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2-{[1-(3,4-Dihydroxyphenyl)methylidene]amino}benzoic acid immobilized Amberlite XAD-16 as metal extractant

Gopalan Venkatesh, Ajai K. Singh*

Department of Chemistry, Indian Institute of Technology, New Delhi 110016, India

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Abstract

2-{[1-(3,4-Dihydroxyphenyl)methylidene]amino}benzoic acid (DMABA) was loaded on Amberlite XAD-16 (AXAD-16) via azo linker and the resulting resin AXAD-16-DMABA explored for enrichment of Zn(II), Mn(II), Ni(II), Pb(II), Cd(II), Cu(II), Fe(III) and Co(II). The optimum pH values for extraction are 6.5–7.0, 5.0–6.0, 5.5–7.5, 5.0–6.5, 6.5–8.0, 5.5–7.0, 4.0–5.0 and 6.0–7.0, respectively. The sorption capacity was found between 97 and 515 μmol g^{-1} and the preconcentration factors from 100 to 450. Tolerance limits for foreign species are reported. The kinetics of sorption is fast as $t_{1/2}$ is $\leq$5 min. The chelating resin can be reused for 50 cycles of sorption–desorption without any significant change (<1.5%) in the sorption capacity. The limit of detection values (blank +3 s) are 1.12, 1.38, 1.76, 0.67, 0.77, 2.52, 5.92 and 1.08 μg L^{-1} for Zn(II), Mn(II), Ni(II), Pb(II), Cd(II), Cu(II), Fe(III) and Co(II), respectively. The enrichment on AXAD-16-DMABA coupled with monitoring by flame atomic absorption spectrometry (FAAS) is used to determine all the metal ion ions in river and synthetic water samples, Co in vitamin tablets and Zn in milk samples.

Keywords: 2-{[1-(3,4-Dihydroxyphenyl)methylidene]amino}benzoic acid; Amberlite XAD-16; Metal ions; Chelating resin; Enrichment; Flame atomic absorption spectrometry; Determination

1. Introduction

The interest in ligand immobilized solid phases like silica gel, organic polymer or copolymers and cellulose continues because of their several applications, for example in solid phase metal extraction [1], designing hybrid organic–inorganic catalysts [2] and heterogenization of homogeneous catalysts [3]. The solid phase extraction of metal ions present at micro/trace level in environmental samples, high purity materials, biological samples and other complex matrices, makes possible their determination with cheap and commonly available analytical techniques, such as flame atomic absorption spectrometry (FAAS). Solid phase extraction is preferable over ion exchange and solvent extraction due its advantages like selectivity, eco-friendliness, reusability and high preconcentration factors [4]. Amberlite XAD-2 has been found to be a good support to load the chelating ligands and design chelating resins for solid phase extraction [5–15]. It has been reported recently that Amberlite XAD-16 (AXAD-16), which is chemically divinyl polystyrene copolymer (marketed by Aldrich (USA)) on ligand immobilization gives chelating resins of better sorption capacities than those of Amberlite XAD-2-based chelators [16–19]. The improvement in the sorption capacity may result due to higher surface area of Amberlite XAD-16 in comparison to that of Amberlite XAD-2 [20–21]. Thus, anchoring of a multidentate ligand 2-{[1-(3,4-dihydroxyphenyl)methylidene]amino}benzoic acid (DMABA) on Amberlite XAD-16 may result chelating resin of very high capacity. It was, therefore, thought worthwhile to design AXAD-16-DMABA and study resulting chelating resin to enrich Zn(II), Mn(II), Ni(II), Pb(II), Cd(II), Cu(II), Fe(III) and Co(II). The enrichment of these metal ions by the newly designed resin coupled with their determination by flame atomic absorption spectrometry has been applied

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* Corresponding author. Tel.: +91 11 2659 1379; fax: +91 11 2658 1037.
E-mail addresses: aksingh@chemistry.iitd.ac.in, ajai57@hotmail.com (A.K. Singh).

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to determine all eight metal ions in water samples, cobalt in vitamin tablets and zinc in milk. The details of these investigations and their results are reported in this paper.

2. Experimental

2.1. Instruments

A flame atomic absorption spectrometer of the Perkin-Elmer Instruments, Shelton, USA, model Aanalyst 100 equipped with air–acetylene flame was used for metal ion determination. The wavelengths used for monitoring Zn, Mn, Ni, Pb, Cd, Cu, Fe and Co are 213.9, 279.8, 231.1, 217.0, 228.8, 324.8, 248.8 and 240.7 nm, respectively. The calibration curves were linear in the ranges 0.02–1.00, 0.07–5.00, 0.20–5.00, 0.19–20.00, 0.28–2.00, 0.08–5.00, 0.19–20.00 and 0.10–3.50 $\mu g\,mL^{-1}$ for Zn, Mn, Ni, Pb, Cd, Cu, Fe and Co, respectively. A Nicolet (Madison, USA) FT-IR spectrometer, model Protégé 460, was used to record IR spectra (in KBr) in the range 400–4000 cm^{-1}. The pH was measured with digital pH meter (Toshniwal Instruments, Ajmer, India). Thermogravimetric analysis (TGA) was carried out on a Dupont (Wilmington, Delaware, USA) 2100 thermal analyzer and Perkin-Elmer (Rotkreuz, Switzerland) elemental analyzer, model 240C, was used for elemental analyses. The flow of solution through the column was controlled using peristaltic pump (Watson–Marlow Model 101/U/R, Falmouth, UK). The sorption and desorption studies of the metal on the chelating matrix were generally carried out on columns of 1 cm diameter (Pharmacia, Bromma, Sweden) and 10 cm in length equipped with adjustable frits. A mechanical shaker equipped with an incubator (Hindustan Scientific, New Delhi, India) with a speed of 200 strokes min^{-1} was used for batch equilibration.

2.2. Reagents

Amberlite XAD-16 (non-ionic divinyl polystyrene; specific area 800 $m^2\,g^{-1}$ and bead size, 20–60 mesh) was procured from Aldrich (Milwaukee, USA). 3,4-Dihydroxybenzaldehyde obtained from ACROS ORGANICS (New Jersey, USA) and anthranilic acid obtained from Merck India Ltd. was used as received. The stock solutions of metal ions (1000 $mg\,L^{-1}$) were prepared from analytical reagent grade metal salts as described earlier [8–11]. They were standardized [22] and working solutions of the metal ions were made by suitable dilution of the stock solutions with doubly distilled water. The 0.1 $mol\,L^{-1}$ HCl and NaOH (pH 2 and 3), 0.1 $mol\,L^{-1}$ acetic acid–acetate buffer (pH 4 and 5), 0.1 $mol\,L^{-1}$ phosphate buffer (pH 6 and 7) and 0.1 $mol\,L^{-1}$ ammonia–ammonium chloride buffer (pH 8 and 9) were used to adjust the pH of the solutions, wherever suitable. Water samples from the Ganges river (Haridwar, India) and tap water (New Delhi, India) were collected, acidified with 2% HNO_3, filtered and stored in glass bottles. The glassware were washed with chromic acid and soaked in 5% HNO_3 overnight and cleaned with doubly distilled water before use.

2.3. Synthesis of 2-{[1-(3,4-dihydroxyphenyl)methylidene]amino}benzoic acid and DMABA loaded Amberlite XAD-16 (AXAD-16-DMABA)

3,4-Dihydroxybenzaldehyde (0.138 g, 1 mmol) and anthranilic acid (0.137 g, 1 mmol) were dissolved in dry diethyl ether and the mixture was stirred at room temperature for 3 h. The solvent was removed on a rotary evaporator to get red coloured Schiff's base DMABA, which was recrystallized from ethanol. Analyses: found C, 64.22; H, 4.31; N, 5.84%; calculated for $C_{14}H_{11}NO_4$: C, 65.37; H, 4.28; N, 5. 45%.

The procedure published [8,9] for nitration of Amberlite XAD-2 beads was used for Amberlite XAD-16 also. The nitrated Amberlite XAD-16 was also reduced to amino resin by the reported method [8,9]. The amino resin was suspended in 200 mL of ice-cold water and treated with a equimolar mixture of 1 $mol\,L^{-1}$ HCl and $NaNO_2$ solution at −5 °C, until the reaction mixture started to change the colour of starch iodide paper to violet. The diazotized polymer was filtered at −5 to 0 °C to avoid its disintegration and treated with DMABA (10 g taken in a mixture of 400 mL water and 50 mL of 2% sodium hydroxide) at 0 to 5 °C for 24 h. The resulting dark brownish crimson coloured beads were filtered and washed with 4 $mol\,L^{-1}$ HCl and doubly distilled water successively and finally air-dried.

Analyses: AXAD-16-DMABA: found C, 62.73; H, 5.56; N, 9.90%;

2.4. Recommended procedure for preconcentration and determination of metal ions

The column and batch methods employed for the preconcentration of metal ions are as follows.

2.4.1. Column method

Amberlite XAD-16 loaded with DMABA (1.0 g) was swollen for 24 h, packed in a glass column C10/10 (Pharmacia; 10 cm × 10 mm), between frits, using the method recommended by the manufacturer [23]. The column was treated with 4 $mol\,L^{-1}$ HCl or HNO_3 (50 mL) and washed with doubly distilled water until free from acid. A suitable aliquot of the sample solution containing Zn(II), Mn(II), Ni(II), Pb(II), Cd(II), Cu(II), Fe(III) or Co(II) in the concentration range 0.0044–1.0 $\mu g\,mL^{-1}$ (500–100 mL depending upon concentration) was passed through the column after adjusting its pH (in the range 6.5–7.0, 5.0–6.0, 5.5–7.5, 5.0–6.5, 6.5–8.0, 5.5–7.0, 4.0–5.0 and 6.0–7.0, respectively, for Zn(II), Mn(II), Ni(II), Pb(II), Cd(II), Cu(II), Fe(III) and Co(II)) at a flow rate of 1.0–5.0 $mL\,min^{-1}$, controlled with a peristaltic pump. The column was washed with distilled water to remove free metal ions. The bound metal ions were stripped from the column with HCl or HNO_3 (10–25 mL) of optimum concentration

Table 1
Optimum experimental conditions for the sorption and desorption of metal ions on AXAD-16-DMABA

Experimental parameters	Metal ion							
	Zn(II)	Mn(II)	Ni(II)	Pb(II)	Cd(II)	Cu(II)	Fe(III)	Co(II)
pH range	6.5–7.0	5.0–6.0	5.5–7.5	5.0–6.5	6.5–8.0	5.5–7.0	4.0–5.0	6.0–7.0
Flow rate (mL min^{-1})	1.0–5.0	2.0–4.0	1.5–4.0	1.0–5.0	1.0–5.0	1.0–5.0	2.0–5.0	1.0–4.0
HCl/HNO$_3$ concentration for desorption (mol L^{-1})	1.5–3.5	2.0–4.0	1.0–2.5	1.0[a]	1.5–2.0	1.5–4.0	1.0–3.0	1.0–4.0
Sorption capacity (μmol g^{-1})	198	178	269	128	97	468	515	221
Average recovery (%)	98.6	98.4	99.2	98.8	97.4	98.0	99.8	98.8
standard deviation[b]	0.027	0.021	0.022	0.031	0.039	0.038	0.022	0.043
Relative standard deviation (%)	2.740	2.090	2.290	3.147	4.020	3.820	2.170	4.370

[a] HNO$_3$ was used for desorption.
[b] For five determinations of 0.25 μg mL^{-1} (0.5 μg mL^{-1} for Pb).

given in Table 1, passed at flow rate 2.0–6.0 mL min^{-1}. The concentration of the metal ion in the eluates was determined by flame atomic absorption spectrometry, standardized previously. Dilution with double distilled water was performed before aspiration when the eluates were sufficiently concentrated to exceed the working range of FAAS.

2.4.2. Batch method

A sample solution (100 mL) containing 0.1–26.5 μg mL^{-1} of Zn(II), Mn(II), Ni(II), Pb(II), Cd(II), Cu(II), Fe(III) or Co(II) was placed in a glass stoppered bottle (250 mL) after adjusting its pH to the optimum value. The DMABA loaded Amberlite XAD-16 (0.1 g) was added. The bottle was 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 HCl or HNO$_3$ (25 mL of optimum concentration given in Table 1). The resin was filtered off and the filtrate was aspirated into the flame of pre-standardized FAAS, after suitable dilution, if required.

3. Results and discussion

3.1. Synthesis and characterization of the Amberlite XAD-16 loaded with DMABA

The AXAD-16-DMABA was synthesized by the reactions of Scheme 1. The TGA curve of freshly prepared AXAD-16-DMABA shows a weight loss of 11.66% at 200 °C. On aging the weight loss at 150 °C lowers down to 5.02% only. This variation may be due to the presence of surface adsorbed water. The FT-IR spectrum of DMABA has bands at 1653, 1556, 1363 and 1263 cm^{-1} due to ν(C=O), ν_{symm}(C=N), O–H bending and ν(C–O), respectively. In the FT-IR spectrum of AXAD-16-DMABA, new bands appear at 1686, 1616, 1569, 1346 and 1243 cm^{-1}, which may be assigned to ν(C=O), ν_{symm}(C=N), ν(N=N), O–H bending and ν(C–O), respectively. These similarities between the spectra of ligand DMABA and the resin made by anchoring it support the loading of DMABA onto Amberlite XAD-16. The surface area of AXAD-16-DMABA was found to be 375.4 m^2 g^{-1}.

3.2. Optimum conditions for sorption and desorption

The multivariate approach was used to optimize the working conditions; each optimum condition was, however, rechecked after standardizing the remaining ones. The optimum conditions for sorption of Zn(II), Mn(II), Ni(II), Pb(II), Cd(II), Cu(II), Fe(III) and Co(II) on the column packed with the DMABA anchored Amberlite XAD-16 (pH and flow rate) and desorption (acid concentration and volume of eluent) were established by varying one of them and following the recommended column procedure. The results are summarized in Table 1. A typical process for optimization of pH for Cu is as follow. A set of solutions (volume: 100 mL), containing 0.25 μg mL^{-1} of Cu was taken. The pH of the solutions of the set was adjusted to different values in the range 2.0–9.0. The enrichment of the metal ion from these solutions was studied by the recommended column procedure. The optimum pH range for maximum recovery of each metal ion is reported in Table 1 (pH profile is shown in Fig. 1). The effect of pH on sorption was also studied by using the recommended batch method and the results are found to be consistent with those of the column method. The use of 5–10 mL of acetate, phosphate and ammonia buffer to adjust the pH does not affect the sorption behavior. The metal ions are not significantly

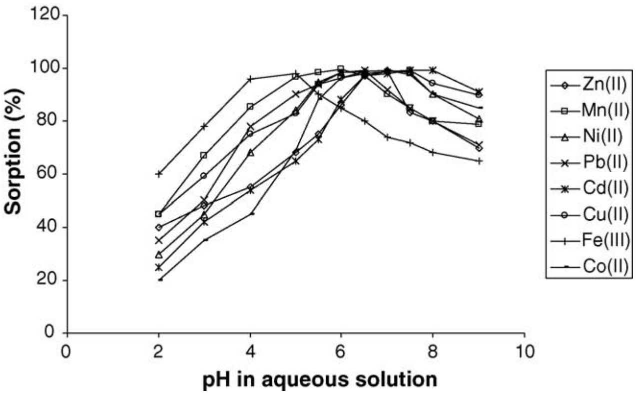
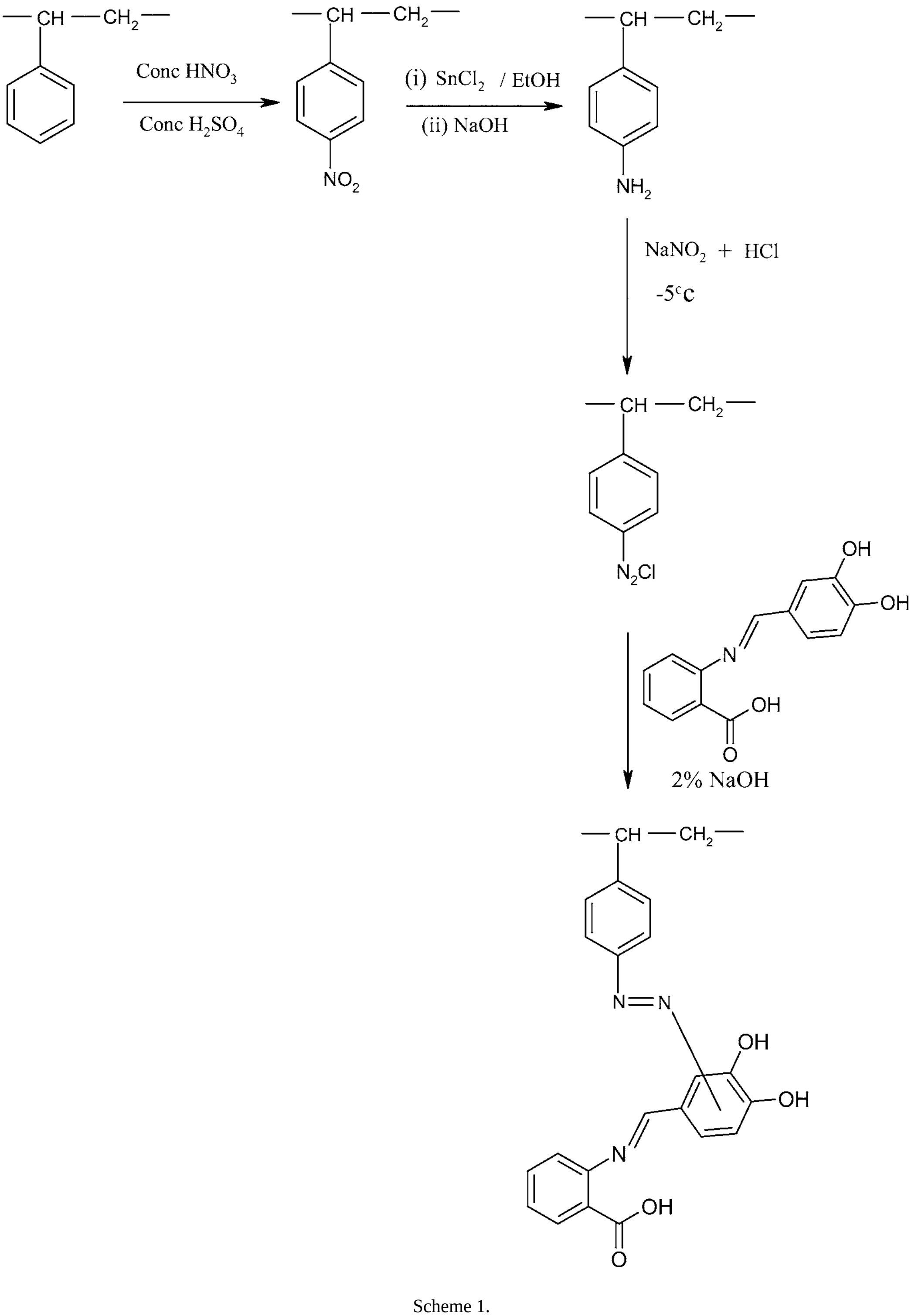


Fig. 1. Effect of pH on sorption of Zn(II), Mn(II), Ni(II), Pb(II), Cd(II), Cu(II), Fe(III) and Co(II) onto DMABA loaded Amberlite XAD-16.



Scheme 1.

desorbed (<2%) by distilled water; therefore, chelation contributes predominantly to the retention of metal ions.

3.3. Effect of flow rate and eluent

The metal ion sorption on a DMABA loaded Amberlite XAD-16 (1 g) packed column was studied at various flow rates of the metal ion solutions controlled with a peristaltic pump. The optimum flow rate for loading all these metal ions was 1.0–5.0 mL min^{-1}. A flow rate <1.0 mL min^{-1} was not employed to avoid the longer time of analysis. At flow rate >5.0 mL min^{-1}, there was a decrease in the percentage of sorption, probably because the metal ions do not equilibrate sufficiently with the matrix. HCl and HNO_3 were found to be the most suitable for stripping off the bound metal ions. For stripping the metal ions from the matrix flow rates 2.0–6.0 mL min^{-1} were found most effective. To study the effect of concentration of stripping solution on desorption of metal ions, the metal ions were eluted from the column with 10–25 mL of HCl/HNO_3 of varying concentration (1–4 mol L^{-1}) at optimum flow rate. The optimum concentration for maximum instant recovery (>97.0 %) of each individual metal ion is given Table 1. The 2 mol L^{-1} HCl was found sufficient for quantitative recovery of all the metal ions except Pb, which was quantitatively eluted with 1 mol L^{-1} HNO_3.

3.4. *Kinetics of metal sorption*

The kinetics of sorption was studied by batch method. DMABA-loaded Amberlite XAD-16 (0.5 g) was shaken with 50 mL of solution containing 40 μg mL^{-1} of one of the eight metal ions for different equilibration times (2, 5, 10, 15, 20, 25, 30, 40 min and 5 h) under optimum conditions. The concentration of metal ions loaded onto the matrix as well as present in the supernatant solution was determined with FAAS after appropriate dilution if needed. The variation of sorption as a function of time for all the metal ions is shown in Fig. 2. The shaking for 2 min was found to give >50% sorption for Mn, Ni, Cu and Fe. In 5 min, >50% sorption of Zn, Pb, Cd and Co is achieved.

3.5. *Effects of electrolytes and cations*

The chloride, nitrate, sulphate and phosphate anions (constituents of natural water samples) have the capability to complex with many metal ions. Therefore, in their presence, the efficiency of the ligand loaded on the matrix to bind metal ions may be hampered, resulting in the reduction of over all extraction. Thus, the effects of NaCl, NaBr, $NaNO_3$, Na_2SO_4, Na_3PO_4, NaI and other foreign species on the sorption efficiency of Zn(II), Mn(II), Ni(II), Pb(II), Cd(II), Cu(II), Fe(III) and Co(II) (25 μg each) onto AXAD-16-DMABA, were studied using the recommended column method under the optimum conditions given in Table 1. A species is considered to interfere when it lowers the recovery of metal ions more than 3% in comparison to the value observed in its absence. Each reported tolerance/interference is in the preconcentration and not in the determination by AAS, as checked with the help of reagent matched standard solutions. The tolerance limits of various foreign species in the sorption of all the metal ions are given in Table 2. These values indicate that sorption on Amberlite XAD-16-DMABA is not much sensitive to foreign species.

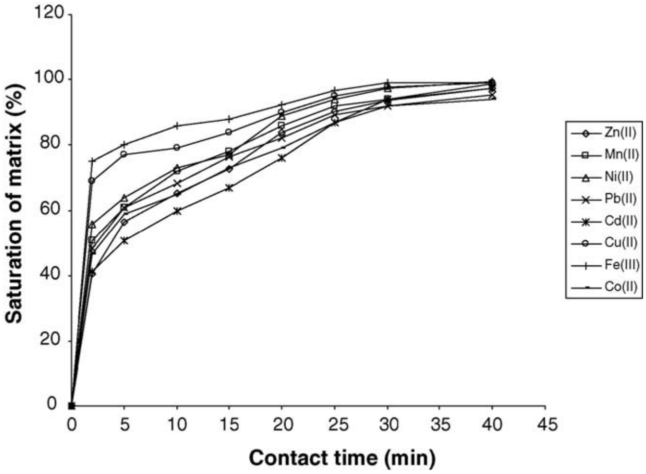


Fig. 2. Kinetics of the sorption of metal ions on DMABA loaded Amberlite XAD-16.

3.6. *Sorption capacity*

The sorption capacities of DMABA loaded Amberlite XAD-16 were determined by batch method. The resin (0.1 g) was saturated with Zn(II), Mn(II), Ni(II), Pb(II), Cd(II), Cu(II), Fe(III) or Co(II) ion solution (concentration: 50 μg mL^{-1}) by equilibration on a mechanical shaker under optimum conditions. The solid matrix was filtered and

Table 2
Tolerance limit of electrolytes, Ca(II), Mg(II) and other foreign species with AXAD-16-DMABA

Foreign species	Metal ion							
	Zn(II)	Mn(II)	Ni(II)	Pb(II)	Cd(II)	Cu(II)	Fe(III)	Co(II)
$NaNO_3$ (mol L^{-1})	0.070	0.140	0.440	0.050	0.190	0.480	0.120	0.020
NaCl (mol L^{-1})	0.350	0.150	0.200	0.010	0.080	0.600	0.270	0.140
NaBr (mol L^{-1})	0.011	0.100	0.020	0.032	0.010	0.090	0.022	0.030
Na_3PO_4 (mol L^{-1})	0.090	0.180	0.010	0.030	0.010	0.110	0.050	0.020
Na_2SO_4 (mol L^{-1})	0.080	0.040	0.270	0.580	0.160	0.690	0.420	0.190
NaI (mol L^{-1})	0.230	0.030	0.100	0.060	0.010	0.050	0.210	0.130
Humic acid (μg mL^{-1})	10.0	16.0	15.0	6.0	12.0	25.0	30.0	8.0
Ascorbic acid (mmol L^{-1})	0.220	0.180	0.650	0.050	0.760	0.400	0.160	0.550
Citric acid (mmol L^{-1})	0.160	0.650	0.120	0.560	0.850	1.200	1.800	0.470
EDTA (mmol L^{-1})	0.003	0.007	0.001	0.001	0.011	0.006	0.004	0.001
Tartaric acid (mmol L^{-1})	0.520	0.440	1.700	0.230	0.310	0.070	0.150	0.340
Ca(II) (mol L^{-1})	0.300	0.010	0.240	0.160	0.080	0.250	0.130	0.140
Mg(II) (mol L^{-1})	0.450	0.220	0.510	0.270	0.020	0.600	0.350	0.170

Table 3
Enrichment factors and enrichment limits of metal ions (AXAD-16-DMABA)

Metal ion	Total volume (mL)	Concentration (ng mL^{-1})	Final volume (mL)	Recovery %	Preconcentration factor
Zn(II)	3000	5.0	10	98.6	300
Mn(II)	2500	10.0	10	99.3	250
Ni(II)	1000	20.0	10	98.3	100
Pb(II)	2500	8.0	10	98.8	250
Cd(II)	2500	10.0	10	97.6	250
Cu(II)	3000	6.7	10	98.3	300
Fe(III)	4500	4.4	10	99.6	450
Co(II)	2500	8.0	15	98.2	167

washed with distilled water. Its loaded metal ions were desorbed with 100 mL of 2 mol L^{-1} HCl/1 mol L^{-1} HNO_3 and determined with FAAS to calculate the capacity. After filtering off the solid matrix the filtrate was diluted suitably (to bring the metal ion concentration in the working range) and also subjected to FAAS determination to determine the capacity. The sorption capacities are reported in Table 1. For iron it was found to be highest. The column method was also used to determine the sorption capacity. It was found to be nearly same (variation: <2.0%) by the two methods. Same sorption capacity values were found when 0.1 g of either resin was equilibrated with metal ion solution having concentration 200 μg mL^{-1}.

3.7. *Resin stability and reusability*

The stability of DMABA-loaded Amberlite XAD-16 was studied in acid (1–6 mol L^{-1} HCl/HNO_3). It was shaken with acid solutions of varying concentrations for 4 h and filtered. The solid was washed with distilled water until free from acid, air-dried and its sorption capacity was determined using batch method. The sorption capacity of the acid treated was resin was found to be similar (variation: <3%) to that of the untreated one. This shows that the present resin can withstand acid concentration up to 6 mol L^{-1}. It can also be reused for 50 cycles of sorption–desorption without any significant change in the sorption capacity (<1.5%).

3.8. *Preconcentration and recovery of metal ions*

Enrichment factor was determined by increasing the dilution of metal ion solution while keeping the total amount of loaded metal ion fixed at 15 μg for Mn, 20 μg for Fe, Cd or Pb and 25 μg for Zn, Cu, Co or Ni and applying the recommended column procedure. These were guided by middle concentration value of calibration curve of each metal ion, as it should be available in the final eluate so that error is least. The preconcentration factors and feed volumes are given in Table 3 (recovery (%) is at lowest concentration). The limit of detection values (defined as (blank +3s)) are 1.12, 1.38, 1.76, 0.67, 3.92, 0.77, 2.52 and 1.08 μg L^{-1} for Zn(II), Mn(II), Ni(II), Pb(II), Cd(II), Cu(II), Fe(III) and Co(II), respectively, and corresponding limit of quantification (blank +10 s) values are 1.57, 1.82, 1.96, 0.96, 5.53, 1.06, 2.86 and 1.43 μg L^{-1}, respectively.

4. Applications of the method

4.1. *Determination of metal ions in water samples*

AXAD-16-DMABA was used to preconcentrate Cu(II), Zn(II), Fe(III), Ni(II), Mn(II), Co(II), Cd(II) and Pb(II) ions in water samples collected from the Ganges (Haridwar) and municipality taps (New Delhi), followed by their determination with FAAS. The estimation of all the eight metal ions was made with and without (referred as direct determination) standard addition (S.A.) by passing 1000 mL of water sample (spiked with 50–100 μg of each of the seven metal ions in the case of standard addition method) through the column packed with 1.0 g of matrix 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 HCl except for Pb for which 1 M HNO_3 was used. The results are given in Table 4 and reflect the suitability of the resin for water analysis. The concentrations reported in Table 4 as estimated by standard addition method are the values obtained by subtracting the amount of metal added

Table 4
Determination of metal ions in water samples using AXAD-16-DMABA

Origin of sample	Method	Metal ion (μg L^{-1})							
		Zn (R.S.D.)	Mn (R.S.D.)	Cd (R.S.D.)	Ni (R.S.D.)	Pb (R.S.D.)	Fe (R.S.D.)	Cu (R.S.D.)	Co (R.S.D.)
Ganges river, Haridwar	Direct	3.8 (3.7)	6.0 (3.4)	4.4 (5.3)	5.5 (3.7)	3.1 (8.0)	53.5 (0.6)	20.5 (0.9)	13.1 (1.8)
	S.A.	3.7 (6.4)	5.9 (2.4)	4.6 (2.9)	5.8 (6.0)	2.9 (5.0)	53.8 (0.2)	20.7 (1.1)	13.2 (1.0)
Tap water New Delhi	Direct	14.3 (1.0)	14.9 (1.6)	6.7 (3.0)	7.5 (2.7)	13.1 (2.3)	95.5 (0.2)	27.9 (0.8)	15.7 (1.2)
	S.A.	14.4 (1.0)	14.5 (2.2)	6.8 (2.2)	7.7 (4.3)	12.9 (1.9)	95.8 (0.3)	27.6 (1.0)	15.8 (1.3)

Direct, recommended procedure is directly applied; S.A., standard addition method; RSD (%), for four determinations.

for spiking from the total metal recovered. The closeness of results of direct and SA method indicates the reliability of present results of metal analyses in water samples.

4.2. *Determination of Co in pharmaceutical samples*

Solid phase extraction with AXAD-16-DMABA coupled with FAAS method of determination was applied to determine cobalt in pharmaceutical samples. Ten tablets (weighing 3.25 g) of Polybion (Merck, Mumbai, India) were digested in a beaker containing 25 mL of concentrated HNO_3 by slowly increasing the temperature of the mixture to 400 K. The mixture was further heated till a solid residue was obtained. It was allowed to cool and dissolved in 20 mL of concentrated HNO_3. The solution was gently evaporated on a steam bath until a residue was left again. It was mixed with 50 mL of distilled water and concentrated HNO_3 was added drop wise until a clear solution was obtained on gentle heating. The pH of the solution was adjusted to optimum value (Table 1) and the concentration of cobalt was estimated by the recommended column procedure using FAAS. The average (four determinations) amount of cobalt was found to be 1.96 $\mu g\,g^{-1}$ of tablet with an R.S.D. of 4.8%. The reported value of cobalt in the tablet is 1.99 $\mu g\,g^{-1}$ of tablet.

4.3. *Determination of Zn in a milk sample*

A sample of powdered milk (1.0 g) was heated in a beaker containing mixture of concentrated sulphuric acid (20 mL) and nitric acid (8 mL) till a clear solution was obtained. It was allowed to cool and most of the acid was neutralized with sodium hydroxide. The pH was adjusted to optimum value and the volume was made up to 1000 mL. The concentration of zinc was estimated by passing the solution through the column packed with DMABA loaded Amberlite XAD-16. The metal ion was eluted from the column using 2 $mol\,L^{-1}$ HCl (as per recommended procedure) and determined using FAAS. The average (four determinations) amount of zinc was found to be 37.50 $\mu g\,g^{-1}$ (R.S.D. ~4.21%). The reported value of zinc in the milk sample is 38 $\mu g\,g^{-1}$.

4.4. *Analysis of synthetic water samples*

To check the validity and accuracy of the present matrix coupled with FAAS for metal ion monitoring, the recommended procedure was applied to determine copper and iron content in synthetic water samples (1000 mL) having composition similar to certified water samples SLRS-4 (National Research Council, Ottawa, Ontario, Canada). The average of four determinations of copper was found to be 1.80 $\mu g\,L^{-1}$ (R.S.D. 4.5%). The iron in these synthetic samples was found to be 102.0 $\mu g\,L^{-1}$ (R.S.D. 4.8%). The amount ($\mu g\,L^{-1}$) of two metal ions present in synthetic sample was: Cu, 1.81 and Fe, 103.

5. Conclusion and comparison with other chelating matrices

The sorption capacities of the present resin are compared with those of other chelating matrices in Table 5. It shows higher capacities in comparison to others (particularly those having Amberlite XAD-2 as support) with very few exceptions. One of them is *N*-(3,4-dihydroxy)benzyl-4-amino-3-hydroxynaphthalene-1-sulphonic acid loaded Amberlite XAD-16. The values reported for this matrix are many

Table 5
Comparison of sorption capacities ($\mu mol\,g^{-1}$)

Support: immobilized ligand	Zn	Mn	Ni	Cd	Pb	Cu	Fe	Co
Amberlite XAD-2								
Thiosalicylic acid [11]	47		310	198	89	214	66	106
Chromotropic acid [8,15]	148		103	83	186	134	58	65
Pyrocatechol [12,15]	28		53	41	105	93	74	23
o-Aminophenol [9]	45		55	30	16	53		58
Tiron [10]	170	182	215	84	60	220	100	110
Pyrogallol [14]	69	82	70	46	32	71	83	70
Quinalizarin [13]	22	17		15	26	50		28
1-(2-Pyridylazo)-2-naphthol [24]				23	7	108		
Amberlite XAD-7								
Xylenol orange [25]	28		45	18	17	25	29	44
Amberlite XAD-16: DMABA(present matrix)	198	178	269	128	97	468	515	221
N-(3,4-dihydroxy)benzyl -4-amino,3-hydroxynaphthalene-1-sulphonic acid [21]			1210	760	880	2050		780
Silica gel								
Resacetophenone [26]	191		254	58	67	186	272	365
5-Formyl-8-hydroxy quinoline[27]	177		255	92	158	448	386	205
Cellulose 2,3-DHP [28]	315		208	70	83	343	431	146
Pyrocatechol [29]	85		140	116	104	186	109	159
8-Hydroxyquinoline [30]	349		178	114	94	630	256	205
Pyrogallol [31]	123		148	99	92	202	160	168

Table 6
Comparison of preconcentration factors

Support: immobilized ligand	Zn	Mn	Ni	Cd	Pb	Cu	Fe	Co
Amberlite XAD-2								
Thiosalicylic acid [11]	200		200	200	100	200	400	180
Chromotropic acid [8,15]	200		200	100	200	100	120	150
Pyrocatechol [12,15]	100		200	200	200	100	80	200
o-Aminophenol [9]	40		65	50	40	50		100
Tiron [10]	180	64	150	48	25	200	80	56
Pyrogallol [14]	160	120	120	40	25	65	140	65
Quinalizarin [13]	100	65		50	50	100		40
1-(2-Pyridylazo)-2-naphthol [24]	50				50	50		
Amberlite XAD-7								
Xylenol orange [25]	100		100	50	50	50	100	100
Amberlite XAD-16								
DMABA(present matrix)	300	250	100	250	250	300	450	167
N-(3,4-dihydroxy)benzyl-4-Amino,3-hydroxynaphthalene-1-sulphonic acid [21]	300		333	267	234			300
Silica gel								
Resacetophenone [26]	150		200	250	250	250	200	300
5-Formyl-8-hydroxy quinoline [27]	200		200	150	250	300	300	250
Cellulose 2,3-DHP [28]	200		125	200	200	250	300	100
Pyrocatechol [29]	180		75	250	200	300	300	100
8-Hydroxyquinoline [30]	250		90	250	200	300	300	100
Pyrogallol [31]	200		133	250	200	300	250	133

times of the capacity values generally observed for chelating solid phase extractors. The exceptional performance of *N*-(3,4-dihydroxy)benzyl-4-amino-3-hydroxynaphthalene-1-sulphonic acid loaded Amberlite XAD-16 cannot be completely attributed to the organic polymer (due to its high surface area) used to support the chelating ligand. In Table 6, the preconcentration factors of the present chelating matrices are compared with those of other chelating extractors. The performance of AXAD-16-DMABA is superior than most of the other matrices. The preconcentration factors reported for *N*-(3,4-dihydroxy)benzyl-4-amino-3-hydroxynaphthalene-1-sulphonic acid loaded Amberlite XAD-16 are not exceptionally high unlike the sorption capacities.

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