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Preparation of a Chelating Resin by Immobilizing 3-((E)-(2-amino phenyl imino) methyl) phenol on Amberlite XAD-16 and Its Application of Solid Phase Extraction of Fe(II),Cu(II), Mn(II), and Zn(II) in Natural Water Samples

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ABSTRACT

A polystyrene divinylbenzene resin (Amberlite XAD-16) functionalized by **3-((E)-(2-amino phenyl imino) methyl) phenol** has been synthesized and its sorption properties have been investigated for preconcentration of Fe(II),Cu(II), Mn(II), and Zn(II) in natural water samples. The new resin (XAD-16-PAN) was characterized by thermo gravimetric analysis and infrared spectrometry. The analytical parameters including pH, sample volume etc. for the quantitative recoveries of the analyte ions using XAD-16-APMP resin were investigated. The effects of alkaline, earth alkaline ions and some anions on the sorption of analyte ions were also examined. The recovery values were greater than 95%.

Keywords: Chelating Resin; Preconcentration; XAD-16-APMP; Natural Waters; AAS.

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INTRODUCTION

Separation and preconcentration techniques such as coprecipitation, electrodeposition, solvent extraction, cloud point extraction, membrane filtration, solid phase extraction [1–5] for the trace heavy metal ions are an important part of modern analytical chemistry. The most common technique available for the separation/preconcentration of metals from aqueous samples is solid phase extraction method using adsorbents such as sephiolite, thiol cotton, activated carbon, green tea leaves, microcrystalline naphthalene, cellulose, and Diaion HP-20.[6–11]The synthesis of chelating resins from the commercial adsorption resins has been popular in the last decade.[12–18] In particular, studies on the synthesis of resins by the reaction of a commercial resin and a suitable chelating agent and sorption characterization of chelating resin available for interesting metal ions have been extensively carried out in a number of analytical laboratories because both their sorption capacities and sorption selectivity are superior to those of ion exchangers intrace levels. For that purpose, especially Amberlite XAD copolymers have been widely used. [19–24] Saxena and co-workers[19] have used Amberlite XAD-2-Alizarin Red-S chelating resin for the preconcentrationof lead(II), cadmium(II), zinc(II) and nickel(II). In another study,Pyrocatechol Violet immobilized Amberlite XAD-2 resin has been synthesized by Saxena and Singh[20] and its adsorption characters has beenidentified. Dev et al. [15] established a new method for the sorption behavior of lanthanum(III), neodymium(III), terbium(III), thorium(IV) anduranium(VI) on Amberlite XAD-4 resin functionalized with bicine ligands.Amberlite XAD-16 is a polystyrene divinylbenzene copolymer. It has no ionizable functional groups. It has been used for the preconcentration and separation of trace heavy metal ions from various media including natural waters, urine, dialysis concentrate, etc., by our group.[26–31] It is used as a solid matrix for synthesis of chelating resin and separation of organic materials which has hydrophobic properties. The preparation of new chelating resins by using Amberlite XAD-16 and some chelating agents have been performed by some researchers.[32–34] Lee and co-workers [32,33] synthesized a new chelating resin by using Amberlite XAD-16 and 4-(2-thiazolylazo) resorcinol. They investigated the adsorption properties of the new resin. Lee and coworkers[33,34] synthesized two different chelating resins by using 4-(2-thiazolylazo) resorcinol and 1-(2-thiazolylazo)-2-naphthol as chelating agent and XAD-16 as support for the preconcentration of trace metal ions including uranium.1-(2-pyridylazo) 2-naphtol (PAN) is a reagent for the spectrophotometric determination of lots of transition metal ions. A preconcentration method using tri-n-octylmethyl ammonium chloride-di-isobutyl ketone for the determination of trace metals in natural water samples was studied by Furuya and Nakayama [35]. The trace metals were analysed using ICP-AES in natural water samples by Grasse and Stevenson[36].In the present work, a chelating resin was synthesized by 3-((E)-(2-amino phenyl imino) methyl) phenol (APMP) on Amberlite XAD-16 (XAD-16- APMP) and characterized. Its application of preconcentration of some metal ions in natural water samples was performed. The optimal analytical conditions including pH, resin amounts, flow rates of sample and elution solutions and matrix effects were also investigated.

MATERIALS AND METHODS

EXPERIMENTAL

Apparatus

A Varian Spectra AA55 atomic absorption spectrometer was used for the determination of metal ions. All measurements were carried out in air/acetylene flame and without background correction. The instrumental parameters were set as recommended by the manufacturer. pH measurements were performed with a Elico pH 160 digital pH meter and combined glass electrode. The nebulizer uptake rate was adjusted to give the optimum response for conventional sample introduction, the resulting rate being 6.0 mL/min. An acetylene flow rate of 2.5 L/min was used with an airflow rate of 8.0 L/min. IR spectra were recorded on a Jasco 300 FTIR spectrometer. A mechanical shaker was used for batch experiments.

Reagents

All solutions were prepared with deionized water. Unless otherwise stated analytical-grade acetone, acids and other chemicals used in this study, were obtained from Merck, Darmstadt, Germany. Stock solutions of all metals, containing 1000 mg/L (Merck, Darmstadt) were used for preparation of the standards for the calibration curve. The correlation coefficient of the calibration curves were generally 0.999.Ammonium acetate buffer solutions (0.1 M) were prepared by adding an appropriate amount of acetic acid (Merck, Darmstadt) to ammonium acetate solutions for pH 2–6 and ammonium chloride buffer solutions (0.1 M) were prepared by adding an appropriate amount of ammonia (Merck, Darmstadt) to ammonium chloride solutions for pH 8–10. Amberlite XAD-16 resin (Sigma Chem. Co.) was purchased as 20–40 mesh (specific area: 750m^2/g).

Synthesis of Chelating Resin

The procedure given by Saxena et al.[19] with some little modifications was applied to the synthesis of the XAD-16-APMP chelating resin.10.0 g of Amberlite XAD-16 was treated with a nitrating mixture, containing 20mL of concentrated nitric acid and 50mL of concentrated sulfuric acid and stirred for 1 h at 60^{0}C on a water-bath. The nitrate mixture was poured into ice-cold water. It was further filtered, washed repeatedly with distilled water until free from acid. Then it was reduced with $SnCl_2$ (40 g), concentrated hydrochloric acid (45mL), and ethanol(60 mL), and refluxed for 12 h at 40^{0}C. The amino polymer was filtered off and washed with mixture of HCl-ethanol, water, and 2M NaOH so as to get the free amino polymer. The amino polymer was treated with 100mL of 2M HCl for 30 min, washed with distilled water in order to remove excess of HCl, suspended in 250mL of ice cold water and mixed with 1M HCl and 1M $NaNO_2$ in aliquots of 2.0mL each time with constant stirring. The diazotized resin was filtered and washed with ice-cold water. It was reacted with APMP (2.0 g taken in 100mL solution in water/ethanol mixture) at room temperature for 1 h. The resulting resin was filtered and washed with distilled water. The formula of XAD-16- APMP resin is given in Fig. 1.

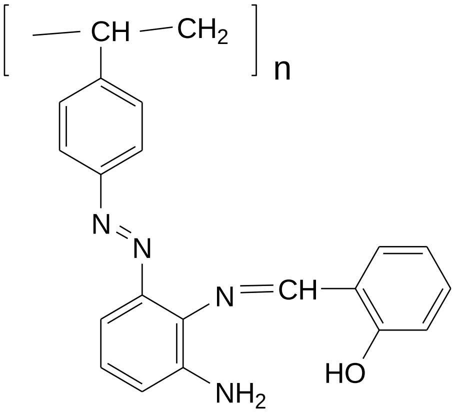

Fig.1.For of New Chelating resin

SYNTHESIS OF LIGANDS

Synthesis of 3-((E)-(2-amino phenyl imino) methyl) phenol benzene-1,2-diamine and 2-hydroxybenzaldehyde equimolar ratio added methanol were refluxed for 1 h, and the contents were cooled to room temperature for separating the formed yellow solid product was filtered, washed with water, dried and recrystallized from hot aqueous methanol (m.p. 174°C-178^{0}C, 89 % yield as shown in Scheme-1). The band at 3490 cm^{-1} is due to the –OH group and absorption bands at 1593 cm^{-1}are due to the C=N group of reagent and the IR spectra as shown in Fig.4.

Column Preparation

The glass column, having a stopcock and a porous disk, was 10 cm long, and 1.0 cm in diameter. A small amount of glass wool was placed on the disc to prevent disturbing of the XAD-16- APMP resin beads during sample loading. Then, 600 mg of XAD-16- APMP chelating resin was slurried in water, and then poured into the column. The bed height of resin in the column was approximately 15 mm. It was washed successively with water, acetone, and water, respectively, then conditioned with 10–15mL of buffer of pH 9. After each use, the resin in the column was washed with large volumes of water and stored in water for the next experiment.

Preconcentration Procedure

The XAD-16- APMP column method was tested with model solutions prior to the determination of trace metal ions in natural water samples. For the metal determinations 100mL of solution containing 10–20 mg of the metal ions was added to 10mL of buffer solution (desired pH between1 and 11). The column was preconditioned by passing buffer solution. The buffered metal solution was passed over the column at a flow rate of 4mL/min by the aid of a vacuum aspirator. After passing of this solution, the column was rinsed twice with 10mL of water. The adsorbed metals on the column were eluted with 8–10mL portion of 1M HCl in acetone. The eluent was evaporated over a hot plate to near dryness. The residue is dissolved with 5mL of 1.0MHCl. The eluent was analyzed for the determinations of metal concentrations by AAS. The results are given Table.4

Analysis of Water Samples

The water samples were collected in prewashed (with detergent, doubly de-ionised distilled water, dilute HNO_3 respectively) polyethylene bottles. The samples were filtered through a Millipore cellulose nitrate membrane of pore size 0.45 mm. The samples were stored in polyethylene bottles and acidified to 1% with nitric acid and were subsequently stored at 4^0C in a refrigerator. For application of the method, 1000mL of water sample was taken in a beaker, then the pH of the sample was adjusted to pH 9 with ammonia/ ammonium buffer solution. The preconcentration method given above was applied. The concentrations of the investigated analyte ions in the final solution were determined by AAS.The results are given Table.3.

RESULTS AND DISCUSSION

Characteristics of XAD-16-PAN Chelating Resin

When the infrared spectra Amberlite XAD-16 and XAD-16-PAN resins were compared, in the chelating resin two additional bands at 1629 and 3450 cm−1 that may be assigned to azo and phenolic O–H stretching vibrations. Four mini columns containing 600 mg of XAD-16- APMP resin for each investigated ions were prepared and saturated with each metal ions, separately in the optimal conditions. The columns were washed with buffer solution and water, respectively, and then the saturated resins were dried on air. Their IR spectra were recorded and compared with IR spectra of XAD-16- APMP resin. The band (1629 cm−1) due to azo group undergoes a red shift of 8–15 cm−1 when a metal ion was adsorbed on the XAD-16-PAN resin. This suggests that the coordination of the metal ions with azo group is very much responsible for their sorption onto the XAD-16- APMP resin.

Effects of pH on the Retentions

The influence of pH on the retentions of **Fe(II),Cu(II), Mn(II), and Zn(II)** on the XAD-16-APMP resin were investigated in the pH range of 2–11. For this purpose column experiments were performed by using 50–60mL of test solutions containing 10–20 mg of each analyte ions. The pHs of the model solutions were adjusted by using buffer solutions given in the experimental section. The results are depicted in Fig.2. The investigated ions were quantitatively (>95%) recovered for all metal ions in the pH range of 9–11 except copper. The recoveries of copper were quantitative in the pH range of 8–11.The volume of the buffer solution had no effect. In all further studies,10mL ammonium chloride buffer solution for pH 9 was used.The model studies at pH 9 and 10 were also repeated by adjusting the pH of the solutions with 1M NaOH. While at pH 9, iron and copper were quantitatively recovered with 1M NaOH, quantitative values were obtained at pH 10 for manganese and zinc

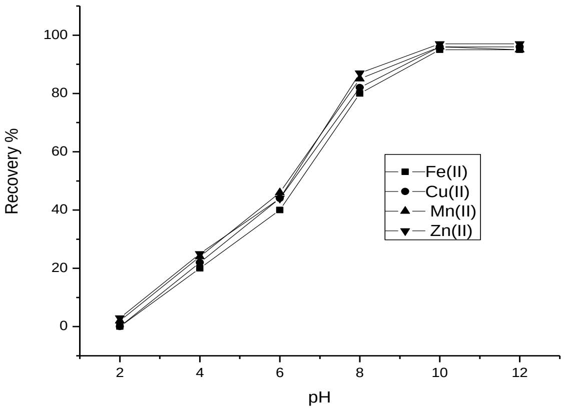

Fig .2 Effect of pH on the retention of analyte ions on XAD-16-PAMP resin

Influences of Eluent Type and Eluent Volume

The effects of eluent type are an important factor in the solid phase extraction studies. The effects of 10mL of various eluents on the recoveries were studied. The results are given in Table 1. The quantitative recoveries of Fe(II),Cu(II), Mn(II), and Zn(II) were obtained for all analyte ions by using 1M HCl in acetone as an eluent. However selective recoveries of metal ions were also possible.The effects of volume of 1M HCl in acetone as an eluent were also investigated in the range of 5–15mL. Quantitative recovery values(>95 %) for analytes were obtained after 7.0mL of 1M HCl in acetone. In all further studies, 10 mL of 1M HCl in acetone was used as eluent.

Table .1 Effect of type and concentration on the recoveries of metal ions(n=4)

Eluent type	Volume (ml)	Recovery (%)			
		Fe	Cu	Mn	Zn
3 M HNO_3	10	85	87	83	84
2 MHNO_3	10	88	9	85	89
3 M HCl in acetone	10	96	95	95	88
1 M HCl in acetone	10	103	99	98	99
2M HCl	10	92	90	93	94
3M HCl	10	93	92	94	95
2 M HCl in acetone	10	90	87	90	91
1 M HCl	10	89	90	91	92

Effects of Resin Amount

The influences of the amount of XAD-16- APMP resin on the mini column were also investigated in the range of 300–700 mg (Fig. 3).The recovery values for the investigated ions were not quantitative till 500 mg of the resin. With more than 500 mg of XAD-16- APMP resin quantitative recovery values obtained. In all subsequent studies 600 mg of XAD-16- APMP resin was used.

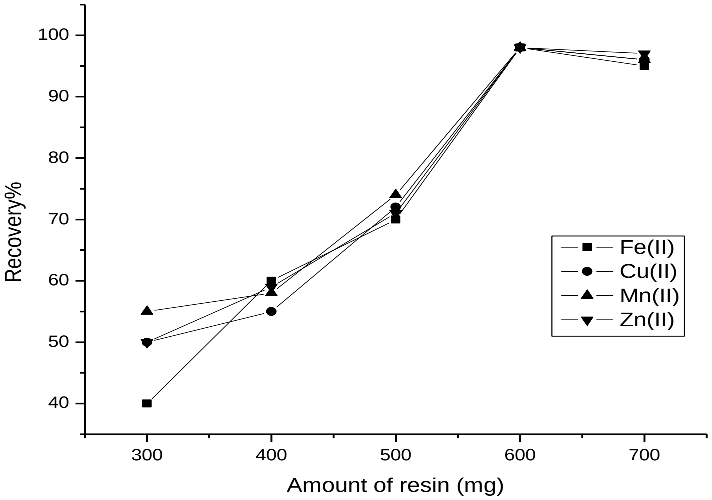

Fig.3. Effect of resin amount on the revcoveries of investigated ions(N=4 eluent; 1M HCl in acetone)

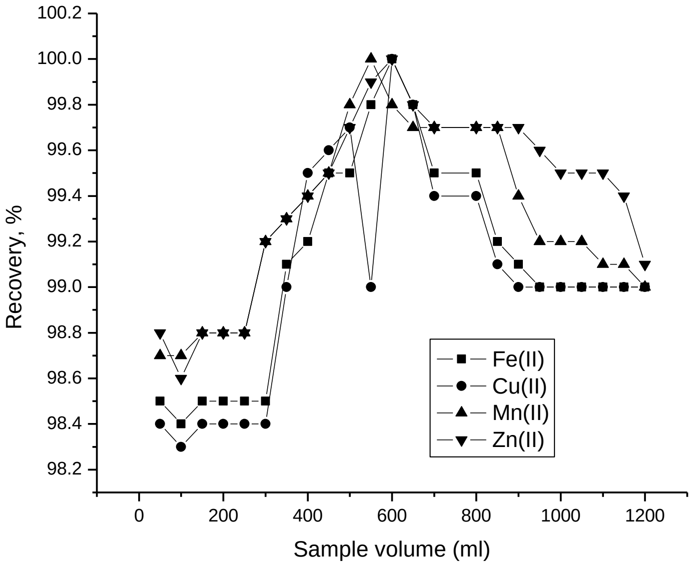

Fig .4 Influences of sample volume on the recoveries of analyte ions(N=4,eluent; 1M HCl in acetone)

Effect of Sample Volume on the Recoveries

In order to explore the possibility of enriching low concentrations of the analyte ions from the large sample volume, the influences of the sample volume on the recovery of the metal ions were also investigated. The metal amounts were 10–20 mg and in the model solution, the metal amounts were held constant while increasing the sample volume. The effect of sample volume on the sorption of metal ions was also investigated by passing 50–1200 mL volumes through the XAD-16- APMP column.

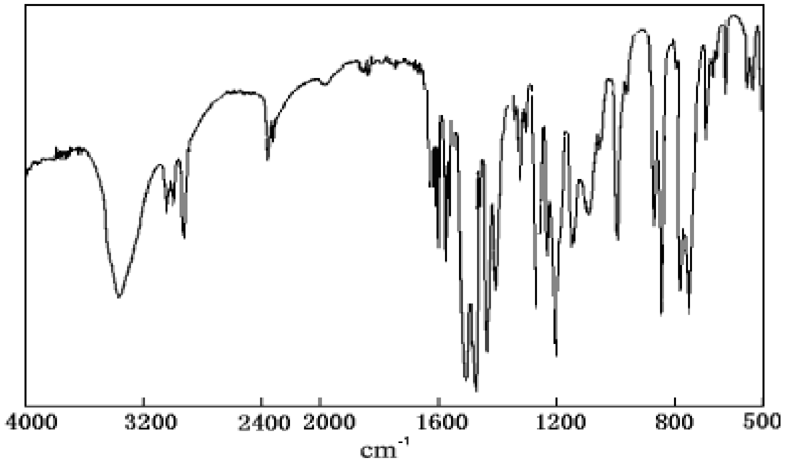

Fig.4 IR spectra of 3-((E)-(2-amino phenyl imino) methyl) phenol

Flow Rates of Sample and Eluent Solutions

Sample and eluent flow rates are important parameters to obtain quantitative retention and elution of analyte ions, respectively. The influences of the flow rates were investigated in the range of 1–10 mL/min. The retentions for the analyte ions on XAD-16-APMP were virtually quantitative for sample flow rates up to 4mL/min. Variation of the elution flow rate in the range of 1.0–4.0 mL/min has no effect on the elution efficiency. In consequence, 4mL/min was selected as flow rate for sample loading and sample elution from the XAD-16- APMP resin.

Effects of Some Cations and Anions

In order to evaluate the possibility of selective recovery of Fe(II),Cu(II), Mn(II), and Zn(II) on XAD-16- APMP resin in the presence of some cations and anions in the natural water samples,the procedure has been performed with 100mL solutions containing these ions. The results are given in Table 2. It can be mentioned that the low ion recoveries for these ions are helpful in the determination of heavy metals at trace levels in natural waters. These results are desired in view of applications to natural water samples. The recoveries of Ca, Mg, K, and Na were determined by AAS and approximately found to be less than 1%.

Table 2 Effects of the matrix ions on the recoveries of the examined metal ions

Ion	Added As	Tolerance Limit Ion (mg L^{-1})
Na^+	NaCl	1000
K^+	KCl	1000
Cl^-	NaCl	1000
SO_4^{2-}	Na_2SO_4	8500
Mg^{+2}	$MgCl_2$	800
HCO_3^-	$NaHCO_3$	800
PO4 $^{3-}$	Na_3PO_4	900
Zn^{+2}, Ba^{+2}, Ca^{+2}	As Nitrates	1000
Ag^+, Al^{+3}, Cr^{+3}	As Nitrates	250

Application to Natural Water Samples

The Amberlite XAD-16- APMP method has been employed for the preconcentration of **Fe(II),Cu(II), Mn(II), and Zn(II)** in natural water samples. For that purpose, the procedure given in Experimental was applied. The results, which are shown in Table 3, have been calculated on the assumption of 100% recovery of working elements.

Table.3 Determination of trace metals in natural water samples after preconcentration on APMP coated resin

	Concentration(µg/L)			
Sample	**Fe(II)**	**Cu(II)**	**Mn(II)**	**Zn(II)**
Kalyanidam	3.91±0.23	1.84±0.93	3.03±0.60	3.90±0.20
Swarna mukhi	4.49±0.37	1.68± 1.07	3.01±0.20	4.22±0.50
Mallimadugu	5.26±0.32	1.54± 1.47	1.34±0.39	3.67±0.42
Srikalahasti area	5.12±0.56	1.25±0.41	1.20±0.45	3.67±0.06

Table.4 Recovery of metal ions from aqueous solution after preconcentration on APMP coated Amberlite XAD-2 resin

Element	Concentration of each element added (µg/100 ml)	Resin coated with APMP		
		Found (µg/l)	Recovery	R.S.D
Fe	25.00	24.98	99.92	1.04
	50.00	49.38	98.76	3.92
Cu	25.00	24.89	99.56	0.88
	50.00	48.34	96.68	4.90
Mn	25.00	24.99	99.96	1.28
	50.00	49.41	98.82	3.12
Zn	25.00	24.97	99.88	1.64
	50.00	49.77	99.54	3.96

CONCLUSION

Based on these results found in the present study, it can be concluded that XAD-16-APMP resin is an effective material for the separation and preconcentration of traces metal ions in the natural water samples. The new resin can be used at least 40 times. Future works will be focused on the usage of the resin solid phase extraction of the metal ions and on the application of the method to other samples containing high salinity such as dialysis solution and urine etc.

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