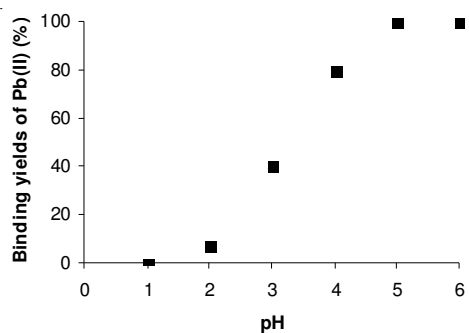

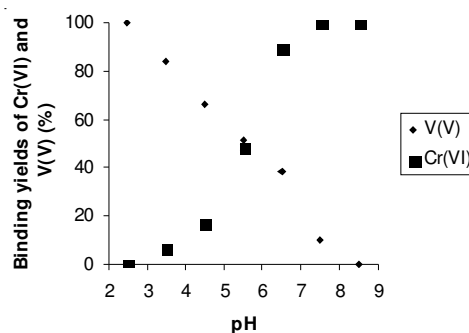Fig. 7.   Effect of pH on binding yield of Pb(II)

Fig. 8.   Effect of pH on binding yield of Cr(VI) and V(V)

Effect of electrolytes on binding yield: In the experiment performed to determine effect of electrolytes on binding yield of Pb(II), Cr(VI) and V(V) such as NaCI, Na_2SO_4, $NaNO_3$, Na_2HPO_4, NaH_2PO_4 were used and the results are shown in Table-1.

Determination of batch capacity of the functionalized resin and loading half-time: Batch capacity of the resin to Pb(II), Cr(VI) and V(V) was determined under optimum conditions (time and pH) and the results are shown in Table-2.

TABLE-1
EFFECT OF ELECTROLYTES ON BINDING YIELD

Electrolytes	Binding yield of Pb(II) (%)	Binding yield of Cr(VI) (%)	Binding yield of V(V) (%)
NaCl	101.00 ± 2.52	80.01 ± 3.10	78.13 ± 2.73
NaNO$_3$	104.20 ± 3.89	99.98 ± 3.23	78.13 ± 2.73
Na$_2$SO$_4$	99.73 ± 1.64	59.98 ± 1.29	66.47 ± 1.75
NaH$_2$PO$_4$	100.73 ± 4.32	99.99 ± 2.06	103.11 ± 3.97
Na$_2$HPO$_4$	101.48 ± 2.92	99.99 ± 2.09	97.62 ± 4.33

TABLE-2
BATCH CAPACITY AND LOADING HALF-TIME

Ion	Batch capacity (mg g^{-1} resin)	Loading half-time (t$_{1/2}$) (min)
Pb(II)	29.78 ± 1.14	15.0
Cr(VI)	5.27 ± 0.34	7.5
V(V)	7.86 ± 0.61	10.0

Effect of eluent concentration on eluation yield: In the experiment performed to determine optimum concentration of eluent in the eluation process for Pb(II), Cr(VI) and V(V), the proper concentrations of eluent were 1.2 mol L^{-1} HNO$_3$, 0.3 mol L^{-1} H$_2$C$_2$O$_4$ and 0.1 mol L^{-1} H$_2$C$_2$O$_4$ for Pb(II), Cr(VI) and V(V), respectively and the results are shown Figs. 9 and 10.
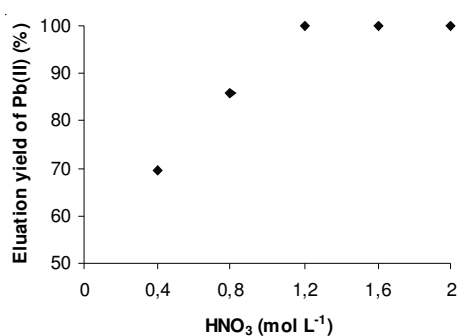

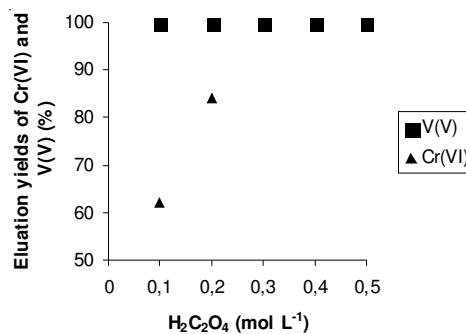Fig. 9.   Effect of eluent concentration on elution yield of Pb(II)

Fig. 10. Effect of eluent concentration on elution yield of Cr(VI) and V(V)

Speciation of V(V)-Cr(VI) by using Amberlite XAD-16-dithioethylenedi-amine-Pb(II) as a function of pH: It was established that the selective separation of Cr(VI)-V(V) was studied in terms of pH, it was determined that V(V) separated in 98.24 ± 1.21 % yield from the solution containing Cr(VI)-V(V) and Cr(VI) remained in the solution at pH 2.5, while Cr(VI) separated in 101.43 ± 3.09 % yield from the solution containing Cr(VI)-V(V) and Cr(VI) remained in the solution at pH 8.5 by using Amberlit XAD-16-dithioethylenediamine-Pb(II) and the results are shown in Fig. 11.
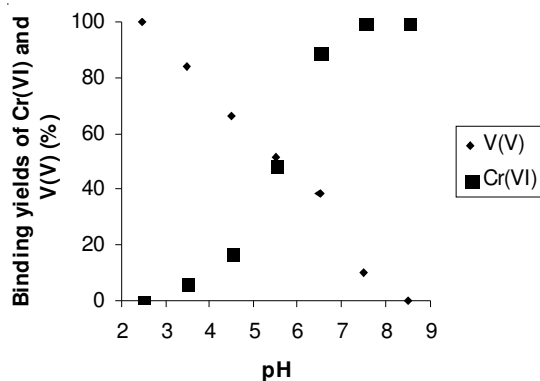
Fig. 11. Speciation of V(V)-Cr(VI) by Amberlite XAD-16-dithioethylenediamin-Pb(II) as a function of pH

Preconcentration

Preconcentration of Pb(II) by using Amberlite XAD-16-dithioethylenediamine: For this purpose, 10 μg L^{-1} of Pb(II) was used. The flow rate of sample solution was adjusted to 5 mL min^{-1}. 5000 mL of samples solution containing 10 μg L^{-1} of Pb(II) were passed through the column under optimum conditions. The recovery of Pb(II) was found to be 96.00 ± 3.02 %, respectively with 500 times preconcentration factor and the results are shown in Table-3.

TABLE-3
PRECONCENTRATION FACTOR AND CONCENTRATION LIMIT OF ENRICHMENT

Ion	Maximum volume of solution (mL)	Concentration limit (μg L^{-1})	Preconcentration factor	Recovery (%)
Pb(II)	5000	10	500	96.00 ± 3.02
Cr(VI)	5000	10	500	100.64 ± 2.24
V(V)	5000	10	500	98.20 ± 3.00

Preconcentration of Cr(VI) and V(V) by using Amberlite XAD-16-dithioethylenediamine-Pb(II): For this purpose, 10 μg L^{-1} of Cr(VI) and V(V) was used. The flow rate of sample solution was adjusted to 5 mL min^{-1}. 5000 mL of samples solution containing 10 μg L^{-1} of Cr(VI) and V(V) were passed through the column under optimum conditions. The recovery of Cr(VI) and V(V) was found to be 100.64 ± 2.24 and 98.20 ± 3.00 %, respectively, with 500 times preconcentration factor and the results are shown in Table-3.

Conclusion

In this study, it was basically aimed to separate V(V) and Cr(VI). Thus, the studies were performed by Amberlit XAD-16-dithioethylenediamine-Pb(II). The experiments were carried out at room temperature and the batch binding periods for Pb(II), V(V) and Cr(VI) were 30, 20 and 15 min, respectively. Maximum binding

yields of Pb(II), V(V) and Cr(VI) in terms of pH were found to be 5-6, 2-3 and 7-8, respectively.

Among alien electrolytes (NaCl, Na_2SO_4, $NaNO_3$, Na_2HPO_4, NaH_2PO_4) only Na_2SO_4 and to some extent NaCl had impact on binding yields of V(V) and Cr(VI) by using Amberlit XAD-16-dithioethylenediamine-Pb(II). Thus, before treatment of the solutions, separation of Na_2SO_4 and NaCl from the solution is seen fit in order to perform the study.

It was established that the selective separation of Cr(VI)-V(V) was studied in terms of pH, it was determined that V(V) separated in 98.24 ± 1.21 % yield from the solution containing Cr(VI)-V(V) and Cr(VI) remained in the solution at pH 2.50, while Cr(VI) separated in 101.43 ± 3.09 % yield from the solution containing Cr(VI)-V(V) and Cr(VI) remained in the solution at pH 8.5 by using Amberlit XAD-16-dithioethylenediamine-Pb(II). When both ions were eluted by $H_2C_2O_4$, V(V) and Cr(VI) separated from the resin to be V(III) and Cr(III), respectively and passed into the solution without separation of Pb(II) from the resin.

For preconcentration, 10 µg L^{-1} of Pb(II), Cr(VI) and V(V) was used. The flow rate of sample solution was adjusted to 5 mL min^{-1}. 5000 mL of samples solution containing 10 µg L^{-1} of Pb(II), Cr(VI) and V(V) were passed through the column under optimum conditions. The recovery of Pb(II), Cr(VI) and V(V) was found to be 96.00 ± 3.02, 100.64 ± 2.24 and 98.20 ± 3.00 %, respectively, with 500 times preconcentration factor.

In this study, it was concluded that the Amberlit XAD-16-dithioethylenediamine-Pb(II) could be used successfully, in both separation and preconcentration of Cr(VI) and V(V).

ACKNOWLEDGEMENT

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Contact:
Dr. K. Usha, Convener, AOP-2010
Centre for Environment Education and Technology (CEET)
Kiranam, Arpookara East P.O., Kottayam 686008, Kerala, India
Ph: +91-9447779269 ,+91-9447391168, +91-481-2591010,
Fax:+91-481-2594458
E-mail: icaop2010@gmail.com
Website: http://www.ceetindia.org/aop2010