

Preconcentration and determination of trace metal ions from aqueous samples by newly developed gallic acid modified Amberlite XAD-16 chelating resin

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ABSTRACT

Gallic acid was immobilized on Amberlite XAD-16 by coupling it through $-N=N$ group. The resulting chelating resin AmberliteXAD-16 gallic acid, characterized by thermogravimetric analysis (TGA), infrared (IR) spectra and BET analysis, was used to preconcentrate Cr(III), Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) ions. The resin was employed for the preconcentration of the metal ions present in river water and industrial area aqueous samples. Several parameters like effect of pH, effect of time, effect of sample volume and flow rate of sample were investigated. The sorption capacities for the resin were $216 \mu\text{mol g}^{-1}$, $180 \mu\text{mol g}^{-1}$, $403 \mu\text{mol g}^{-1}$, $281 \mu\text{mol g}^{-1}$, $250 \mu\text{mol g}^{-1}$ and $344 \mu\text{mol g}^{-1}$ for Cr(III), Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) respectively. The preconcentration factors for Cr(III), Mn(II), Fe(III), Ni(II), Co(II) and Cu(II) were found out to be 300, 200, 400, 285.7, 300 and 400 respectively. The effect of various interfering ions was also studied. Results were validated by using standard addition method for river water sample.

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1. Introduction

The tremendous increase in the use of heavy metals over the past few decades has inevitably resulted in an increased flux of metallic substances in the environment. Major sources of heavy metals in the environment include metal extraction, metal refining, electroplating, paints and pigments, the manufacture of batteries as well as metal discharges from industrial facilities. So, there is a critical need for preconcentration and separation of the of trace metals from matrices prior to their determination, due to their frequent presence in environmental samples and higher matrix interferences.

Separation and preconcentration techniques such as coprecipitation [1], electrodeposition, liquid–liquid extraction [2,3] and membrane filtration for the heavy metal ions have been used. Of all these techniques liquid–liquid extraction has been used extensively for the separation and preconcentration of different analytes. Solid-phase extraction (SPE) is preferable over all these techniques due its advantages like selectivity, eco-friendliness, reusability and high preconcentration factors [4–14]. Moreover, the use of chelating sorbents can provide a better separation of interferent ions, high efficiency and higher rate of process, and the possibility of combining with different determination methods. SPE is also superior for preconcentration of trace metals in respect to minimum solvent

waste generation and sorption of the target species on the solid surface in a more stable chemical form [15–17].

Various solid phases including chelex 100 [18], silica gel [19,20], Amberlite XAD resins [21–26], polyurethane foam [27], and activated carbon [28] have been used for the solid-phase extraction of traces heavy metals in environmental samples prior to their instrumental analysis.

Recently, several chelating matrices have been developed using modified Amberlite XAD series. Important advantage of Amberlite XAD series over other supports is their good physical properties such as their porosity, uniform pore size distribution, high surface area as chemical homogeneous non-ionic structure, and good adsorbent properties for great amounts of uncharged compounds [29–32]. The most widely used support materials for the purpose are XAD-2 and XAD-4 in the Amberlite XAD series. Amberlite XAD-16 has an edge over these resins due to the high surface area in comparison to the XAD-2 and XAD-4 resins [33]. The large surface area also makes it possible to increase the number of chelating sites and to make them more accessible towards the adsorption of metal ions. This can be achieved by selecting a ligand of small size and a polymeric support of moderate cross-linking such as Amberlite XAD-16. Generally, resins having largest surface area are preferred. Due to these properties, Amberlite XAD-16 has been selected as a solid-phase extraction support for metal chelates for the present work.

In continuance to the research going on in our laboratory [4–7], an approach for the removal of trace metal ions using newly synthesized gallic acid (GA) coupled with Amberlite XAD-16 via diazo

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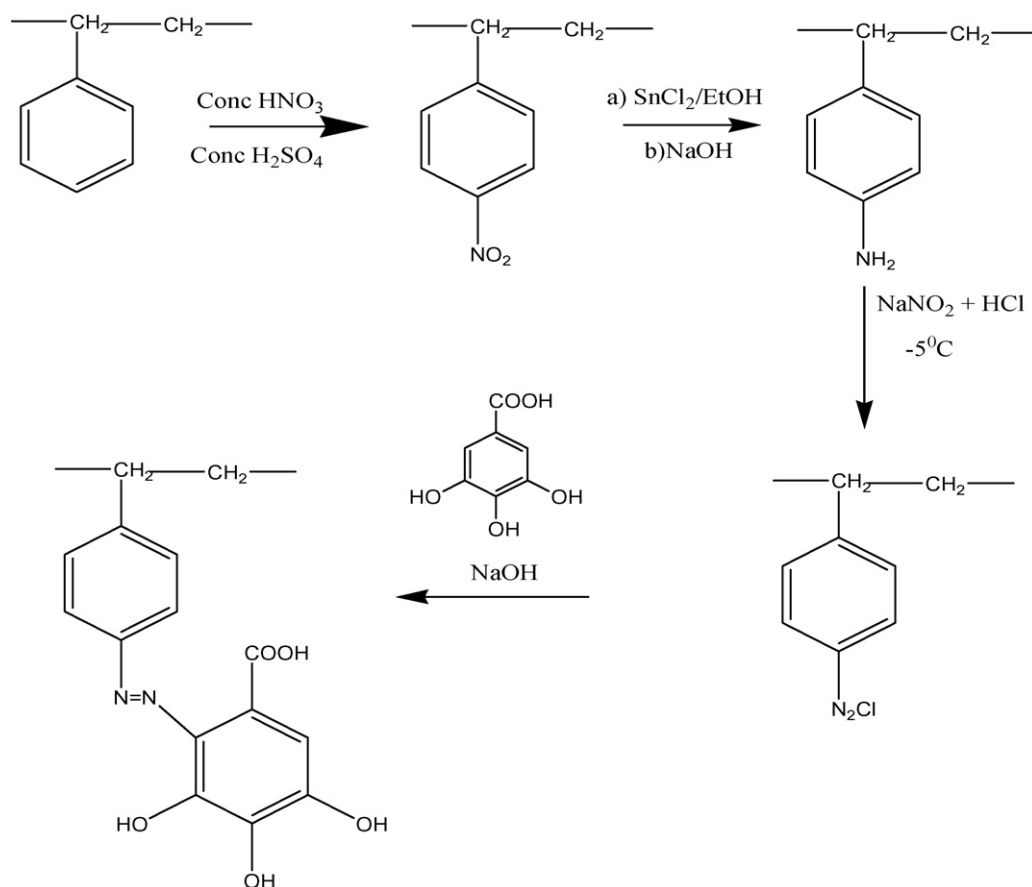


Fig. 1. Steps involved in the synthesis of XAD-16-gallic acid.

group [29,34] was adopted and its application for the preconcentration of metal ions in natural water samples was studied. The optimal analytical conditions including pH, rate of sorption, flow rates of sample, preconcentration factor, sorption capacity and matrix effects were also investigated. The use of present resin for preconcentration of metal ions overcomes many drawbacks of the traditional method of liquid–liquid extraction.

Since, the present work helps towards “Greening” the extraction process by replacing the use of large quantities carcinogenic solvents which are used in liquid–liquid extraction (thereby reducing the environmental impact of processes) with an added advantage of reusability of modified resin, multiple number of times, for removal of metal ions. So, the present work focuses on the green chemistry approach for addressing the problem of removal of metal ions from various aqueous samples.

2. Experimental

2.1. Instruments

The pH measurements were carried out using ELICO LI 120 pH meter, PerkinElmer Analyst 200 flame atomic absorption spectrometer was employed for determination of metal ions. The operating parameters for working elements were set as recommended by the manufacturer.

Thermogravimetric analysis was performed on DTG-60 Shimadzu instrument, equipped with TG units. Infrared (IR) spectra ($4000\text{--}400\text{ cm}^{-1}$) were recorded on PerkinElmer Spectrum 2000 FTIR spectrometer. The surface area of the prepared resin was determined by using Surface Area Analyser, Micrometrics ASAP 2010.

2.2. Reagents

Amberlite XAD-16 (non-ionic divinyl polystyrene; surface area $800\text{ m}^2\text{ g}^{-1}$ and bead size, 20–60 mesh) was procured from Alfa Aesar, USA. Stock solutions of Cr(III), Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) containing 1000 mg/l of metal ion (Merck, Germany) were used for preparation of the standards for the calibration curve.

All solutions were prepared with double distilled water. Unless stated, analytical-grade acids and other chemicals used in this study, were obtained from Merck.

Acetate buffer solutions were prepared by adding an appropriate amount of acetic acid (0.2 M) (Merck) to sodium acetate (0.2 M) solutions for pH 2–6 and ammonium chloride buffer solutions were prepared by adding an appropriate amount of ammonia, ammonium chloride solutions (0.2 M) for pH 8.

2.3. Synthesis of chelating resin

10.0 g of Amberlite XAD-16 was treated with a nitrating mixture, containing 20 ml of concentrated nitric acid and 50 ml of concentrated sulfuric acid for 1 h at 60°C on a water-bath. The nitrated mixture was poured into ice-cold water. It was further filtered, washed repeatedly with distilled water until free from acid. It was then reduced by refluxing with SnCl_2 (40 g), concentrated hydrochloric acid (45 ml), and ethanol (60 ml), for 12 h at 40°C . The amino polymer was filtered off and washed with mixture of HCl–ethanol, water, and 2 M NaOH so as to get the free amino polymer. The amino polymer was treated with 100 ml of 2 M HCl for 30 min, washed with distilled water in order to remove excess of HCl, suspended in 250 ml of ice cold water and mixed with 1 M

Table 1
Optimum experimental parameters for sorption and desorption of analytes

Experimental Parameters	Cu	Co	Cr	Fe	Mn	Ni
pH range	6–7	6–7	3–5	4–6	5–6	6–7
HNO ₃ for desorption	2 M	2 M	2 M	2 M	2 M	2 M
Metal sorption capacity	344	281	216	403	180	250
Lower limit of detection (ng ml ⁻¹)	20	10	10	20	10	10
Breakthrough volume (ml)	2000	2000	1000	2000	2000	1500
Preconcentration Factor (2 M HNO ₃)	400	285.7	200	400	200	300

HCl and 1 M NaNO₂ in aliquots of 2.0 ml each time with constant shaking. The diazotized resin was filtered and washed with ice-cold water and coupled with gallic acid (10.0 g taken in 250 ml of 2% NaOH solution) below 5 °C for 24 h. The resulting resin was filtered and washed with distilled water. The steps involved in the synthesis of XAD-16-gallic acid resin are given in Fig. 1.

2.4. Procedures adopted for carrying out different studies

2.4.1. Column method

A glass column, 15 cm long, having a stopcock and a fritted porous disc (4.5 cm in diameter) was used for sample loading. Then, 50 mg of XAD-16-gallic acid chelating resin was placed inside the column. It was washed, conditioned to the desired pH with 10 ml of buffer for doing the experimentation. Then the sample solutions (10 ml each) were loaded onto the resin beads. The adsorbed metal ions were desorbed with 2 mol l⁻¹ HNO₃ and determined with FAAS to calculate the capacity. After filtering off the solid matrix the filtrate was diluted suitably (if required) (to bring the metal ion concentration in the working range) and subjected to FAAS determination. After each use, the resin in the column was washed with large volumes of water and stored for the next experiment. The optimum experimental parameters for quantitative metal ion sorption and desorption are listed in Table 1.

2.4.2. Batch method

Sample solutions (10 ml) containing 5 µg ml⁻¹ each of Cr(III), Co(II), Cu(II), Mn(II), Ni(II) and Fe(III) were placed in separate glass stoppered bottles (250 ml) after adjusting its pH to the optimum value. The gallic acid loaded Amberlite XAD-16 (0.05 g) was added to each bottle. The bottles were stoppered and shaken for 30 min. The resin was filtered and the metal ions from the resin were desorbed by shaking the resin beads with HNO₃ (10 ml). The resin was filtered off and the filtrate was aspirated into the flame of pre-standardized FAAS.

3. Results and discussion

3.1. Characteristics of XAD-16-gallic acid chelating resin

The thermogravimetric analysis (TGA) curve of the XAD-16-GA chelating resin shows two-step degradation. In the first step, a mass loss of 10.07% up to 110 °C is due to physisorbed water on the resin. In the second step mass loss is 33.37% from 274 °C up to 553 °C corresponding to loss of -COOH and three -OH moieties attached to gallic acid. When the infrared spectra Amberlite XAD-16 and XAD-16-GA resin were compared, and it was found that, the chelating resin is showing two additional bands at 1507 cm⁻¹ and 1652 cm⁻¹ that can be assigned to azo and carbonyl stretching vibrations. The surface area of XAD-16-GA was found to be 453 m² g⁻¹ by BET method. The BET method is widely used for the calculation of surface areas of solids by physical adsorption of gas molecules (for present study nitrogen adsorption was used). The surface area obtained gives the direct measure of sites available for nitrogen adsorption. So, the decrease in surface area of modified resin in comparison to unmod-

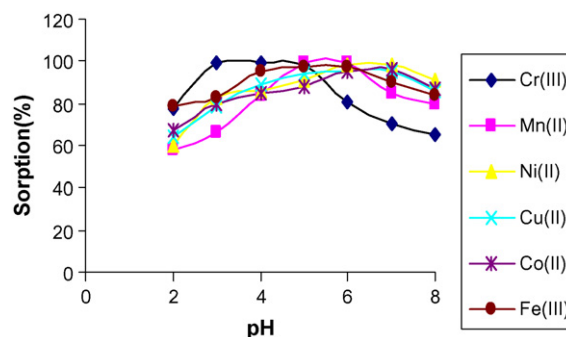


Fig. 2. Effect of pH on sorption of Cr(III), Mn(II), Ni(II), Cu(II), Co(II) and Fe(III) onto gallic acid loaded Amberlite XAD-16.

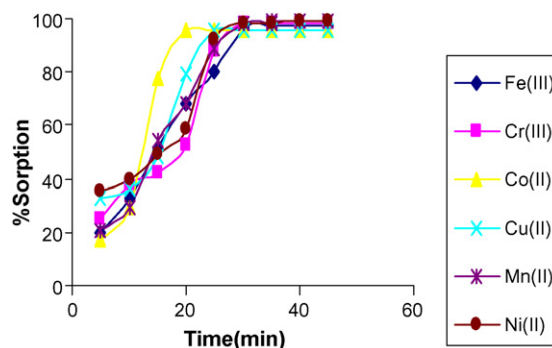


Fig. 3. Rate of metal sorption for Cr(III), Mn(II), Ni(II), Cu(II), Co(II) and Fe(III) ions onto gallic acid loaded Amberlite XAD-16.

ified Amberlite XAD-16 confirms the incorporation of Gallic acid to Amberlite XAD-16.

3.2. Effect of pH on enrichment of metal ions

The influence of pH on the retentions of Cr(III), Ni(II) and Mn(II), Cu(II), Fe(III) and Co(II) on the XAD-16-GA resin was investigated in the pH range of 2–8. Experiments were performed by passing 10 ml of test solutions containing 5 µg ml⁻¹ of each analyte ion at a flow rate of 2 ml/min. The pH of the solutions was adjusted by using buffer solutions. The bound metal ions were stripped from the column with HNO₃ (10 ml) passed at a flow rate of 2 ml/min. Quantitative recoveries were obtained in the pH range 6–7 for Ni(II), 3–5 for Cr(III), 6–7 for Cu(II), 5–6 for Mn(II), 4–6 for Fe(III) and 6–7 for Co(II). The results are depicted in Fig. 2.

Table 2

The eluent solution type and % recovery of the metal ions (sample volume: 10 ml, concentration of metal solution: 0.5 mg l⁻¹, n = 3)

Eluent	Recovery (R.S.D.)%					
	Cr	Mn	Fe	Co	Cu	Ni
0.2 N HCl	22 (4.7)	56 (2.1)	50 (1.9)	32 (1.7)	34 (4.5)	65 (3.7)
0.5 N HCl	51 (3.2)	75 (1.4)	55 (4.7)	40 (3.3)	48 (1.7)	79 (1.3)
1.0 N HCl	58 (4.6)	95 (3.8)	70 (1.8)	63 (3.7)	81 (4.6)	96 (2.8)
2.0 N HCl	89 (1.8)	95 (3.6)	89 (1.6)	76 (2.9)	85 (2.1)	95 (3.4)
3.0 N HCl	91 (2.6)	93 (1.7)	85 (2.5)	80 (4.3)	80 (2.7)	89 (4.7)
0.2 N HNO ₃	41 (4.3)	32 (3.8)	53 (3.6)	56 (1.0)	67 (4.2)	41 (1.1)
0.5 N HNO ₃	49 (3.6)	50 (4.2)	75 (4.7)	72 (3.3)	76 (3.9)	71 (4.9)
1.0 N HNO ₃	79 (2.8)	88 (1.7)	93 (3.4)	90 (2.9)	92 (2.3)	96 (3.5)
2.0 N HNO ₃	98 (2.3)	98 (3.3)	96 (2.6)	95 (4.4)	95 (2.9)	97 (2.7)
3.0 N HNO ₃	91 (1.7)	96 (1.3)	94 (1.5)	95 (2.7)	98 (3.4)	95 (4.5)

Table 3
Enrichment factors and enrichment limits of metal ions (AL-XAD-16-GA)

Metal ion	Total volume (ml)	Lower limit of detection (ng ml ⁻¹)	Final volume (ml) (volume of eluent used)	% Recovery	Preconcentration factor
Cr(III)	1000	10	5	99.4	200.0
Mn(II)	2000	10	10	99.0	200.0
Ni(II)	1500	10	5	97.0	300.0
Co(II)	2000	10	7	98.2	285.7
Cu(II)	2000	20	5	96.1	400.0
Fe(III)	2000	20	5	99.2	400.0

3.3. Rate of metal sorption

In order to find out the rate of sorption of the six metal ions, 0.1 g of resin was fed with 100 ml of 0.5 $\mu\text{g ml}^{-1}$ of metal solution maintained at optimum pH and the adsorption was studied by taking small aliquots of metal solutions at the time interval of 5 min up to 45 min.

The variation of sorption as a function of time for all the metal ions is shown in Fig. 3. Maximum adsorption of metal ions was achieved in less than 30 min for all the metal ions.

3.4. Influence of eluent type

For selection of the eluent, effect of HCl and HNO₃ on the preconcentration yields of the metals was studied under the optimum conditions. The results are given in Table 2. The quantitative recoveries of Cr(III), Mn(II), Ni(II), Cu(II), Fe(III) and Co(II) were obtained for all analytes ions by using 2 M HNO₃ as an eluent. Therefore 2 M HNO₃ was selected as an eluent for further applications.

3.5. Reuse of chelating resin

The stability and regeneration of the XAD-16-GA resin were examined. The column was reused after regeneration with 10 ml of 2 M HNO₃ and 100 ml distilled water, respectively, and is stable up to 20 runs without appreciable loss of sorption capacity.

3.6. Effect of sample volume on the recoveries and preconcentration factor

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 investigated. The metal amounts were 10 ng ml⁻¹ and 20 ng ml⁻¹ in the model solution, the metal amounts were held constant while increasing the sample volume. The concentration of metal ion solution (given in ng ml⁻¹), below which the adsorption decreased by 5% is defined as the 'lower limit of detection' for the metal ion for XAD-16-GA. The effect of sample volume on the sorption of metal ions was also investigated by passing 1000–2000 ml volumes through the XAD-16-GA column. The results are depicted in Table 3. The adsorption of the metal ions with 0.1 g resin was not affected by sample volume till 1000 ml. The highest preconcentration factor was 400 for Cu(II) and Fe(III) ions when volume of eluent used was 5.0 ml.

3.7. 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 1–5 ml/min. The retentions for the analyte ions on XAD-16-GA were virtually quantitative for sample flow rates (rate at which sample solution was introduced to the column) up to 2 ml/min. Variation

of the elution flow rate (rate at which the sample solution came out of column) in the range of 1.0–4.0 ml/min has no effect on the elution efficiency. In consequence, 2 ml/min was selected as flow rate for sample loading and sample elution from the XAD-16-GA resin.

3.8. Sorption capacity of XAD-16-GA resin

The sorption capacities of gallic acid loaded Amberlite XAD-16 were determined by batch method. The resin (0.1 g) was saturated with Cr(III), Mn(II), Ni(II), Cu(II), Co(II) and Fe(III) solution (50 ml of 100 $\mu\text{g ml}^{-1}$) by equilibration on a shaker under optimum conditions. The sorption capacities were found out to be 216 $\mu\text{mol g}^{-1}$, 180 $\mu\text{mol g}^{-1}$, 250 $\mu\text{mol g}^{-1}$, 281 $\mu\text{mol g}^{-1}$, 344 $\mu\text{mol g}^{-1}$ and 403 $\mu\text{mol g}^{-1}$ for Cr(III), Mn(II), Ni(II), Co(II), Cu(II) and Fe(III) respectively. The column method was also used to determine the sorption capacity. The results in both the cases were found to be comparable.

3.9. Effects of some cations and anions

In order to evaluate the possibility of selective recovery of Cr(III), Mn(II), Ni(II), Co(II), Cu(II) and Fe(III) on XAD-16-GA resin in the presence of some cations and anions in the natural water samples, the effect of presence various interfering ions was also studied. The study of role of electrolyte in presence of metal ions is very important from application point of view, since these electrolytes might have the ability to interfere with the adsorption of metal ions by forming complexes with the resin and hence avoiding the resin to form chelate with target metal ion. So, the test of ability of resin to selectively target the metal ions of interest in presence of the electrolyte species become important.

The concentration of matrix ions was varied from 0.001 to 0.5 mol l⁻¹. Tolerance limits of investigated electrolytes are given in Table 4. Quantitative recoveries were obtained for analyte ions. The reported tolerance limit is defined as the ion concentration causing a relative error $\leq \pm 5\%$ in the sorption of metal ion. As can be seen from the results that the synthesized resin possess reasonably high tolerance limits for the salts, which are commonly found in saline water and natural water bodies, so XAD-16-GA can be successfully applied for extraction of metal ions from such systems.

Table 4
Tolerance limits of electrolytes

Metal ion	Metal Conc. ($\mu\text{ mol l}^{-1}$)	Electrolytes (mol l^{-1})					
		NaCl	KCl	KI	Na ₂ SO ₄	CaCl ₂	NaNO ₂
Cu(II)	0.786	0.010	0.010	0.100	0.010	0.100	0.001
Ni(II)	0.852	0.001	0.050	0.100	0.050	0.001	0.010
Fe(III)	0.895	0.500	0.100	0.500	0.100	0.010	0.500
Mn(II)	0.910	0.001	0.010	0.010	0.001	0.010	0.001
Co(II)	0.848	0.050	0.010	0.100	0.100	0.005	0.010
Cr(III)	0.961	0.001	0.001	0.001	0.001	0.050	0.050

Table 5

Determination of metal ions in river water (sample volume 250 ml, final volume of eluent used 10 ml)

Metal ion	Added ($\mu\text{g ml}^{-1}$) (S.A.)	Found ($\mu\text{g ml}^{-1}$)		% Recovery
		Reading	R.S.D.	
Cr(III)	–	0.320	3.2	95.4
	1.00	1.260	2.5	
Mn(II)	–	0.218	2.7	97.8
	1.00	1.192	3.1	
Ni(II)	–	1.502	1.4	97.5
	1.00	2.440	3.6	
Cu(II)	–	2.100	0.9	97.0
	1.00	3.008	2.9	
Co(II)	–	0.045	2.8	99.4
	1.00	1.039	2.3	
Fe(III)	–	0.601	1.3	98.6
	1.00	1.580	4.1	

4. Applications of the method

4.1. Determination of metal ions in river water and industrial area aqueous samples

AL-XAD-16-GA was used to preconcentrate Co(II), Cu(II), Cr(III), Mn(II), Ni(II) and Fe(III) ions in water samples collected from the Ganges (Varanasi) and Wazirpur Industrial Area (Delhi). The estimation of the six metal ions in case of water from Ganges was made with and without (referred as direct determination) standard addition (S.A.) by passing 250 ml of water sample (spiked with $1 \mu\text{g ml}^{-1}$ of each of the six metal ions in the case of standard addition method) through the column packed with 1.0 g of modified resin after adjusting the pH to an optimum value and determining the metal ion as described in the recommended column procedure. The elution was made with 2 M HNO_3 . The results are given in Table 5.

For the analysis of aqueous sample from industrial area (Wazirpur, Delhi, India) appropriate dilutions were done in order to check the efficiency of resin. The sample was diluted 1000 times to bring

Table 6

Recovery of Cr(III), Mn(II), Ni(II) and Cu(II) from industrial area sample (sample volume 250 ml, final volume of eluent (2 M HNO_3 = 10 ml)

Metal ion	Concentration in sample ($\mu\text{g ml}^{-1}$) reading (% R.S.D.)		Concentration in eluent ($\mu\text{g ml}^{-1}$) reading (% R.S.D.)		% Reading
Cr(III)	0.1825 (3.0)		4.4000 (2.4)		96.7
Mn(II)	0.0280 (1.1)		0.6810 (1.7)		97.1
Ni(II)	0.0301 (2.2)		0.7500 (0.5)		99.7
Cu(II)	0.1070 (2.6)		2.6500 (1.5)		99.0

the concentration of sample in the working range of resin. And the diluted sample (250 ml of above sample) was given to 1.0 g of matrix after adjusting the pH to an optimum value and the metal ions were determined as described in the recommended column procedure. The elution was done with 10 ml of 2 M HNO_3 . The results obtained are shown in Table 6.

4.2. Accuracy of the results

A good agreement in Table 5 was obtained between the added and measured analyte amounts. The recovery values calculated for the added standards were always higher than 95%, thus confirming the accuracy of the procedure and its independence from the matrix effects. These results confirm the validity of the proposed method.

4.3. Comparison with other preconcentrating matrices

The sorption capacities and preconcentration factors of present Resin are compared with other matrices in Tables 7 and 8, respectively.

The comparison of sorption capacities of ALXAD-16-GA with sorption capacities of Amberlite XAD-2 and XAD-7 supported resins shows the superiority of the present resin for the adsorption of the trace metal ions over thiosalicylic acid [35], chromotropic acid [36], pyrocatechol [37], *o*-aminophenol [38], tiron [39], pyrogallol [40], quinalizarin [41], 5-palmitoyl-8-hydroxyquinoline [42], ammonium pyrrolidine dithiocarbamate [43], 2,6-diacetylpyridine [44], xylene orange [45]. Much higher sorption capacities are obtained for AL-XAD-16-GA than AL-XAD-16 supported 1-(2-pyridylazo)2-naphthol [29] for all the investigated metal ions. Better sorption

Table 7

Comparison of Sorption Capacities ($\mu\text{mol g}^{-1}$)

Support: immobilized ligand	Co	Cu	Cr	Mn	Ni	Fe
Amberlite XAD-2						
Thiosalicylic acid [35]	106	214			310	60
Chromotropic acid [36]	65	134			103	58
Pyrocatechol [37]	23	93			53	74
<i>o</i> -Aminophenol [38]	58	53			55	
Tiron [39]	110	220		182	215	100
Pyrogallol [40]	70	71		82	70	83
Quinalizarin [41]	28	50		17		28
5-Palmitoyl-8-hydroxyquinoline[42]	27	28	21		24	22
Amberlite XAD-4						
Ammonium pyrrolidine dithiocarbamate [43]		174		157	123	
2,6-diacetylpyridine [44]	255	264		261	290	
Amberlite XAD-7						
Xylene orange[45]	44	25			45	29
Amberlite XAD-16						
Gallic acid (present work)	281	344	216	180	250	403
2-[[1-(3,4-Dihydroxyphenyl) methylidene]amino]benzoic acid [46]	221	468		178	269	515
1,3-Dimethyl-3-aminopropan-1-ol [47]	270	460			550	
1-(2-Pyridylazo)2-naphthol [29]	79	78	96			
Silica Gel						
Resacetophenone [48]	365	186			254	272
8-hydroxyquinoline [49]	178	400			220	348
3-Hydroxy-2-methyl-1,4-naphthoquinone [50]	10	10				10

Table 8
Comparison of preconcentration factors

Support: immobilized ligand	Co	Cu	Cr	Mn	Ni	Fe
Amberlite XAD-2						
Thiosalicylic acid [35]	180	200			200	400
Chromotropic acid [36]	150	100			200	120
Pyrocatechol [37]	200	100			200	80
<i>o</i> -Aminophenol [38]	100	50			65	
Tiron [39]	56	200		64	150	80
Pyrogallol [40]	65	65		120	120	140
Quinalizarin [41]	40	100		65		
5-Palmitoyl-8-hydroxyquinoline[42]	50	50	50		50	50
Amberlite XAD-4						
Ammonium pyrrolidine dithiocarbamate[43]		230		55	59	
2,6-diacetylpyridine [44]	–	–	–	–	–	–
Amberlite XAD-7						
Xylenol orange [45]	100	50			100	100
AmberliteXAD-16						
Gallic acid (present work)	285.7	400	300	200	300	400
2-([1-(3,4-Dihydroxyphenyl)methylidene] amino)benzoic acid. [46]	167	300		250	100	450
1,3-Dimethyl-3-aminopropan-1-ol [47]	300	400			300	
1-(2-Pyridylazo)2-naphthol [29]	200	200	200			
Silica Gel						
Resacetophenone [48]	300	240			300	272
8-hydroxyquinoline [49]	250	300			200	300
3-Hydroxy-2-methyl-1,4-naphthoquinone [50]	–	–				–

capacities for Co(II) and Mn(II) are shown by the present resin when compared with 2-([1-(3,4-dihydroxyphenyl) methylidene]amino) benzoic acid [46] though results for Ni(II) is comparable. AL-XAD-16-GA proves to be much better than silica supported resins resacetophenone [48], 8-hydroxyquinoline [49] and 3-hydroxy-2-methyl-1,4-naphthoquinone [50] where the sorption capacities are much lesser than that of present resin.

The preconcentration factors of AL-XAD-16-GA for the investigated metal ions is much higher than Amberlite XAD-2 supported resins like thiosalicylic acid [35], chromotropic acid [36], pyrocatechol [37], *o*-aminophenol [38], tiron [39], pyrogallol [40], quinalizarin [41], 5-palmitoyl-8-hydroxyquinoline [42]. Similarly, higher preconcentration factors are obtained for present resin when compared with Amberlite XAD-4, XAD-7 ammonium pyrrolidine dithiocarbamate [43] supported xylenol orange [45] and AXAD-16 supported 1-(2-pyridylazo)2-naphthol [29] and modified silica supported resacetophenone [48] (except for Co(II) where the results are comparable), 8-hydroxyquinoline [49]. ALXAD-16-GA also shows higher sorption capacity and preconcentration for Cr(III).

5. Conclusion

The present chelating matrix shows an enrichment factor in range of 250–410 $\mu\text{mol g}^{-1}$ for different metal ions studied, which is better to most promising chelating resins reported till date. As can be seen from Tables 7 and 8, not many chelating resins having high sorption capacity and preconcentration factor for Cr(III) have been reported so far on Amberlite XAD-16 functionalized polymeric support so, Amberlite XAD-16-GA promises to be competent enough for Cr(III) adsorption.

Based on the results found in the present study, it can be concluded that Amberlite XAD-16-GA is an effective resin for the separation and preconcentration of the trace metal ions in the natural water samples. The method gives higher preconcentration factors for all the six studied metal ions in comparison to most of the resins listed in Table 5. The new resin can be used at least 20 times and high preconcentration factors can be achieved at very low costs of chemicals incurred.

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