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

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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 eluent on separation and preconcentration of Pb(II), Cr(III) and Cr(VI) were studied. In addition, the batch capacity for each ion was determined under the optimum conditions. The preconcentration yields of Pb(II), Cr(III) and Cr(VI) were found to be 96.60 ± 3.02, 102.20 ± 3.00 and 100.64 ± 2.24 %, respectively, with 500 times preconcentration factor under the optimum conditions. The speciation of Cr(III)-Cr(VI) was studied, it was determined that Cr(III) separated in 93.24 ± 2.21 % yield from the solution containing Cr(III)-Cr(VI) by using Amberlit XAD-16-dithioethylenediamine and Cr(VI) remained in the solution at pH 4, while Cr(VI) separated in 101.43 ± 3.09 % yield from the solution containing Cr(III)-Cr(VI) and Cr(III) remained in the solution at pH 7.50 by using Amberlit XAD-16-dithioethylenediamine-Pb(II).

Key Words: Removal, Preconcentration, Speciation, 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 capable 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. This can be achieved by selecting a ligand of small size and a polymeric support of

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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] thiosalicilyc acid[5], polydithiocarbamate[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.

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[11]. 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)[12-15].

In this study, removal of Pb(II), Cr(III) and Cr(VI) from solution, their preconcentration and speciation of Cr(III) and Cr(VI) were investigated systematically by Amberlite XAD-16 functionalized by using dithioethylenediamine.

EXPERIMENTAL

Perkin-Elmer Analyst 200 PC/400 model atomic absorption spectrometer was used to determine Pb(II) and total chromium, Shimadzu UV-vis spectrophotometer was used to determine Cr(VI) by using diphenylcarbazide method 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: $Pb(NO_3)_2$ (100 mg L^{-1} Pb(II) in 0.1 mol L^{-1} HNO_3), K_2CrO_4 (100 mg L^{-1} Cr(VI) in double bidistiled water), $CrCl_3$ (100 mg L^{-1} Cr(III) in 0.1 mol L^{-1} in double bidistiled water), (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-CH_2Cl: 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 under reflux in 20 mL ethanol for 2 h.

Reduction of Amberlite XAD-16-CH_2-rubeanic acid with $NaBH_4$: Amberlite XAD-16-CH_2-rubeanic acid in 50 mL methanol was reacted with 0.5 g $NaBH_4$. 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 several times.

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

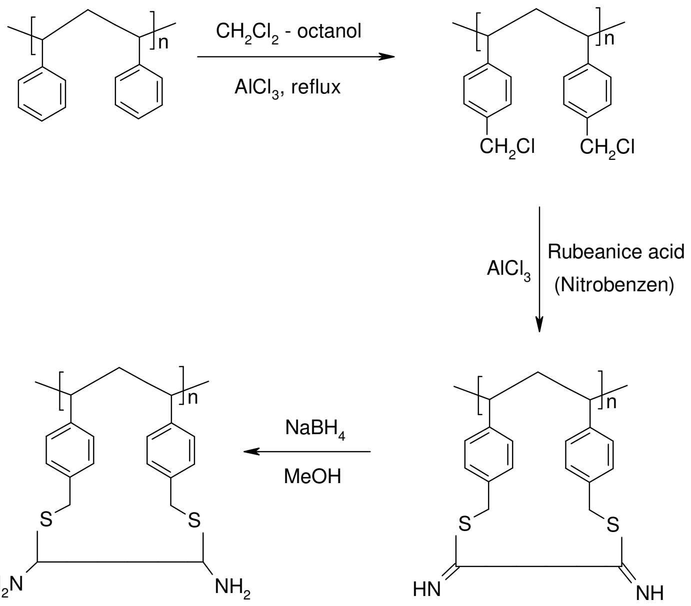

Fig. 1. Reaction sequence for various stages of the preparation of the Amberlite XAD-16 resin functionalized with dithioethylenediamine

Characterization studies: The FTIR spectra of Amberlit XAD-16 and dithioethylenediamine 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.

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(III) and Cr(VI) removal from solution. A glass-wool plug was rested on stopcock of the column

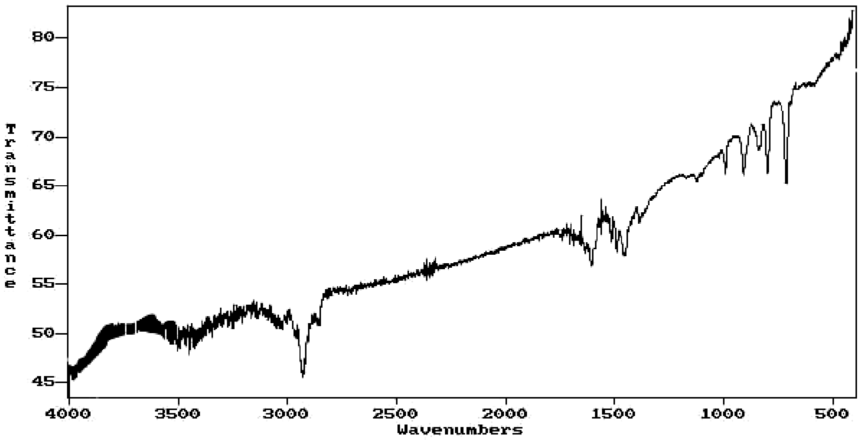

Fig. 2. IR spectrum of Amberlit XAD-16

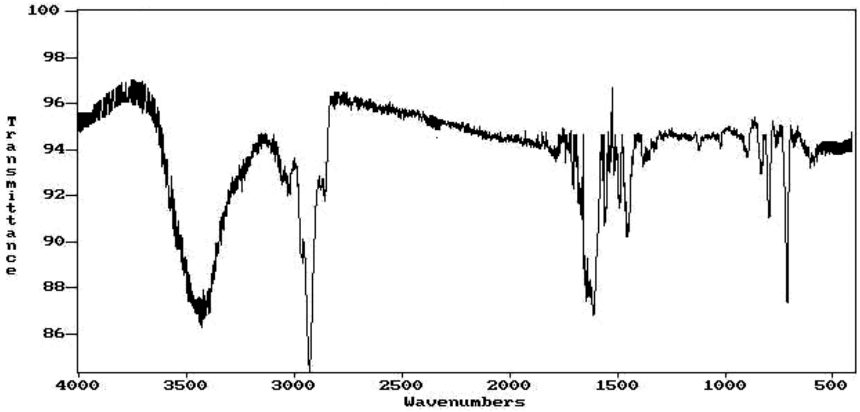

Fig. 3. IR spectrum of Amberlit XAD-16-rubeanic acid

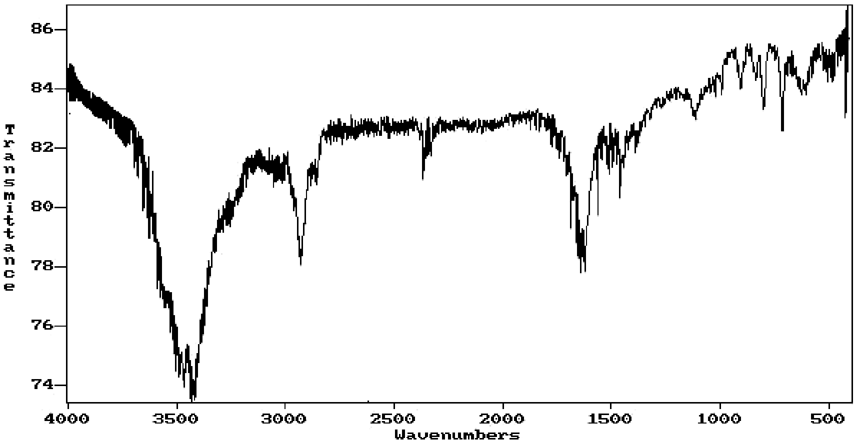

Fig. 4. IR spectrum of Amberlit XAD-16-dithioethylenediamine

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.

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, Cr(III) were eluted with 0.4 mol L^{-1} HNO_3 and Cr(VI) were eluted 0.3 mol L^{-1} $H_2C_2O_4$ and determined in eluted by AAS.

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.

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 and of each batch contact, the metal loaded sorbent was filtered off and the metal remaining in the filtrate was measured by AAS.

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 10 min for Cr(III) 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.

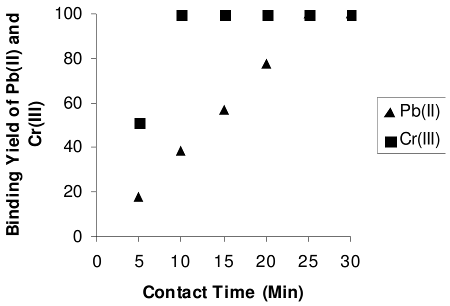

Fig. 5. Effect of contact time on binding yield of Pb(II) and Cr(III)

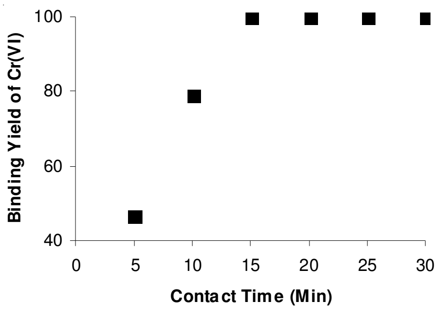

Fig. 6. Effect of contact time on binding yield of Cr(VI)

Effect of pH on binding yield: It was established that optimum pH was 5-6 for Pb(II), 7-8 for Cr(VI) and 4-5 for Cr(III) were sufficient in the experiments performed to determine optimum pH in removal of Pb(II), Cr(VI) and Cr(III) from the solutions and the results are shown in Figs. 7 and 8.

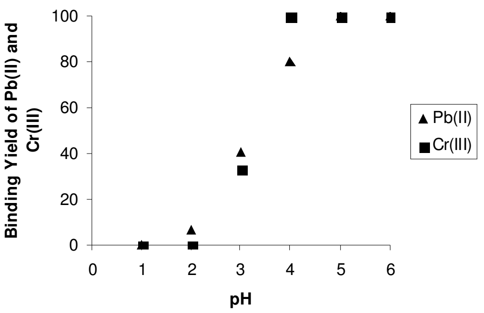

Fig. 7. Effect of pH on binding yield of Pb(II) and Cr(III)

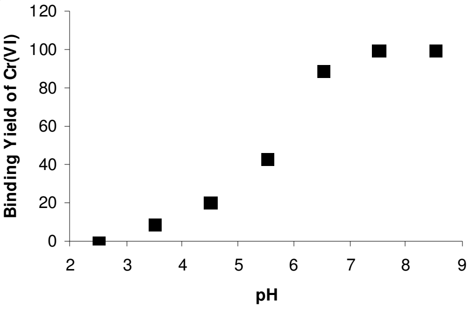

Fig. 8. Effect of pH on binding yield of Cr(VI)

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

TABLE-1
EFFECT OF ELECTROLYTES ON BINDING YIELD

Electrolytes	Binding yield of Pb(II) (%)	Binding yield of Cr(III) (%)	Binding yield of Cr(VI) (%)
NaCl	101.00 ± 2.52	99.30 ± 4.81	80.01 ± 3.10
$NaNO_3$	104.20 ± 3.89	102.32 ± 1.89	99.98 ± 3.23
Na_2SO_4	99.73 ± 1.64	100.61 ± 2.99	59.98 ± 1.29
NaH_2PO_4	100.73 ± 4.32	103.61 ± 5.28	103.11 ± 3.97
Na_2HPO_4	101.48 ± 2.92	98.81 ± 1.11	97.62 ± 4.33

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

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
Cr(III)	4.20 ± 0.61	5.0

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 Cr(III), the proper concentrations of eluent were 1.2 mol L^{-1} HNO_3, 0.3 mol L^{-1} $H_2C_2O_4$ and 0.4 mol L^{-1} HNO_3 for Pb(II), Cr(VI) and Cr(III), respectively and the results are shown Figs. 9 and 10.

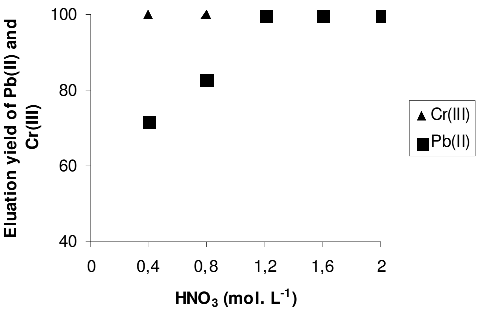

Fig. 9. Effect of eluent concentration on eluation yield of Pb(II) and Cr(III)

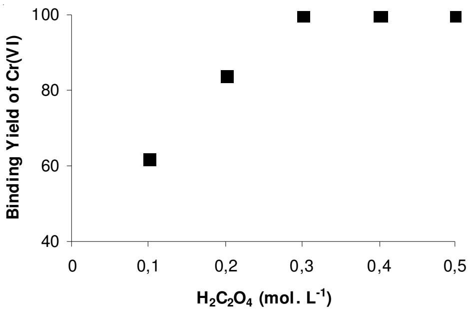

Fig. 10. Effect of eluent concentration on eluation yield of Cr(VI)

Speciation of Cr(III) and Cr(VI): It was established that the speciation of Cr(III)-Cr(VI) was studied, it was determined that Cr(III) separated in 93.24 ± 2.21 % yield from the solution containing Cr(III)-Cr(VI) and Cr(VI) remained in the solution at pH 4 by using Amberlit XAD-16-dithioethylenediamine, while Cr(VI) separated in 101.43 ± 3.09 % yield from the solution containing Cr(III)-Cr(VI) and Cr(VI) remained in the solution at pH 7.50 by using Amberlit XAD-16-dithio-ethylenediamine-Pb(II).

Preconcentration

Preconcentration of Pb(II) and Cr(III) by using Amberlite XAD-16-dithioethylenediamine: For this purpose, 10 μg L^{-1} of Pb(II) and Cr(III) 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) and Cr(III) were passed through the column under optimum conditions. The recovery of Pb(II) and Cr(III) was found to be 96.0 ± 3.02 and 102.20 ± 3.00, 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
Cr(III)	5000	10	500	102.20 ± 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) 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) passed through the column under optimum conditions. The recovery of Cr(VI) was found to be 100.64 ± 2.24 %, respectively, with 500 times preconcentration factor and the results are shown in Table-3.

In this study, it was basically aimed to speciation Cr(III) and Cr(VI). Thus, the studies were performed by Amberlit XAD-16-dithioethylenediamine. The experiments were carried out at room temperature and the batch binding periods for Pb(II), Cr(III) and Cr(VI) were 30, 10 and 15 min, respectively. Maximum binding yields of Pb(II), Cr(III) and Cr(VI) in terms of pH were found to be 5-6, 4-5 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 yield of 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.

For preconcentration, 10 µg L^{-1} of Pb(II), Cr(III) and Cr(VI) 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(III) and Cr(VI) were passed through the column under optimum conditions. The recovery of Pb(II), Cr(III) and Cr(VI)was found to be 96.00 ± 3.02, 102.20 ± 3.00 and 100.64 ± 2.24 %, respectively, with 500 times preconcentration factor.

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

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