

RESIDUES AND TRACE ELEMENTS

A New Chelating Resin for Preconcentration and Determination of Mn(II), Ni(II), Cu(II), Zn(II), Cd(II), and Pb(II) by Flame Atomic Absorption Spectrometry

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A new polychelator, AXAD-16-1,2-diphenylethanolamine, was developed by chemically modifying Amberlite XAD-16 with 1,2-diphenylethanolamine to produce an effective metal-chelating functionality for the preconcentration of Mn(II), Ni(II), Cu(II), Zn(II), Cd(II), and Pb(II) and their determination by flame atomic absorption spectrometry. Various physicochemical parameters that influence the quantitative preconcentration and recovery of metal were optimized by both static and dynamic techniques. The resin showed superior extraction efficiency with high-metal loading capacity values of 0.73, 0.80, 0.77, 0.87, 0.74, and 0.81 mmol/g for Mn(II), Ni(II), Cu(II), Zn(II), Cd(II), and Pb(II), respectively. The system also showed rapid metal-ion extraction and stripping, with complete saturation in the sorbent phase within 15 min for all the metal ions. The optimum condition for effective metal-ion extraction was found to be a neutral pH, which is a great advantage in the preconcentration of trace metal ions from natural water samples without any chemical pretreatment of the sample. The resin also demonstrated exclusive ion selectivity toward targeted metal ions by showing greater resistivity to various complexing species and more common metal ions during analyte concentration, which ultimately led to high preconcentration factors of 700 for Cu(II); 600 for Mn(II), Ni(II), and Zn(II); and 500 for Cd(II) and Pb(II), arising from a larger sample breakthrough volume. The lower limits of metal-ion detection were 7 ng/mL for Mn(II) and Ni(II); 5 ng/mL for Cu(II), Zn(II), and Cd(II), and 10 ng/mL for Pb(II). The developed resin was successful in preconcentrating metal ions from synthetic and real water samples, multivitamin-multimineral tablets, and curry leaves (*Murraya koenigii*) with relative standard deviations of $\leq 3.0\%$ for all analytical measurements, which demonstrated its practical utility.

One of the most difficult analytical tasks involved in trace metal analysis is quantification, a complicated process because of the presence of various complex matrixes encapsulated in large amounts along with the analytes, in sources such as seawater and other natural systems (1). The best approach to obtain reliable and reproducible results is to separate the analytes of interest from the source before analysis. For this purpose, 2 separation techniques, namely, solvent extraction (SE) and solid-phase extraction (SPE), have played a major role in analyte preconcentration. The use of SE is often laborious and time-consuming because of multiple extraction steps and problems associated with the disposal of large amounts of organic waste (2). The use of SPE is an effective alternative, which benefits both the analysis and the environment.

SPE, a hybrid of liquid-liquid extraction and ion-exchange techniques, is emerging in its field with significant features such as ecofriendliness, faster kinetics, greater reusability, and cost effectiveness (3, 4). The use of SPE started with various solid supports such as silica gel, kieselguhr, and activated charcoal, but the current development involves the use of functionalized styrene copolymers that provide a system of high flexibility, durability, and workability under a wide range of experimental conditions, with a variety of organic ligands (5–13). Significant development has been achieved by using chelating polymers, such as Amberlite XAD (AXAD) resins, 9, 14–22 which have proved quite effective. AXAD resins are available commercially in various pore sizes, volumes, and internal diameters with such names as AXAD-2, -4, -12, and -16. The use of AXAD-16 as a solid support appeared promising because of its larger pore size and volume, which favor enhancement of ligand functionality; the system also showed greater water regaining capacity, which ultimately favors increased surface contact with the aqueous phase, as demonstrated by the resin's faster kinetic behavior. Notable work has been done with AXAD-2, -4, and -12, but the use of AXAD-16 has been limited (23–27). Based on these features, a new polychelator, AXAD-16-1,2-diphenylethanolamine, was developed. The metal-chelating properties of the new resin system were studied, and extractive behavior under various experimental parameters was investigated and optimized. Table 1 shows the superiority of the developed resin matrix in terms of its metal-loading capacity and preconcentration factor over those reported for other AXAD resin matrixes. The

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Table 1. Comparison of AXAD-16-1,2-diphenylethanolamine with other chelating matrixes in terms of metal-ion sorption capacity and preconcentration factor

Functionalized AXAD resin matrix ^a	Metal-ion sorption capacity, mmol/g ^b					
	Mn(II)	Ni(II)	Cu(II)	Zn(II)	Cd(II)	Pb(II)
AXAD-16-1,2-diphenylethanolamine	0.73 (600)	0.80 (600)	0.77 (700)	0.87 (600)	0.71 (500)	0.81 (500)
AXAD-16-1,3-dimethyl-3-aminopropan-1-ol (23)	0.62 (300)	0.55 (300)	0.46 (400)	0.25 (250)	0.21 (300)	0.23 (500)
AXAD-4-1-hydrozinophthalazine (15)	—	0.82 (50)	1.24 (50)	0.74 (50)	0.96 (50)	0.86 (50)
AXAD-4- <i>p</i> - <i>tert</i> -butylcalix[8]arene (6)	—	0.44 (58)	0.78 (50)	0.72 (50)	0.70 (50)	0.70 (50)
AXAD-4-Bicine (22)	—	0.39 (50)	0.38 (50)	0.38 (50)	—	0.40 (50)
AXAD-4- <i>o</i> -vanillinthio semicarbazone (8)	—	—	0.01 (90)	0.02 (140)	0.01 (100)	—
AXAD-2-thiosalicylic acid (12)	—	0.31 (200)	0.21 (200)	0.05 (200)	0.20 (200)	—
AXAD-2-tiron (18)	0.18 (64)	0.21 (150)	0.22 (200)	0.17 (180)	0.08 (48)	0.06 (25)
AXAD-2- <i>o</i> -aminophenol (22)	—	0.06 (65)	0.05 (50)	0.05 (40)	0.03 (50)	—

^a Values in parentheses are reference numbers.

^b Values in parentheses are preconcentration factors.

developed ion-selective resin was tested for its practical applicability with various real and synthetic samples, including curry leaves (*Murraya koenigii*).

Experimental

Apparatus

(a) *Spectrometer*.—A Varian SpectrAA-20 (Varian Techtron, Springvale, Australia) atomic absorption spectrometer was used for the determination of Mn(II), Ni(II), Cu(II), Zn(II), Cd(II), and Pb(II).

(b) *Transform spectrometer*.—IR spectra and FIR spectra for characterization of the chemically modified matrix were recorded by using a Bruker Model IFS 66V Fourier transform spectrometer (Bruker, Ettlingen, Germany).

(c) *Analyzer*.—A Elementar Vario EL analyzer (Varian Techtron) was used for elemental (CHN) analysis. A Perkin-Elmer thermal analyzer was used for thermogravimetric analysis (TGA) studies.

(d) *pH meter*.—All pH adjustments were made by using a Digusun DI-707 pH meter (Instruments and Equipment, Mumbai, India).

(e) *Mechanical shaker*.—An Orbitek Model DL (Scigenics, Chennai, India) mechanical shaker at 200 rpm was used for all the static studies.

Reagents

All reagents used were analytical grade.

(a) *Standard solutions of Mn(II), Ni(II), Cu(II), Zn(II), Cd(II), and Pb(II)*.—Prepared by dissolving appropriate amounts of MnCl₂·4H₂O, NiSO₄·6H₂O, CuSO₄·5H₂O, ZnSO₄·7H₂O, 3CdSO₄·8H₂O, and Pb(NO₃)₂ in water; the solutions were slightly acidified with the corresponding acid before they were diluted to the required volume.

(b) *Glycine-HCl (pH 1–3), sodium acetate-acetic acid (pH 4–6.5), and ammonium acetate-ammonia (pH 7–8)*.—0.02M concentrations. Used to make pH adjustments.

(c) *AXAD-16*.—With surface area of 825 m²/g, pore diameter of 20–50 mesh, and bead size of 0.3–1.2 mm (Fluka Chemie, Buchs, Switzerland); used as the polymer backbone for the synthesis of the chelating resin. A 10 g portion of the resin was soaked in 4M HCl overnight and washed with distilled water until the pH was neutral. It was further washed with ethanol, filtered, dried, and vacuumized before use.

(d) *Benzoin and sodium borohydride*.—Used as received without any further purification (Merck Ltd, Mumbai, India).

Synthesis of AXAD-16-1,2-diphenylethanolamine

A 5 g portion of the vacuumized AXAD-16 was treated with the nitrating mixture (25 mL H₂SO₄ plus 10 mL HNO₃) at 70°C for 2 h. The yellow nitrated resin was refluxed with 40 g SnCl₂, 45 mL concentrated HCl, and 50 mL absolute ethanol for 9 h at 90°C to form the amino resin after an NaOH wash (8). The alkali-free amino resin was refluxed with a 4 Å molecular sieve with 5 g benzoin dissolved in absolute alcohol to produce yellow imine resin beads, which were washed with hot ethanol to remove excess benzoin. The imine resin was reduced to the more stable AXAD-16-1,2-diphenylethanolamine by using 5 g NaBH₄ in dry methanol under ice-cold conditions (23). The resin was washed with distilled water until the pH was neu-

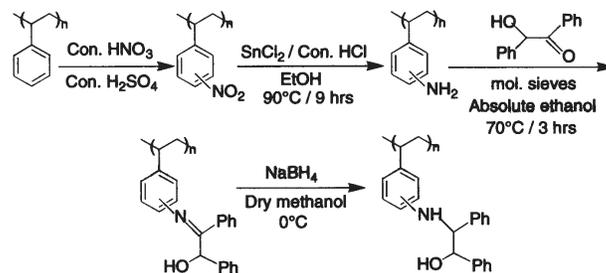


Figure 1. Synthesis of the chelating-resin matrix.

Table 2. Optimum experimental parameters for sorption and desorption of metal ions

Experimental parameter	Mn(II)	Ni(II)	Cu(II)	Zn(II)	Cd(II)	Pb(II)
pH range	7.0–7.5	7.0–8.0	7.0–8.0	6.5–8.0	6.5–7.0	6.5–7.0
$t_{1/2}$, min	4.0	2.5	4.9	2.8	3.2	4.2
Metal sorption capacity, mmol/g	0.73	0.80	0.77	0.87	0.74	0.81
Concn of HCl for desorption, mol/L	3.0	4.0	2.0	2.0	3.0	4.0
Avg. recovery, %	99.9	100.0	100.0	99.6	99.9	99.8
Optimum flow rate, mL/min	2.0–7.0	2.0–9.0	2.0–7.0	2.0–9.0	2.0–7.0	2.0–7.0
Preconcentration factor	600	600	700	600	500	500

tral, filtered, and vacuum-dried. The synthesized resin was characterized by using IR, FIR, TGA, and CHN analysis. The synthetic route resulting in the desired chelating-resin matrix is depicted in Figure 1.

Recommended Procedure for Sorption Studies of Mn(II), Ni(II), Cu(II), Zn(II), Cd(II), and Pb(II)

(a) Static method.—A 50 mg portion of the resin matrix was equilibrated with 50 mL metal-ion solution (10 $\mu\text{g/mL}$) at 200 rpm in a mechanical shaker in a 125 mL well-stoppered reagent bottle for 1 h after the sample was adjusted to optimum pH, at which maximum sorption was observed. The resin was filtered, washed, and stripped with 10 mL of the optimum desorbing agent. The concentrations of the desorbed Mn(II), Ni(II), Cu(II), Zn(II), Cd(II), and Pb(II) were determined by using flame atomic absorption spectrometry (FAAS). The optimum parameters for the sorption and desorption of the analytes of interest are listed in Table 2. The resin beads were reused after they were washed with distilled water until the pH was neutral.

(b) Dynamic method.—A 1 g portion of the resin beads (preconditioned earlier with suitable buffer solution) was packed by the slurry method in a glass column (13 \times 0.6 cm) to a bed height of 5 cm, which was washed with water before use. The sample solution of 1000–8000 mL was passed through the column under optimized flow rates ranging from 2 to 9 mL/min, depending on the nature of the metal ions to be extracted, as shown in Table 2. The sorbed metal ions were preconcentrated by using 10 mL of the optimum eluant, and their concentrations were determined by FAAS. The used resin beads were washed with distilled water until the pH was neutral and preconditioned by the method described earlier for subsequent preconcentration studies.

Results and Discussion

Characterization of the Polychelator

The IR spectrum for the vacuum-dried functionalized resin showed spectral bands corresponding to -OH and -NH stretching frequencies in the region ranging from 3500 to 3250 cm^{-1} . Furthermore, additional bands at 1502.3 and

1373.1 cm^{-1} due to the C-N stretching frequency confirmed the presence of the chelating ligand moiety attached to the polymeric backbone. The extent of resin functionalization during each stage of the reaction was carefully studied by the appearance and disappearance of the stretching frequencies of the corresponding functional groups.

The IR spectrum of the metal-chelated resin matrix showed a red shift in the range of 15–20 cm^{-1} for C-N and -OH stretching frequencies, indicating the active participation of the chelating sites in the process of metal chelation. This was evident from FIR data in the region of 500–100 cm^{-1} , which showed spectral bands in the region of 500–400 and 290–120 cm^{-1} , indicating $\nu_{\text{N-M}^{n+}}$ and $\nu_{\text{O-M}^{n+}}$ vibrational frequencies of the chelating active sites.

The CHN analyses were also performed for each step, and the results agreed with the corresponding theoretical values. The CHN elemental analysis for the desired final step showed percentage values of C, 82.71; H, 6.94; and N 4.53, which compares with the theoretical values of C, 83.8; H, 6.66; and N, 4.44 showed the incorporation of at least one ligand moiety per repeating unit of the polymer matrix. These results are supported by IR data as discussed above. The slight deviation from the theoretical data implies the incomplete conversion at each stage of resin functionalization.

TGA data showed a gradual weight loss of about 6% up to 110°C, indicating the presence of water molecules in the pores

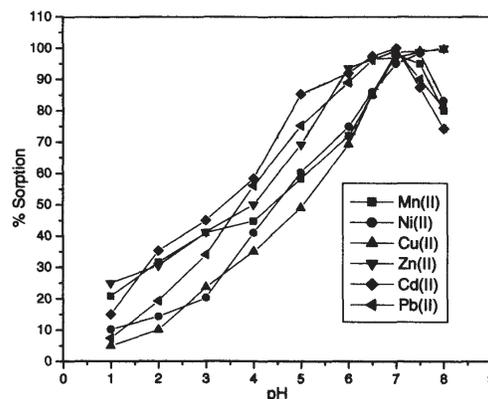


Figure 2. Effect of solution pH on exchange capacity.

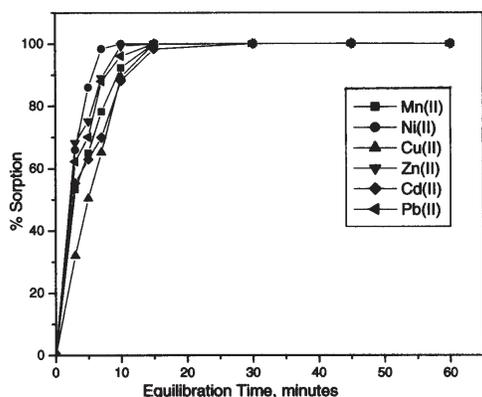


Figure 3. Kinetics studies of metal-ion extraction.

of the polymeric matrix, thereby ensuring a better hydrophilicity character for the resin beads.

Optimization of Parameters by Using the Static Method

(a) *Effect of solution pH on metal-ion sorption.*—The pH at which the resin functions at its maximum extracting capacity was investigated by equilibrating 0.05 g resin with metal-ion solutions (50 mL, 10 $\mu\text{g/mL}$) over a wide range of equilibrium pH by using corresponding buffer solutions. The resin beads were filtered, and the sorbed metal ions were desorbed using 4M HCl. Metal-ion analysis was performed by using FAAS, and the metal-ion extracting capability of the resin under various values of solution pH is shown in Figure 2. The maximum sorption for all the metal ions studied was found at near neutral conditions; this finding allowed the analysis of natural water samples without any chemical pretreatment.

(b) *Recovery studies.*—The quantitative metal-ion recovery from the sorbent phase was studied by equilibrating 0.05 g resin matrix with metal-ion solution (50 mL, 10 $\mu\text{g/mL}$) under optimum pH conditions. The metal ion sorbed to the resin phase was shaken with different concentrations of HCl acid as eluting agents, and the quantitative recoveries were determined by FAAS; the results are shown in Table 2. Quantitative

recoveries were obtained with 4M HCl in the case of Ni(II) and Pb(II), whereas other metal ions were recovered with even low acid concentrations, indicating a more stable metal-polymer complex by Ni(II) and Pb(II).

(c) *Kinetics studies.*—The rate of metal-ion sorption to the sorbent phase was studied by shaking 0.05 g resin with individual metal-ion solutions (50 mL, 5 $\mu\text{g/mL}$) under optimum pH for various time periods as shown in Figure 3. The sorbed metal ions were recovered, and their concentrations were determined. The sorbent phase requires ≥ 15 min for metal-ion saturation, indicating a faster accessibility of the chelating sites to the metal ions.

(d) *Metal sorption capacity of the resin.*—The maximum metal sorption capacity of the developed polychelator was studied by shaking 0.05 g resin with an excess of each of the individual metal ions (50 mL, 200 $\mu\text{g/mL}$) under optimum solution pH for 6 h. The metal-ion concentration in the resin phase was estimated after desorption. The maximum resin-sorption capacities of 0.73, 0.80, 0.77, 0.87, 0.74, and 0.81 mmol/g were obtained for Mn(II), Ni(II), Cu(II), Zn(II), Cd(II), and Pb(II), respectively. With the assumption of 1:1 complex formation with the matrix, the theoretical resin capacity based on CHN analysis was calculated to be 3.31 mmol/g from experimental CHN data, calculated in terms of a single repeating unit of chelating polymer. The decrease in the actual sorption capacity for each individual ion may be attributed mainly to the nonaccessibility of some of the chelating sites and also to the formation of complexes in different metal-ligand ratios.

(e) *Stability and reusability of the developed polychelator.*—The reliability of the developed analytical method was studied by shaking 0.05 g resin beads with a sample solution (50 mL, 10 $\mu\text{g/mL}$) under optimum pH conditions. The resin beads were filtered, washed, and leached, and the metal ions were determined. The same resin beads were subjected to similar treatment several times, and the results showed good reproducibility and reusability for >30 cycles, with a precision of 3.2% for triplicate measurements, even with the treatment of high acid concentrations, reflecting the good chemical and mechanical durability of the resin.

Table 3. Tolerance limits of diverse electrolyte species

Electrolyte species	Tolerance limit, mol/L					
	Mn(II)	Ni(II)	Cu(II)	Zn(II)	Cd(II)	Pb(II)
NaCl	0.655	0.684	0.578	0.668	0.590	0.571
KNO ₃	0.380	0.395	0.335	0.475	0.412	0.435
MgSO ₄	0.091	0.087	0.125	0.089	0.087	0.088
CaCl ₂	0.123	0.136	0.147	0.162	0.175	0.231
Na ₃ PO ₄	0.083	0.073	0.096	0.031	0.081	0.096
NaF	0.321	0.476	0.485	0.430	0.452	0.315
NH ₄ ⁺	0.052	0.127	0.113	0.056	0.054	0.060

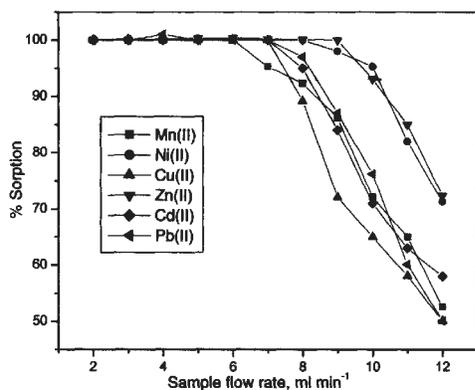


Figure 4. Effect of sample flow rate on metal-ion phase equilibration.

(f) *Ion-selectivity studies and tolerance limits of diverse species on metal-ion sorption.*—The tolerance limits of various interfering species that could affect the sorption of the analytes of interest were determined. A solution of the analyte of interest (50 mL, 1 $\mu\text{g/mL}$), along with various concentrations of individual diverse ions at optimum pH, was shaken with 0.05 g resin. The concentrations of the diverse ions were increased to a level at which 0% loss in the analyte signal was observed. The tolerable limits for analyte extraction with various diverse species are shown in Table 3. The results reflect excellent ion selectivity of the resin toward the targeted analytes over major matrix components found in natural samples. This finding is of great significance in the selective extraction of targeted species under high saline conditions.

Studies Performed by Using the Dynamic Method

(a) *Optimization of sample and eluant flow rates.*—The effect of sample flow rate on quantitative metal-ion sorption was examined by passing metal-ion solutions (1000 mL, 0.1 $\mu\text{g/mL}$) at flow rates ranging from 2 to 12 mL/min through the preconditioned resin column, where the flow rates were adjusted by a type of Marriott's apparatus. The results are shown in Figure 4, in which quantitative metal-ion sorption was obtained with flow rates of 8–9 mL/min for Ni(II) and Zn(II) and 6–7 mL/min for the other metal ions, reflecting faster metal-ion equilibration from the aqueous phase to the resin phase. An optimum eluant flow rate of 2 mL/min was found to be effective in all cases for complete metal-ion recovery, thereby reducing the time of analysis.

(b) *Sample and eluant breakthrough volumes.*—Sample breakthrough volume is defined as the volume up to which quantitative sorption is achieved, as determined by passing various sample volumes ranging from 500 to 8000 mL, each spiked with 100 μg metal ion in the presence of various interfering electrolyte species, through the resin column under optimum conditions of flow rate. Recovery of the metal ions after desorption was determined for individual samples. The sample breakthrough-volume curve (Figure 5) shows high preconcentration factors of 700 for Cu(II); 600 for Mn(II), Zn(II), and Ni(II); and 500 for Cd(II) and Pb(II). These val-

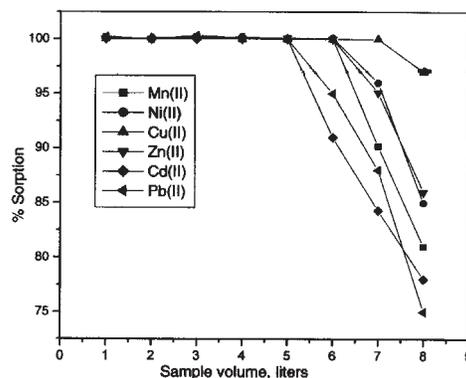


Figure 5. Effect of sample breakthrough volume on metal-ion extraction.

ues, which were found to be predominantly greater when compared with those for developed resins, reflect the capability of the developed resin matrix in preconcentrating metal ions from large sample volumes. An optimum eluant volume of 10 mL was found to be sufficient for quantitative recovery of the analytes.

(c) *Sensitivity of the developed method.*—The sensitivity of the chelating matrix was determined by studying the lower limit of detection, 5000 mL sample containing 10–100 μg metal ions was passed through the resin column, and the sorbed metal ions were desorbed and determined. The sensitivity studies found LODs of 3 ng/mL for Zn(II) and Cd(II), 5 ng/mL for Cu(II), 7 ng/mL for Mn(II) and Ni(II), and 10 ng/mL for Pb(II), with no loss in analyte signal, proving the capability of the resin to extract metal ions at ppb levels.

Applications

(a) *Analysis of a synthetic seawater mixture.*—A 3000 mL volume of a synthetic seawater mixture was prepared by strictly following the published procedure (28). It was then passed through the preconditioned resin column. The metal ions were recovered by using 10 mL 4M HCl, and the concentrations of the metal ions were determined by FAAS, which showed quantitative recoveries of the metal ions. The synthetic mixture spiked with 20 μg of each of the individual metal ions was passed through the resin bed. The recovery values were in the range of 99–100%, reflecting the quantitative extraction of the resin matrix under high saline conditions, and allowing its application as a metal-ion preconcentrator for various real samples.

(b) *Preconcentration and estimation of trace metal ions from natural water samples.*—Real water samples (sea/well/tap/river), 5000 mL each, were passed through a 0.2 μm membrane filter, then through the columns to remove particulate matters. The metal ions from the water samples were preconcentrated without any dilution, the sorbed metal ions were eluted with 10 mL 4M HCl, and their concentrations were determined by FAAS as indicated in Table 4. The analytical reliability was tested by the method of standard additions in which 20 μg of each metal ion was added to the water sam-

Table 4. Application of the chelating matrix in preconcentrating metal ions from water samples

Sample nature, source, and time of collection	Method	Metal-ion concentration, ng/mL (RSD, %) ^a						
		Mn(II)	Ni(II)	Cu(II)	Zn(II)	Cd(II)	Pb(II)	
Seawater, Marina (Chennai; Dec. 2002)	Direct	5.05 ± 0.17 (1.8)	8.24 ± 0.24 (1.6)	14.48 ± 0.35 (1.3)	10.55 ± 0.45 (2.3)	0.71 ± 0.03 (2.1)	0.29 ± 0.01 (1.2)	
	SA ^b	5.11 ± 0.20 (2.1)	8.21 ± 0.30 (2.0)	14.51 ± 0.53 (2.0)	10.62 ± 0.37 (1.9)	0.73 ± 0.04 (2.3)	0.31 ± 0.01 (2.1)	
Seawater, Mahabalipuram (Chennai; May 2002)	Direct	6.02 ± 0.23 (2.1)	9.32 ± 0.36 (2.1)	18.41 ± 0.88 (2.6)	12.31 ± 0.29 (1.3)	0.96 ± 0.04 (2.0)	0.16 ± 0.01 (2.5)	
	SA	6.18 ± 0.27 (2.4)	9.29 ± 0.26 (1.5)	18.20 ± 0.84 (2.5)	12.42 ± 0.52 (2.3)	0.94 ± 0.04 (2.1)	0.21 ± 0.01 (1.3)	
Well water, Broadway (Chennai; Nov. 2002)	Direct	8.35 ± 0.24 (1.6)	14.58 ± 0.45 (1.7)	12.34 ± 0.60 (2.2)	20.30 ± 0.67 (1.8)	1.10 ± 0.03 (1.7)	14.44 ± 0.80 (3.0)	
	SA	8.42 ± 0.34 (2.2)	14.64 ± 0.51 (1.9)	12.60 ± 0.60 (2.6)	20.50 ± 0.56 (1.5)	1.15 ± 0.06 (2.8)	15.23 ± 0.67 (2.4)	
Well water, Trishur (Kerala; Jan. 2003)	Direct	1.81 ± 0.09 (2.9)	2.98 ± 0.11 (2.0)	14.46 ± 0.58 (2.2)	35.77 ± 1.38 (2.1)	0.62 ± 0.02 (1.7)	9.05 ± 0.45 (2.7)	
	SA	1.84 ± 0.07 (2.1)	2.91 ± 0.16 (3.0)	14.41 ± 0.45 (1.7)	35.79 ± 1.64 (2.5)	0.66 ± 0.03 (2.7)	9.06 ± 0.40 (2.4)	
River water, Godavari (Andhra Pradesh; Dec. 2002)	Direct	7.10 ± 0.25 (1.9)	16.32 ± 0.84 (2.8)	19.20 ± 0.85 (2.4)	12.34 ± 0.48 (2.1)	2.12 ± 0.07 (1.9)	16.21 ± 0.74 (2.5)	
	SA	7.12 ± 0.31 (2.4)	16.42 ± 0.63 (2.1)	19.18 ± 0.74 (2.1)	12.47 ± 0.34 (1.5)	2.06 ± 0.09 (2.5)	16.30 ± 0.90 (3.0)	
Tap water, IITM (Chennai; Jan. 2003)	Direct	16.31 ± 0.57 (1.9)	9.60 ± 0.33 (1.9)	32.41 ± 1.07 (1.8)	142.50 ± 3.14 (1.2)	1.31 ± 0.06(2.5)	22.35 ± 0.98 (2.4)	
	SA	16.38 ± 0.72 (2.4)	9.84 ± 0.52 (2.9)	32.52 ± 1.31 (2.2)	143.01 ± 6.04 (2.3)	1.26 ± 0.05 (2.1)	22.19 ± 0.65 (1.6)	

^a Triplicate analyses; RSD = relative standard deviation.

^b SA = Standard additions.

ples for preconcentration. The results obtained show good reproducibility of the developed method with low relative standard deviation (RSD) values of <3.0% for triplicate measurements. The deviation of the observed data from the reported literature values was attributed to various human activities that resulted in varying concentrations of metal ions in seawater as well as in ground water, and ultimately either enhanced or reduced values.

(c) *Determination of Cu(II), Ni(II), Mn(II), and Zn(II) in certified multivitamin-multimineral tablets.*—Multivitamin-multimineral tablets, obtained from Nicholas Piramal India Ltd., were analyzed by dissolving and decomposing one tablet by heating in aqua regia 3 times and finally in H₂SO₄–H₂O₂ (1 + 1). The residue was dissolved in dilute HCl, and the solution was adjusted to pH 3 with dilute NaOH solution. The pH was raised to 5 by using sodium solution, and the solution was then filtered. The filtrate was adjusted to optimum pH and then passed through the preconditioned resin bed. The metal-ion concentration in the solid phase was determined by FAAS after leaching with 4M HCl; the results are given in Table 5.

(d) *Determination of Cu(II), Ni(II), Mn(II), and Zn(II) in curry leaves (Murraya koenigii).*—After the curry leaves were air-dried, they were heated to 110°C in an air-oven for 3 h and then powdered. A 5 g portion of the sample was heated with H₂SO₄–H₂O₂ (1 + 1) repeatedly to decompose the organic matter and then evaporated to dryness. The residue was dissolved in water, and the silicate residues were filtered. The solution was adjusted to pH 4.5 with 3M sodium acetate and filtered. The filtrate was adjusted to optimum pH and passed through the resin bed. The reliability of the recoveries of the metal ions was studied by the method of standard addition, whereby 15 µg each of Cu(II), Ni(II), Mn(II), and Zn(II) was added prior to preconcentration; the results are shown in Table 4.

Conclusions

The newly developed polychelator was successful in extracting the analytes of interest from various natural complex matrices, with a high degree of selectivity and sensitivity. Other significant features are its faster metal-extracting capability combined with remarkable metal-loading capacity values, which are much better than the values reported for chelating polymers. The resin was found to have good mechanical stability and chemical durability, as indicated by its extractive behavior, which did not decrease even after 30 cycles of usage and demonstrated its practical applicability and reusability. Moreover, the developed polychelator is very easy to synthesize. Other features of the developed system are its high preconcentration factors for all the analytes and its ability to preconcentrate trace mg 1 mg/L levels of analytes from real samples (collected near various industrial zones), with RSD values of ≤3.0%, which demonstrate its data reproducibility and reliability, as was confirmed by the method of standard additions.

Table 5. Estimation of metal-ion concentrations in curry leaves (*Murraya koenigii*) and certified multiminerall-multivitamin tablet

Sample	Method	Analyte concentration ^a (RSD, % ^b)			
		Mn(II)	Ni(II)	Cu(II)	Zn(II)
Multimineral-multivitamin tablet	Experimental	0.73 ± 0.03 (2.8)	—	1.37 ± 0.05 (1.8)	0.11 ± 0.01 (2.7)
	Theoretical	0.74	—	1.35	0.10
Curry leaves	Direct	10.10 ± 0.41 (2.2)	15.37 ± 0.82 (2.9)	20.31 ± 0.86 (2.3)	10.73 ± 0.35 (1.8)
	SA ^c	10.27 ± 0.45 (2.4)	15.29 ± 0.39 (1.4)	21.37 ± 0.82 (2.1)	10.91 ± 0.44 (2.2)

^a Concentrations in multiminerall-multivitamin tablets are in mg/g; concentrations in curry leaves are in µg/g.

^b RSD = Relative standard deviation.

^c SA = Standard additions.

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