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Synthesis and Preconcentration of Amberlite XAD-4 Resin Modified by Dithioethylenediamine

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In the present work, Amberlite XAD-4 copolymer resin modified by rubeanic acid was synthesized for separation and preconcentration of Cu(II), Co(II), Ni(II)), Cd (II) and Mn(II). The optimization procedure for analytical parameters including pH, contact time, batch capacity, *etc*. was examined in order to obtain quantitative recoveries of metal ions. Preconcentration yields of Cu(II), Co(II), Ni(II), Cd (II) and Mn(II) by Amberlite XAD-4-dithioethylenediamine copolymer resin were found as 103.3 ± 2.6, 96.8 ± 1.7, 102.0 ± 3.0, 90.3 ± 1.7 and 97.2 ± 2.4 %, respectively. Batch capacity of Cu(II), Co(II), Ni(II), Cd(II) and Mn(II) by Amberlite XAD-4-dithioethylenediamine copolymer resin was determined as 0.1243 ± 0.0036, 0.2057 ± 0.0034, 0.2323 ± 0.0043, 0.1757 ± 0.0025 and 0.1888 ± 0.0034 mmol g^{-1} resin, respectively. The preconcentration factor was 500 for Cu (II), Co (II), Ni(II), Cd(II) and Mn(II).

Key Words: Metal(II), Amberlite XAD-4, Rubeanic acid, Dithioethylenediamine.

INTRODUCTION

Preconcentration and separation methods including precipitation[1], solvent extraction[2], ion exchange[3], adsorption[4,5], electrochemical deposition[6], membrane separation[7] and other techniques are frequently used for determination of trace metal levels in environmental matrices. In recent years, chelating resins have proved to be very useful in the separation and preconcentration of metal ions at trace levels[8-13]. Amberlite XAD resins are widely used to develop series several chelating materials[9,12]. This explains the current interest in developing analytical procedures for the quantification of these elements. Although it is true that these elements can be directly determined in water using sensitive analytical techniques, such as electrothermal, atomic absorption spectrometry (AAS) or ICP-MS, in many laboratories, particularly in less developed countries, only flame atomic absorption spectrometry (FAAS) and inductively coupled plasma optical emission spectrometry ICP-OES are available. The sensitivity obtained with FAAS or with ICP-OES is not sufficient to detect these elements in river water, since a preconcentration method is required. To this end the use of supports loaded with chelating reagents is particularly convenient, because such resins containing various functionalized groups are easy to prepare and make these procedures highly selective. Therefore, preconcentration and separation methods for trace metal ions have been developed by using various supports including Amberlite XAD resins[14-21]. Rubeanic acid (dithiooxamide) is a reagent for spectrophotometric determination of traces metal ions[22-24]. Rubeanic acid has been used for preconcentration and determination of heavy metal ion from various media[25-29].

In this study, determination of preconcentration and removal conditions of certain metal(II) ions were investigated systematically by using Amberlite XAD-4 copolymer resin modified by dithioethylenediamine.

EXPERIMENTAL

All chemicals were of analytical reagent grade and were used as received. The concentrations of Cu(II), Co(II), Ni(II)), Cd (II) and Mn (II) were determined using a Unicam AAS 929 atomic absorption spectrometer with an air-acetylene flame. All pH measurements were performed with Metter Toledo pH meter equipped with a glass electrode. The functional groups of the synthesized resin (for Amberlite XAD-4 and Amberlite XAD-4-rubeanic acid) were analyzed in KBr tablets by using a Mattson 1000 FT-IR spectrometer.

In order to remove Cu(II), Co(II), Ni(II), Cd(II) and Mn(II) from solution and determination of optimum conditions, 5 µg mL^{-1} of metal solutions were used. For the purpose of preconcentration, 10 µg L^{-1} of metal solutions were used. For elution of these metal, 0.4-2.0 mol L^{-1} HNO_3 was used. Each experiment was repeated three times and statistical errors were calculated as relative standard deviation (RSD).

Synthesis of Amberlite XAD-4-rubeanic acid: The synthesis was carried out at three stages: (i) chloromethylation (ii) the bonding of rubeanic acid to Amberlite XAD-4-CH_2Cl_2 (iii) reduction of Amberlite XAD-4-CH_2-rubeanic acid with $NaBH_4$.

Chloromethylation: Electrophilic substitution of the Amberlite XAD-4 copolymer with CH_2Cl_2 was carried out by a Friedel-Craft reaction. 10 g of Amberlite XAD-4 copolymer resin in 20 mL of 1-octanol was treated with 40 mL of CH_2Cl_2 in the presence of 5 g of $AlCl_3$ 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 was filtered off and washed with 6 M HCl abundantly. Then, chlorinated resin was washed with $CHCl_3$ and acetone, successively.

Binding of rubeanic acid to Amberlite XAD-4-CH_2Cl_2: The chloromethylated resin of Amberlite XAD-4 in 50 mL of nitrobenzene was treated with 0.25 g rubeanic acid in the presence of 5 g $AlCl_3$. This mixture was shaken at 70 ºC for 72 h. The product was then filtered, washed with 1 M HCl abundantly and washed with ethanol, chloroform and acetone, successively. The product was heated to reflux in 20 mL of ethanol for 2 h.

Reduction of Amberlite XAD-4-CH_2-rubeanic acid with $NaBH_4$: When rubeanic acid was reduced by $NaBH_4$, it was shown that the structure had deteriorated by the released H_2S gas. Thus, when rubeanic acid was bound to resin, it was observed that H_2S gas had not released. The reduction was carried out as follows:

Amberlite XAD-4-CH_2-rubeanic acid in 50 mL of methanol was treated with 0.5 g $NaBH_4$. This mixture was shaken at room temperature for 24 h. The product was filtered, washed with 1 M NaOH and 1 M HCl abundantly.

The reaction sequence for various stages of the preparation of the Amberlite XAD-4 resin modified by rubeanic acid is shown in Fig. 1. It was suggested that the structure could be as shown in Fig. 2.

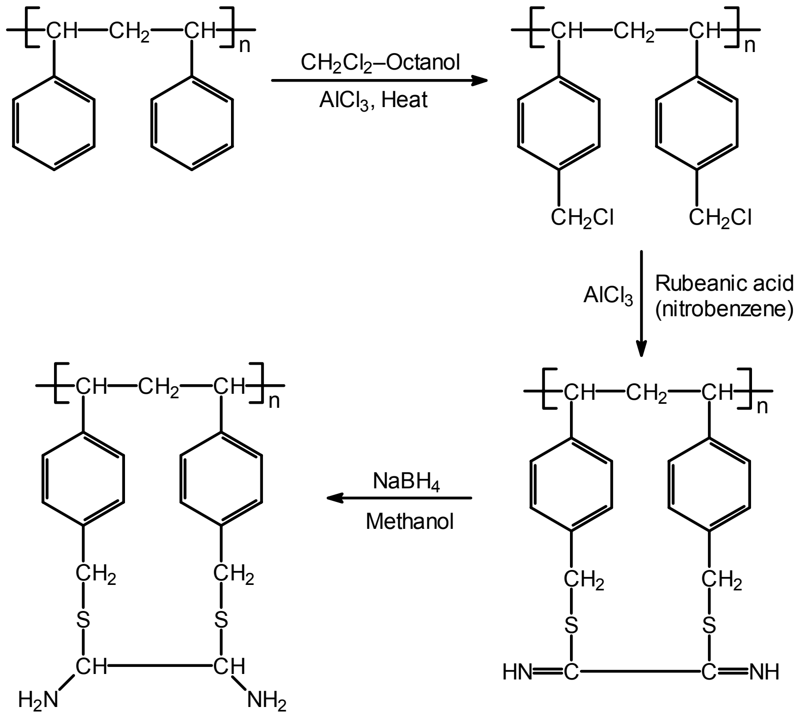

Fig. 1. Reaction sequence for various stages of the preparation of the Amberlite XAD-4 resin modified by dithioethylenediamine

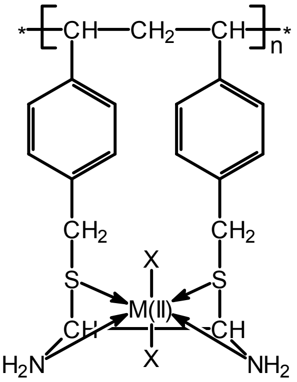

Fig. 2. Structure of M(II) bound to the resin
($X = NO_3^-$, Cl^-, I^-; $M = Cu^{2+}$, Co^{2+}, Ni^{2+}, Cd^{2+}, Mn^{2+})
*dithioethylenediamine (DTEDA)

Characterization of Amberlite XAD-4 resin modified by dithioethylenediamine (Amberlite XAD-4-CH_2- DTEDA): The copolymer resin obtained was characterized by means of IR spectroscopy. The IR spectra of Amberlite XAD-4, Amberlite XAD-4-CH_2Cl_2, Amberlite XAD-4-CH_2-RA and reduced Amberlite XAD-4-CH_2- DTEDA are shown in Figs. 3-6.

In the IR spectrum of reduced state of the Amberlite XAD-4 resin modified by rubeanic acid, the formation of double peaks indicated the amine group (-NH_2) at 3479 and 3419 cm^{-1} and the formation of a weak and spread peak showed the C-S-C group at 625 cm^{-1}. So, IR spectrum confirms that the suggested structure took place.

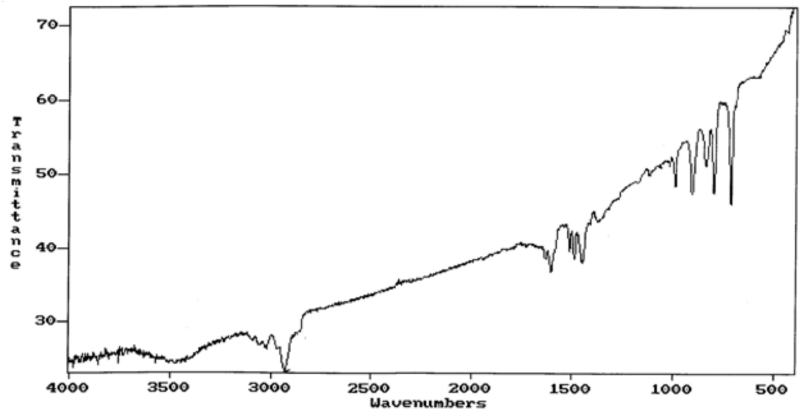

Fig. 3. IR Spectrum of Amberlite XAD-4

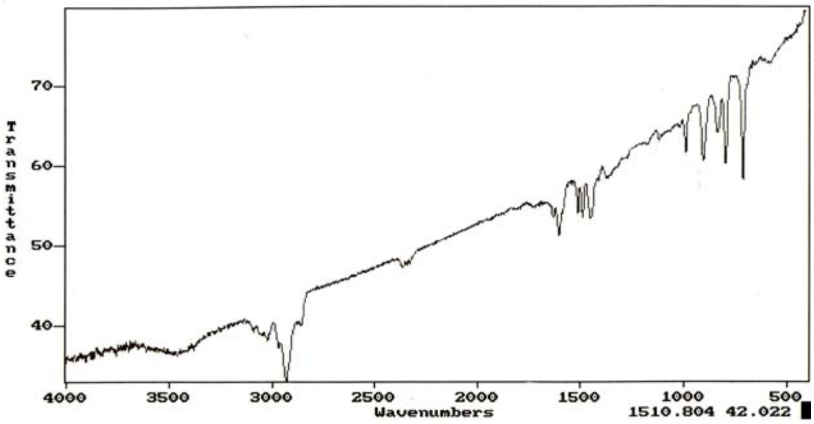

Fig. 4. IR Spectrum of Amberlite XAD-4-CH_2Cl

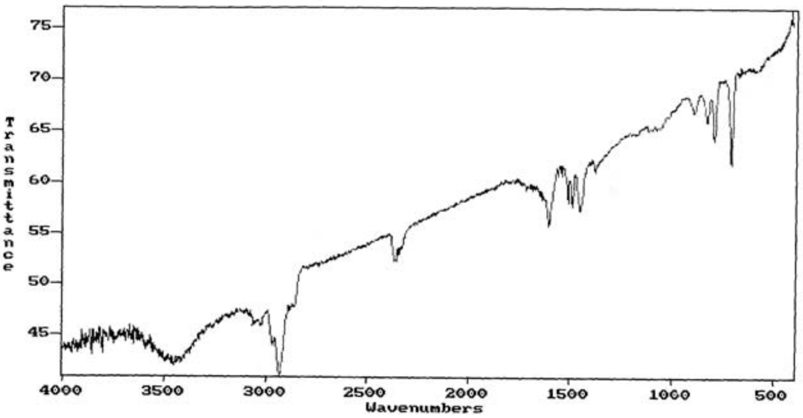

Fig. 5. IR spectrum of Amberlite XAD-4 CH_2-rubeanic acid

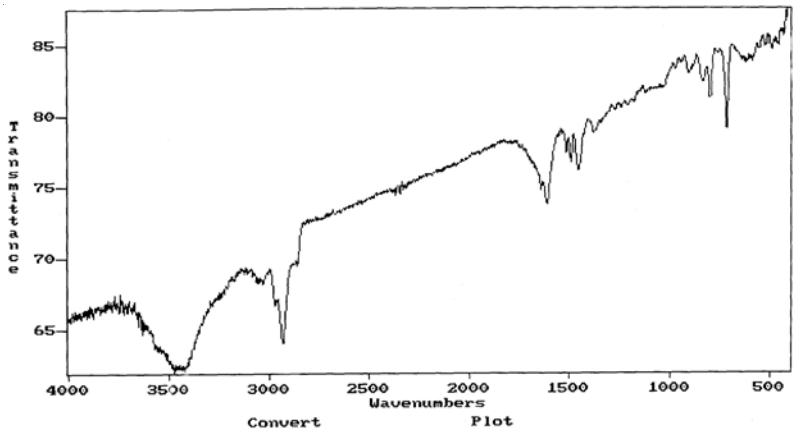

Fig. 6. IR Spectrum of the Amberlite XAD-4 resin modified by dithioethylenediamine

Column preparation: A glass column (30 cm length and 10 mm i.d.) containing 0.10 g of Amberlite XAD-4-CH_2-DTEDA (*ca.* 7.5 cm bed height) has been used for preconcentration of Cu(II), Co(II), Ni(II)), Cd (II) and Mn(II) 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 distribution of the resin during sample passage. HNO_3 and deionized water were passed through the column in order to clean it.

Investigation of the contact time for preconcentration: For preconcentration of Cu(II), Co(II), Ni(II), Cd(II) and Mn (II), 10 µg mL^{-1} of metals and 0.10 g of Amberlite XAD-4-CH_2-DTEDA were used at pH 5.24.

Optimum pH for preconcentration: In order to find the preconcentration factor of the resin for varying analytes (metals), 5.0 µg mL^{-1} of metal ions in 10.0 mL volume were passed through the resin bed; the retained metals were eluted with 10.0 mL of 0.4-2.0 M HNO_3 and determined by AAS.

Effect of acidity on metal desorption efficiency: The effect of eluent acidity on metal desorption efficiency was investigated in the range of 0.4-2.0 M HNO_3.

Effect of the electrolytes: The possible effect of electrolytes was investigated by repeating metal retention experiments in 100-fold greater concentration of electrolyte solutions containing NaI, NaCl, $NaNO_3$, $Na_2C_2O_4$, Na_2HPO_4, NaH_2PO_4 and Na_2SO_4 prepared in the optimal pH range.

Batch capacity: 10 mL of 10000 µg mL^{-1} working solutions of metal were brought to optimal pH and transferred to 250 mL stoppered flask. To each was added 0.1 g of Amberlite XAD-4-CH_2- DTEDA, each was stoppered and agitated for 5, 10, 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.

RESULTS AND DISCUSSION

Effect of contact time on yield of binding of Cu(II), Co(II), Ni(II), Cd(II) and Mn(II) to Amberlite XAD-4 resin modified by DTEDA: The effect of contact time on yield of binding of metal(II) ions to Amberlite XAD-4-CH_2-DTEDA has been investigated separately. For this purpose, 5 µg mL^{-1} of metal ions was used. For 0.1 g of the resin modified by DTEDA, 10 mL of sample solutions containing metal(II) ions were contacted to the resin modified by DTEDA for 5, 10, 20, 25 and 30 min.

It was determined that 100 % of Cu(II), Co(II), Ni(II) and Mn(II) and 26.50 % of Cd (II) were bound to the resin modified by DTEDA at 25, 5, 5, 30 and 5 min, respectively (Fig. 7).

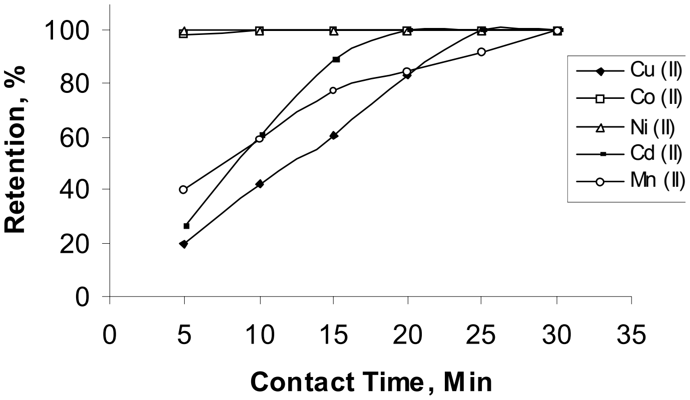

Fig. 7. Effect of contact time on yield of binding of Cu(II), Co(II), Ni(II), Cd(II) and Mn(II) to the resin modified by DTEDA

Effect of pH on yield of binding of Cu(II), Co(II), Ni(II)), Cd(II) and Mn(II) to Amberlite XAD-4 resin modified by DTEDA: Metal(II) retention behaviour as a function of pH (Fig. 8) revealed that the breakthrough pH ranged between pH values of 1.0-8.0 and quantitative retention was achieved at pH 3 for Co(II), Ni(II) and Mn(II), at pH 4 for Cd(II) and at pH 5 for Cu (II).

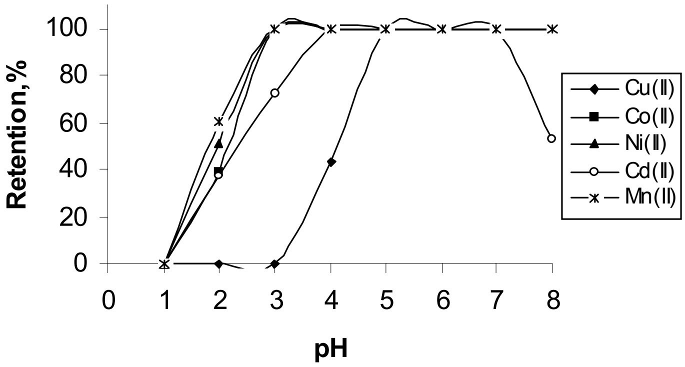

Fig. 8. Effect of pH on yield of binding of Cu(II), Co(II), Ni(II), Cd(II) and Mn (II) to Amberlite XAD-4 resin modified by DTEDA

Effect of inert electrolytes on yield of binding of Cu(II), Co(II), Ni(II), Cd(II) and Mn(II) to Amberlite XAD-4 resin modified by DTEDA: The tested inert electrolytes, NaI, NaCl, $NaNO_3$, $Na_2C_2O_4$, Na_2HPO_4, NaH_2PO_4 and Na_2SO_4 (under the condition that the conjugate bases of acids were brought to the optimal pH values of 5-6 with acid) did not show any effect on metal retention at a 100 fold molar concentration excess of the analytes as shown in Table-1.

TABLE-1
EFFECT OF THE ELECTROLYTES ON AMBERLITE XAD-4 RESIN

Metal ion	pH	Concentration of metal(II) (µg mL^{-1})	Concentration of electrolytes (µg mL^{-1})	Recovery (%)
Cu(II)	5.20	5	500	100
Co(II)	5.50	5	500	100
Ni(II)	5.20	5	500	100
Cd(II)	5.80	5	500	100
Mn(II)	5.50	5	500	100

Batch capacity of Amberlite XAD-4 resin modified by DTEDA: The sorption percentages of the tested metal(II) cations are recorded as a function of time in Fig. 7. The sorption was completed within 0.5 h for all metal ions. Batch capacities are tabulated in Table-2.

TABLE-2
BATCH CAPACITY OF THE AMBERLITE XAD-4 RESIN

Metal ion	Batch capacity mmol M(II) g^{-1} resin	Loading time (min)
Cu(II)	0.1243 ± 0.0036	25
Co(II)	0.2057 ± 0.0034	10
Ni(II)	0.2323 ± 0.0043	5
Cd(II)	0.1757 ± 0.0025	20
Mn(II)	0.1888 ± 0.0034	30

*Determined with the use of 10 mL of 10000 µg metal(II) mL^{-1} solution. Batch capacity was measured under optimum condition.

Effect of volume of elution concentration: For the elution of metal ions, nitric acid has been tested as eluent. As can be seen in Fig. 9, the best elution was obtained by using 10 mL of 0.4 mol L^{-1} HNO_3 for Cu (II), 10 mL of 0.2 mol L^{-1} HNO_3 for Co(II), 10 mL of 1.2 mol L^{-1} HNO_3 for Ni(II), 10 mL of 1.6 mol L^{-1} HNO_3 for Cd(II) and 10 mL of 0.8 mol L^{-1} HNO_3 for Mn(II).

Preconcentration factors: The preconcentration factors of the resin for the studied metals (the most dilute solution being 10 µg mL^{-1}) were 500. The results are shown in Table-3. Flow rate was 5 mL min^{-1} which gave metal recoveries of 90-102 %. HNO_3 was chosen as the eluting agent and 10 mL of the eluent was sufficient for metal desorption.

Application of the method to wastewater: The prepared resin was used for preconcentrating Cu(II), Co(II), Ni(II), Cd(II) and Mn(II) from wastewater sample collected from wastewater purifying plant of Diyarbakir.

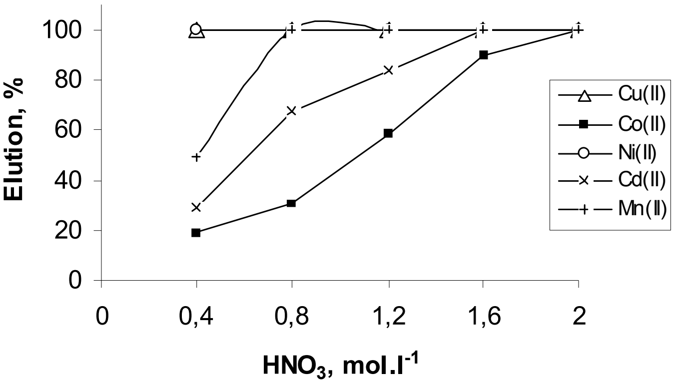

Fig. 9. Effect of eluent concentration on stripping yield of Cu(II), Co(II), Ni(II), Cd(II) and Mn(II)

TABLE-3
EFFECT OF PRECONCENTRATION FACTORS

Metal ion	Acid concentration (M)	Volume of solution (mL)	Concentration limit (μg mL^{-1})	Preconcentration factor	Recovery (%)
Cu(II)	0.4	5000	10	500	103.0 ± 2.6
Co(II)	2.0	5000	10	500	96.8 ± 1.7
Ni(II)	1.2	5000	10	500	102.3 ± 1.7
Cd(II)	1.6	5000	10	500	90.3 ± 1.7
Mn(II)	0.8	5000	10	500	97.2 ± 2.4

The pH of the wastewater sample was 6.86. The sample was filtered through filter paper for removal of suspended matter and was kept in a stoppered polyethylene bottle prior to analysis. The results of analysis are given in Table-4.

TABLE-4
DETERMINATION OF METAL ION CONCENTRATION
FOUND IN THE WASTEWATER

Method	Cu(II) conc. (μg L^{-1})	Co(II) conc. (μg L^{-1})	Ni(II) conc. (μg L^{-1})	Cd(II) conc. (μg L^{-1})	Mn(II) conc. (μg L^{-1})
Direct	992	-	280	-	468

The sample collected from wastewater purifying plant of Diyarbakir diluted to 6000 mL with water. This solution was passed through the resin column at 5 mL min^{-1} at the original pH of the waste water and was eluted with 20 mL of 1 M HNO_3. The results of preconcentration on wastewater of this plant are shown in Table-5.

TABLE-5
APPLICATION OF THE PRECONCENTRATION PROCEDURE TO WASTE WATER

Metal ion	Concentration in column-adsorbed solution (6000 mL) µg L^{-1}	Eluate (20 mL) µg mL^{-1}	Preconcentration factor	Recovery (%)
Cu(II)	49.6	14.64	295	97.77 ± 2.4
Co(II)	–	–	–	–
Ni(II)	14.0	4.13	295	98.40 ± 2.9
Cd(II)	–	–	–	–
Mn(II)	23.4	7.02	300	100.00 ± 2.3

Conclusion

(i) Selective preconcentration process of several cations could be done by Amberlite XAD-4 copolymer resin modified by dithioethylenediamine (DTEDA) that used in preconcentration and separation process. (ii) The proposed preconcentration and separation procedure provides a fast, precise, reliable and simple method for the enrichment of Cu, Co, Ni, Cd and Mn. (iii) It was determined that preconcentration process of not only cations but also that of anions could be done by this synthesized resin. (iv) The recovery yields obtained with standard solutions were in the range of 92.5-103 %, for all elements. A large concentration factor (500 for 5000 mL sample volume) can be reached. (v) On the other hand, since the sorption and elution conditions are similar for Cu, Co, Ni, Cd and Mn, in future the proposed procedure can be applied to simultaneous determination by ICP-OES. (vi) Both cation and anion bind to the resin by forming a neutral structure in the coordination sphere. For instance, if $Pb(NO_3)_2$ salt is used, nitrate binds to the resin together with Pb.

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