Separation and Preconcentration of Cd(II), Cu(II), Ni(II), and Pb(II) in Water and Food Samples Using Amberlite XAD-2 Functionalized with 3-(2-Nitrophenyl)-1H-1,2,4-triazole-5(4H)-thione and Determination by Inductively Coupled Plasma−Atomic Emission Spectrometry

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ABSTRACT: A separation and preconcentration procedure was developed for the determination of trace amounts of Cd(II), Cu(II), Ni(II), and Pb(II) in water and food samples using Amberlite XAD-2 fuctionalized with a new chelating ligand, 3-(2-nitrophenyl)-1H-1,2,4-triazole-5(4H)-thione (Amberlite XAD-2-NPTT). The chelating resin was characterized by Fourier transform infrared spectroscopy (FT-IR) and used as a solid sorbent for enrichment of analytes from samples. The sorbed elements were subsequently eluted with 10 mL of 1.0 M HNO_3, and the eluates were analyzed by inductively coupled plasma−atomic emission spectrometry. The influences of the analytical parameters including pH, amount of adsorbent, eluent type and volume, flow rate of the sample solution, volume of the sample solution, and effect of matrix on the preconcentration of metal ions have been studied. The optimum pH for the sorption of four metal ions was about 6.0. The limits of detection were found to be 0.22, 0.18, 0.20, and 0.16 μg L^{-1} for Cd(II), Cu(II), Ni(II), and Pb(II), respectively, with a preconcentration factor 60. The proposed method was applied successfully for the determination of metal ions in water and food samples.

KEYWORDS: 3-(2-Nitrophenyl)-1H-1,2,4-triazole-5(4H)-thione (NPTT), Amberlite XAD-2, water samples, food samples, ICP-AES

■ INTRODUCTION

Metal pollution and food safety with respect to human health are two important parallel issues all over the world. The occurrence of metals in food may be natural or due to increased incidences of human activities like rapid industrialization and anthropogenic life styles, the latter being considered severe as it commonly allows the persistence of a range of toxic heavy metals including trace metals like cadmium, copper, nickel, and lead in the environment.[1] Copper is an essential metal to sustain biological processes, but excess exposure to copper often results in nausea, vomiting, liver damage, gastrointestinal problems, and hypertension. On the other hand, cadmium, nickel, and lead are considered to be toxic, and their intoxication results in severe detrimental effects. Cadmium-induced toxicity affects the functional and structural integrity of liver and kidneys. Nickel exposure is implicated in lung and skin cancers. Lead affects the brain functions and testicular processes and also affects other vital parts of the body through oxidative stress. Thus, it seems apparent that the essential, moderately toxic, and toxic heavy metals affect almost all compartments of the vital parts and thereby interfere with biochemical and physiological alterations. It has also been reported that many people suffer with Itai−Itai syndrome due to the consumption of fish contaminated with cadmium.[2] Hence, the determination of heavy metals like cadmium, copper, nickel, and lead in food samples plays an important role in environmental protection and food and agricultural chemistry.

Direct analysis of trace levels of metals in environmental and food samples is difficult because of their very low concentrations and high amounts of matrices in the analyzing samples. To solve this problem, separation−preconcentration procedures are often used prior to analysis by inductively coupled plasma−atomic emission spectrometry (ICP-AES). Among the preconcentration procedures, solid phase extraction (SPE) has advantages such as (i) high preconcentration factor, (ii) simple operation, (iii) rapid phase separation, and (iv) the ability to combine with different detection techniques.[3] Amberlite XAD either loaded or functionalized with various ligands, such as o-vanillinthiosemicarbazone,[4] 2-hydroxy-acetophenone-thiosemicarbazone,[5] 3-ferrocenyl-3-hydroxydithioacrylic acid,[6] and dimethylglyoxal bis(4-phenyl-3-thiosemicarbazone),[7] were used for preconcentration and determination of metal ions in different matrices. Thus, the development of functionalized resins that can provide good stability, high sorption capacity for metal ions, and good flexibility in working conditions is important for the accurate monitoring of trace metals in water and food samples.

In view of this, we have developed a sensitive analytical method for the separation and preconcentration of Cd(II), Cu(II), Ni(II), and Pb(II) in water and food samples. A new ligand, namely, 3-(2-nitrophenyl)-1H-1,2,4-triazole-5(4H)-thione (NPTT), was synthesized and used for the functionalization of Amberlite XAD- 2 by covalent coupling of ligand with polymer backbone through azo spacer. The functionalized resin
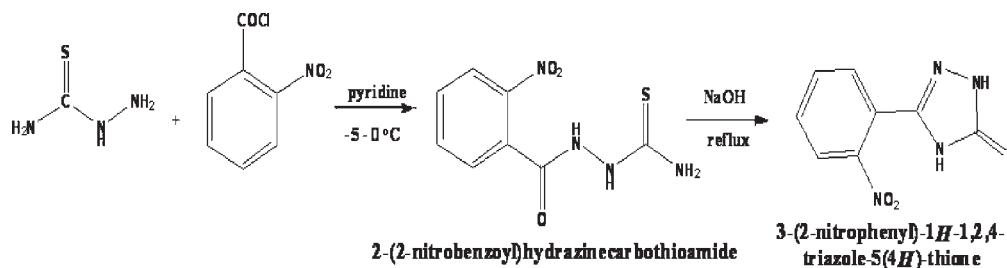
Scheme 1. Representative Schematic for the Synthesis of NPTT

2-(2-nitrobenzoyl)hydrazinecarbothioamide

3-(2-nitrophenyl)-1*H*-1,2,4-triazole-5(4*H*)-thione

was employed as a solid sorbent for separation and preconcentration of metal ions from samples and determined by ICP-AES. Optimal experimental conditions for SPE of metal ions were investigated. The established method was applied for the determination of metal ions in water and food samples.

■ EXPERIMENTAL PROCEDURES

Apparatus. Atomic emission spectrometer (ICP-AES, Varian, Liberty Series II, Australia) with a wiproacer computer was used for the determination of metal ions. The instrumental operating parameters were as follows: photomultiplier tube voltage, 700 V; incident power, 1.1 kW; plasma gas flow, 15.0 L min^{-1}; auxiliary gas flow, 1.5 L min^{-1}; observation height, 14.0 mm; pump rate, 15.0 rpm; and sample uptake, 25 time s^{-1}. The wavelengths used were 226.502 nm for Cd, 324.754 nm for Cu, 221.647 nm for Ni, and 220.382 nm for Pb. The analyte lines were selected on the basis of net and background intensities as well as their freedom from spectral overlaps.

Microwave digestion (MarsXpress, CEM Corp., United States) was used in the preparation of food samples for metal extraction. A Fourier transform infrared (FT-IR) spectrometer (Thermo-Nicolet FT-IR, Nicolet IR-200, United States) was used in the characterization of ligand and functionalized resin. An Elico (LI-129) pH meter was used for pH measurements.

Chemicals and Solutions. All aqueous solutions were prepared with double-distilled water. All of the chemicals used were of analytical reagent grade. The Amberlite XAD-2 resin (Aldrich, Milwaukee, WI) with a particle size of 20−60 mesh, a pore diameter of 90 Å, and a surface area of 330 m^2 g^{-1} was used. Before they were used, the resin beads were purified by treating them with 4 M HCl followed by 2 M NaOH solution to remove both acidic and basic impurities and finally with water until the washings showed neutral pH. The purified resin was filtered, rinsed with ethanol to remove the metal impurities, and vacuum-dried prior to usage.

The following pH solutions were used for the SPE procedure: acetate buffer between pH 2 and 6, borate buffer at pH 7, and ammonium buffer between pH 8 and 10. A multielement standard solution (100 μg mL^{-1}) was prepared by dilution of ICP-AES standards of Cd(II), Cu(II), Ni(II), and Pb(II). Working standards were prepared by appropriate dilution of the multielement standard with double-distilled water.

Synthesis of the 3-(2-Nitrophenyl)-1*H*-1,2,4-triazole-5(4*H*)-thione. To a solution of thiosemicarbazide in absolute pyridine, 2-nitrobenzoyl chloride was added dropwise with stirring at −5 to 0 °C. The reaction mixture was stirred for 3 h at room temperature and poured into H$_2$O to get a precipitate. It was refluxed for 3 h in NaOH (2 N) solution and cooled to room temperature, which resulted in the formation of 3-(2-nitrophenyl)-1*H*-1,2,4-triazole-5(4*H*)-thione as precipitate. The precipitate was filtered off and recrystallized. The schematic representation of reaction sequence of NPTT synthesis is shown in Scheme 1. Yield, 86%. IR (KBr) (υ_{max}, cm^{-1}): 3417, 3051, 1616, 1258,

Scheme 2. Functionalization of Amberlite XAD-2 with NPTT

Amberlite XAD-2-NPTT
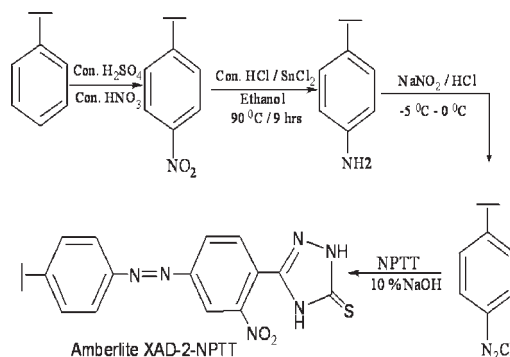
and 1152. ^{1}H NMR (DMSO-d_6): δ 11.64 (1H, s, NH), 8.32−8.30 (d, 2H, Ar), 8.23−8.21 (d, 2H, Ar), 8.19−8.14 (t, 1H, Ar), 7.68−7.64 (t, 1H, Ar), 3.49 (1H, s, NH). ^{13}C NMR (DMSO-d_6): δ 178.6, 148.7, 140.2, 136.5, 133.8, 130.4, 124.2, 121.7. APCI-MS (m/z) 223 [M + H] anal. calcd for C$_8$H$_6$N$_4$O$_2$S: C, 43.24; H, 2.72; N, 25.21. Found: C, 43.18; H, 2.69; N, 25.17.

Functionalization of Amberlite XAD-2 with NPTT. A 5 g sample of Amberlite XAD-2 was treated with a nitrating mixture, containing l0 mL of concentrated HNO$_3$ and 25 mL of concentrated H$_2$SO$_4$, and stirred for 1 h at 60 °C in a water bath. The reaction mixture was poured into ice water, and the nitrated resin was then filtered off and washed with water until the effluents were pH neutral and reduced with a mixture of SnCl$_2$ (40 g) in the presence of concentrated HCl (45 mL) and ethanol (50 mL) and refluxed for 12 h at 90 °C. The amino polymer was filtered off and washed with distilled 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 to remove excess of HCl, and suspended in 250 mL of ice cold water. It was then diazotized by adding 1 mL increments of an equimolar mixture of 1 M HCl and NaNO$_2$ with constant stirring until the reaction mixture showed a permanent blue color with starch-iodide paper. The diazotized Amberlite XAD-2 was filtered at −5 to 0 °C to avoid its disintegration at a higher temperature and treated with NPTT (3 g taken in a mixture of 100 mL of water and 25 mL of 4% sodium hydroxide) at 0−5 °C for 24 h. The dark brownish crimson colored beads obtained were filtered, washed with 4 M HCl and doubly distilled water successively, and finally vacuum-dried. A schematic representation of functionalization of Amberlite XAD-2-NPTT is shown in Scheme 2.

Sample Collection. The vegetable samples, namely, Lady's Finger (*Abelmoschus esculentus*), onion (*Alium sepa*), cauliflower (*Brassica olera* var. *Botrytis*), cucumber (*Cucumis sativus*), sweet potato (*Ipomoea*),
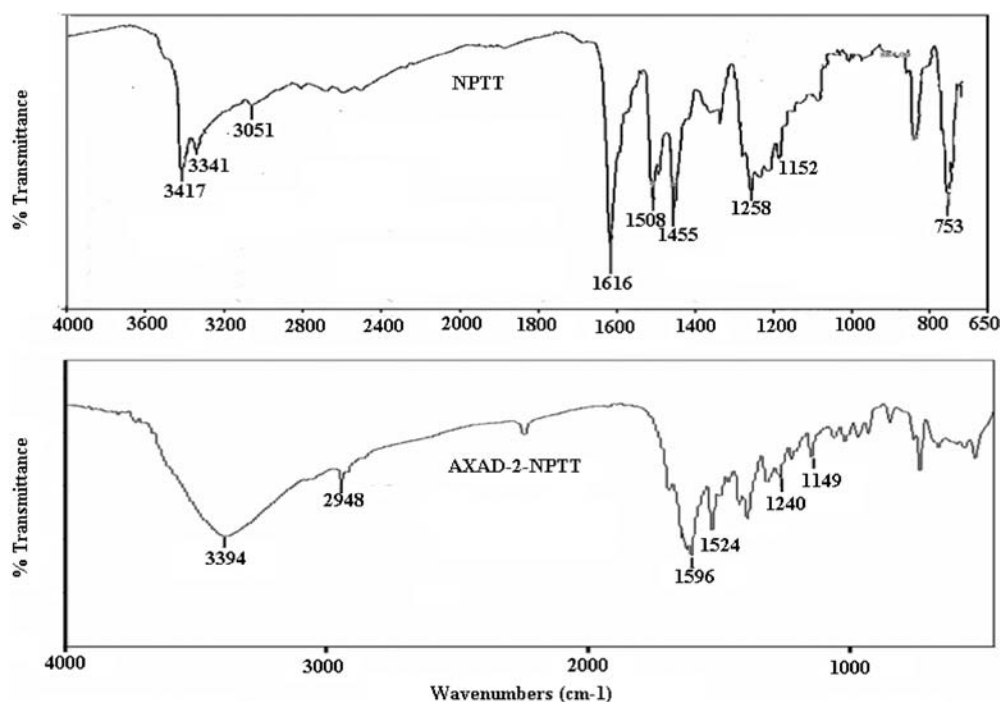
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Figure 1. FT-IR spectra of NPTT and functionalized Amberlite XAD-2-NPTT.

tomato (*Lycopersicum esculentum*), and drumstick (*Moringa oleifera*) were collected in polyethylene bags from the nearby agricultural fields of Tirupati town, A.P, India.

The river and seawater samples were collected in screw-cap polyethylene bottles from the Penner river and Bay of Bengal, Nellore District, A.P, India. The samples were filtered through 0.45 μm membrane filters and stored in a refrigerator at 4 °C until analysis.

Sample Preparation. Sample preparation of vegetable samples was carried out by the following procedure. Vegetable samples were air-dried for 3 days, then cleaned with double-distilled water followed by drying at 105 °C in a hot air oven for 2 h, and then powdered. One gram of each sample was taken in borosilicate flasks, and 5 mL of concentrated nitric acid was added to each flask. After they stood for 8 h, the samples were digested in a microwave system for 10 min at 106 °C. A clear solution was obtained. The digested samples were further made up to 25 mL using double-distilled water and determined as described in the SPE procedure after adjusting the pH to the desired value.

SPE Procedure for Preconcentration and Determination of Metal Ions. A glass column (1.0 cm i.d., length of 10 cm) with a stopcock was taken. Five hundred milligrams of Amberlite XAD-2 functionalized with NPTT was slurred in doubly distilled water and poured in the column. A small amount of glass wool was placed on the disk to prevent the loss of resin beads during sample loading. The column was treated with 2.0 M HCl and washed with doubly distilled water until free from acid. A desired volume of the sample solution containing Cd(II), Cu(II), Ni(II), and Pb(II), with the pH adjusted to 6.0, was passed through the column and washed with double-distilled water. The bound metal ions were stripped from the resin bed using 10 mL of 1.0 M HNO_3. The concentrations of metal ions in eluates were determined by ICP-AES.

Batch Method for the Determination of Sorption Capacity. The sorption capacity of Amberlite XAD-2-NPTT (maximum amount of metal sorbed per gram) of each metal ion was determined by the batch method. The resin (1 g) was saturated with Cd(II), Cu(II), Ni(II), and Pb(II) ion solutions (concentration, 50 μg mL^{-1}) by equilibrating the solutions on a mechanical shaker under optimum conditions. The solid matrix was filtered and washed with distilled water. The sorbed metal ions on the resin were desorbed with 10 mL of 1 M HNO_3 and determined by ICP-AES. The sorption capacities in mg g^{-1} are 4.2 for Cd(II), 4.4 for Cu(II), 3.9 for Ni(II), and 4.8 for Pb(II), respectively.

■ RESULTS AND DISCUSSION

IR Spectral Analysis of NPTT and Amberlite XAD-2-NPTT. FT-IR analysis of NPTT and the functionalized Amberlite XAD-2-NPTT were carried out with as potassium bromide pellets. The FT-IR spectrum of NPTT showed bands at 3417, 3051, 1616, 1258, and 1152 cm^{-1} due to N–H, Ar–H, C=N, C=S, and C–N stretching, respectively. In the FT-IR spectrum of functionalized Amberlite XAD-2-NPTT, bands appeared at 3394, 2948, 1592, 1523, 1228, and 1149 cm^{-1} due to N–H, Ar–H, C=N, N=N, C=S, and C–N stretching, respectively (Figure 1). These similarities between the spectra of ligand (NPTT) and the modified resin support the functionalization of Amberlite XAD-2 with NPTT through azo spacer.

Effect of pH. pH is one of the important factors affecting the efficiency of retention/elution of metal ions by solid support.[8] The formation of metal complexes and their stabilities in aqueous solutions are strongly related to the pH of the medium. The effect of pH was studied by varying the pH in the range of 2.0–9.0 (Figure 2). To evaluate the effect of pH on the extraction efficiency, the pH of the 600 mL sample solutions containing 50 μg each of Cd(II), Cu(II), Ni(II), and Pb(II) was adjusted in the range of 2.0–9.0, and the recommended procedure was applied. The solutions were passed through the column at a flow rate of 2.5 mL min^{-1}. The metal ions sorbed onto resin were then eluted by an appropriate eluent and determined by ICP-AES. In all of the cases, metal retention by the functionalized Amberlite XAD-2-NPTT was increased with increasing pH and reached a maximum (pH 6.0) after which the retention decreased. On the
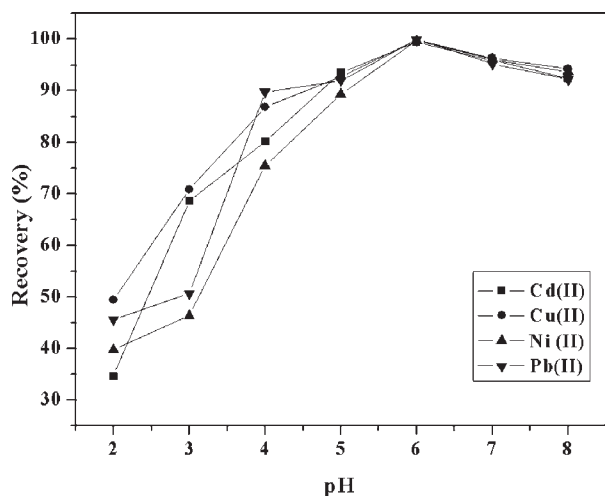
Figure 2. Effect of pH on the recovery (%) of metal ions.

Figure 3. Kinetics of metal ion sorption on Amberlite XAD-2-NPTT resin.

other hand, the progressive decrease in the retention of these metal ions at lower pH is due to the competition of hydrogen ions with the metal ions for the complexation and binding to NPTT. In contrast, at higher pH (>6.0), the decrease in retention is due to the precipitation of metal ions as insoluble $M(OH)_2$ or $M(OH)^+$ in the reaction medium. To achieve the high efficiency and good selectivity, the optimum pH of 6.0 was selected in further studies.

Effect of the Amount of Resin on Preconcentration of Metal Ions. The amount of solid phase in the column is a main parameter for the quantitative recovery of the analyte ions. The efficiency of the functionalized Amberlite XAD-2-NPTT column for the sorption of metal ions was studied by varying amounts ($100-600$ mg) of the functionalized resin. It was observed that by increasing the amount of modified solid phase up to 500 mg, the metal ions Cd(II), Cu(II), Ni(II), and Pb(II) recovered were also increased. Furthermore, increase in the amount of solid phase with a fixed value of sample solution, there was no increase in the recoveries. Hence, in the proposed procedure, 500 mg of Amberlite XAD-2-NPTT resin was used.

Effect of Flow Rate. The effect of flow rate of the sample solution on the retention of the metal ions Cd(II), Cu(II), Ni(II), and Pb(II) on the Amberlite XAD-2-NPTT resin was studied with the column packed with 500 mg of resin. Sample solutions were passed through the column at various flow rates ($1.0-5.0$ mL min^{-1}) maintained by peristaltic pump at the optimum pH 6.0. The optimum flow rate may be defined as the rate of flow of the solution through the column at which more than 98% retention of metal ions takes place. The studies showed that the optimum flow rate for quantitative sorption of metal ions with the resin was between 1.0 and 2.5 mL min^{-1}. The flow rates less than 1.0 mL min^{-1} were not studied to avoid long analysis time. The increase of flow rate more than 2.5 mL min^{-1} caused a gradual decrease in sorption due to insufficient contact time between the resin and the metal ions; hence, 2.5 mL min^{-1} flow rate was chosen as the optimum flow rate for elution of these metals from resin.

Selection of the Best Eluent and Optimization of Its Concentration. For the analytical performance of solid phase preconcentration system, the type and concentration of eluent are also important. Among different concentrations of HCl and HNO$_3$ tried, 1.0 M HNO$_3$ was found to be ideal for quantitative
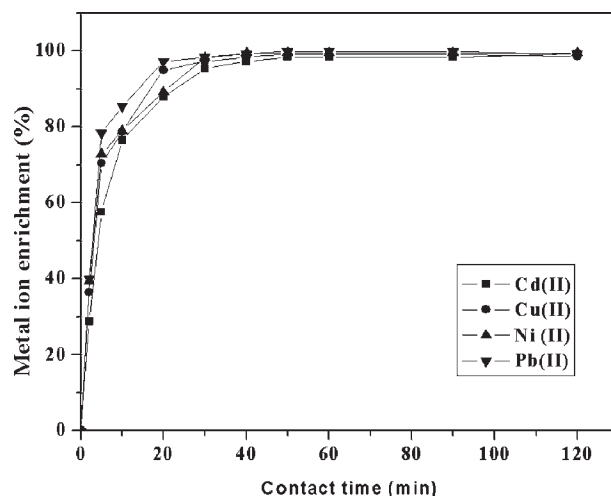
Table 1. Effect of Matrix Ions on Determination of Cd(II), Cu(II), Ni(II), and Pb(II) by the Proposed Method ($n = 5$)

matrix ion	tolerance limit (mg L^{-1})	recovery (%)	matrix ion	tolerance limit (mg L^{-1})	recovery[a] (%)
Na$^+$	28000	98.1 ± 1.1[a]	CH$_3$COO$^-$	10000	95.4 ± 1.2
K$^+$	24000	97.2 ± 1.4	PO$_4{}^{3-}$	2500	95.1 ± 1.7
Ca^{2+}	20000	96.8 ± 0.9	SO$_4{}^{2-}$	16000	96.4 ± 1.5
Mg^{2+}	18000	96.3 ± 0.8	Al^{3+}	100	95.4 ± 1.2
Cl$^-$	23000	98.5 ± 1.6	Cr^{6+}	51	95.1 ± 1.4
NO$_3{}^-$	14000	97.3 ± 1.8	Zn^{2+}	40	95.6 ± 0.9
HCO$_3{}^-$	10000	95.2 ± 1.3	Co^{2+}	44	97.4 ± 1.2

[a] Mean ± SD.

recovery of selected metal ions. Hence, 1.0 M HNO$_3$ was selected as the eluent for the analysis of the metals ions.

Kinetics of Sorption. Sorption kinetics is one of the important parameter that is being studied in SPE methods because it provides the rate of sorption of metals onto resin loaded with a reagent in the dynamic column mode for routine analysis. The rate of uptake of metal ions onto Amberlite XAD-2-NPTT was studied by batch method. One gram of functionalized resin was added to 50 μg of individual metal ion solutions and stirred for 2, 5, 10, 20, 30, 40, 50, 60, 90, and 120 min at a fixed temperature (30 ± 0.1 °C). The metal ions sorbed onto the resin were eluted with 1.0 M HNO$_3$ and analyzed by ICP-AES. The amount of metal sorbed onto the resin with time is graphically presented in Figure 3. The loading half-time, $t_{1/2}$, needed to reach 50% sorption of the total loading capacity has been found to be less than 5 min for each metal ion [Cd(II), 4.0; Cu(II), 3.9; Ni(II), 3.6; and Pb(II), 4.2 min, respectively]. The kinetics of the resin–metal interaction is sufficiently rapid for all of the metal ions at optimum pH. The faster uptake of these metal ions on Amberlite XAD-2-NPTT reflects a good accessibility of the chelating sites of the resin to metal ions.

Effect of Foreign Ions. The effects of common ions that are present in natural samples such as sodium, potassium, calcium, magnesium, chloride, nitrate, bicarbonate, acetate, phosphate, sulfate, aluminum, chromium, zinc, and cobalt on

the preconcentration of Cd(II), Cu(II), Ni(II), and Pb(II) by Amberlite XAD-2-NPTT functionalized resin with optimized conditions have been investigated. The tolerance limits of various foreign species on the sorption of the metal ions are given in Table 1. The tolerance limit of foreign ions was taken as that value which caused an error of not more than 5% in the emission reading. Because of good sorption capacity of the resin, all of the four metal ions can be preconcentrated simultaneously and determined by ICPAES.

Column Reusability. To examine the long-term stability of the resin reagent, it was subjected to successive adsorption and desorption cycles by passing 600 mL of metal solutions through the column. The stability and potential reusability of the column-containing resin were assessed by monitoring the change in the recoveries of the analytes up to 10 runs; there was no change in recovery of metal ions, and after 10 runs, the recoveries of all of the analytes slightly decreased to below 95%.

Analytical Performance. The preconcentration factor assessed by varying the volume of the sample solution in the range of 100−1000 mL revealed that the recoveries were almost the same up to 600 mL of aqueous phase (preconcentration factor ∼60) in the case of Cd(II), Cu(II), Ni(II), and Pb(II). However, the efficiency of the recovery slightly decreased when sample volume was more than 600 mL. Hence, 600 mL of water sample was chosen in the present study.

The sorption capacity values of Amberlite XAD-2-NPTT (maximum amount of metal sorbed per gram of functionalized resin) mg g^{-1} for each metal ion determined by batch method were found to be 4.2 for Cd(II), 4.4 for Cu(II), 3.9 for Ni(II), and 4.8 for Pb(II), respectively.

The method detection limit values defined as the concentration of metal (in μg L^{-1}) that gives an emission reading equal to the mean of the reagent blank prepared as described in the section (Sample Preparation), plus three times the standard deviation (SD) of the blank solution were 0.22, 0.18, 0.20, and 0.16 for Cd(II), Cu(II), Ni(II), and Pb(II), respectively.

The accuracy of the developed procedure was evaluated by determining the metal ions in the standard reference material (NIST 1643e Water). According to results in Table 2, concentrations of the four metal ions determined by the proposed method are in good agreement with the certified values. Results indicate that the developed procedure can be used for the determination of four metals with good accuracy in environmental samples.

Determination of Trace Metal Ions in Water Samples. Water samples were collected from Penner river (Nellore) and seawater (Bay of Bengal, Nellore); the concentrations of Cd(II), Cu(II), Ni(II), and Pb(II) were determined, and the results are

Table 2. Recovery of Metals from Standard Reference Materials after Preconcentration on Amberlite XAD-2-NPTT Resin^a

element	NIST 1643e water (μg l^{-1})	
	certified value	proposed method
Cd(II)	6.51 ± 0.42	6.47 ± 0.26
Cu(II)	22.76 ± 0.31	22.73 ± 0.34
Ni(II)	62.41 ± 0.29	62.38 ± 0.42
Pb(II)	19.58 ± 0.25	19.56 ± 0.24

^{a} The values reported are means of five readings ± SDs.

Table 3. Determination of Trace Metal Ions in Various Water Samples ($n = 5$)^a

sample	ICP-AES method (μg L^{-1})	
	river water	sea water
Cd(II)	0.72 ± 0.16	1.92 ± 0.28
Cu(II)	17.10 ± 0.31	16.27 ± 0.46
Ni(II)	14.32 ± 0.27	17.31 ± 0.24
Pb(II)	15.42 ± 0.56	7.42 ± 0.21

^{a} Means ± SDs ($n = 5$).

Table 4. Determination of Trace Metal Ions in Various Food Samples (mg g^{-1})

		metal ions^a											
		Cd(II)			Cu(II)			Ni(II)			Pb(II)		
botanical name	added	found	recovery (%)	RSD (%)	found	recovery (%)	RSD (%)	found	recovery (%)	RSD (%)	found	recovery (%)	RSD (%)
A. esculentus (Lady's Finger)	0.0	0.021		3.4	0.183		1.6	3.045		1.9	0.058		2.3
	5.0	5.020	98.7	1.1	5.181	99.1	0.9	8.033	99.6	1.2	5.057	99.6	1.1
	10.0	10.020	97.8	0.8	10.180	98.9	0.8	13.012	98.9	1.0	10.057	99.5	1.0
A. sepa (onion)	0.0	0.026		3.2	0.378		1.9	2.043		1.6	0.138		2.3
	5.0	5.025	96.2	1.2	5.377	99.8	1.1	7.029	99.3	0.9	5.137	99.2	1.2
	10.0	10.024	94.8	0.9	10.374	99.2	0.8	12.025	99.1	0.7	10.135	98.2	0.9
C. sativus (cucumber)	0.0	0.027		3.1	0.598		1.8	2.147		1.8	0.129		1.2
	5.0	5.026	98.3	1.1	5.591	98.8	1.2	7.121	98.8	0.9	5.127	98.4	0.9
	10.0	10.025	94.9	0.8	10.589	98.6	1.1	12.116	98.6	0.6	10.128	99.2	0.8
L. esculentum (tomato)	0.0	0.024		3.3	0.602		1.7	1.263		2.8	0.047		3.4
	5.0	5.023	97.3	0.8	5.598	99.5	1.1	6.253	99.2	1.2	5.046	97.8	1.6
	10.0	10.022	95.4	0.7	10.595	98.9	0.8	11.249	98.9	1.0	10.045	96.4	1.4
M. oleifera (drumstick)	0.0	0.028		3.1	0.576		1.7	1.632		2.9	0.096		1.7
	5.0	5.027	96.4	1.0	5.568	98.7	1.3	6.601	98.1	1.5	5.094	98.5	0.8
	10.0	10.026	94.8	0.8	10.565	98.1	1.2	11.598	97.9	1.4	10.093	97.8	0.6

^{a} Mean SD ($n = 5$).

Table 5. Comparison of Proposed Method with Other SPE Methods Based on Use of Amberlite Resins

preconcentration system	analytes	technique	flow rates (mL min^{-1})	PF	detection limit (μg L^{-1})	refs
Amberlite XAD-2/ pyrogallol	Cu(II), Cd(II), Co(II), Ni(II), Pb(II), Zn(II), Mn(II), Fe(III), U(VI)	FAAS	1.5−2.5	64 for Cu(II); 160 for Zn(II);	5.0 for Cu(II); 0.5 for Zn(II)	9
XAD-2000/DDTC	Mn, Fe, Co, Cu, Cd	FAAS	20	100	0.2 for Mn(II); 0.2 for Cu(II)	10
XAD −2000/1-(2-pyridylazo)-2-naphthol (PAN)	Cr(III), Cu(II), Ni(II), Pb(II)	FAAS	10	250		11
Amberlite XAD-4/ dithiocarbamates	Cd(II), Cu(II), Mn(II), Ni(II), Pb(II), Zn(II)	ICP-AES		230 for Cu(II); 120 for Mn(II); 215 for Zn(II)	0.4 for Cu(II); 0.3 for Mn(II); 0.5 for Zn(II)	12
Amberlite XAD-4/ DDTC	Cu, Fe, Pb, Ni, Cd, Bi	FAAS	10	150	4	13
Amberlite XAD-7/ xylenol orange	Cd(II),Co(II), Cu(II), Ni(II), Zn(II), Fe(III)	FAAS	2−4 for Cu(II); 2−5 for Zu(II)	50 for Cu(II); 100 for Zn(II);		14
Amberlite XAD-2-HAPTSC	Cd(II), Cu(II), Ni(II)	ICP-AES	2.5		0.54 for Ni(II); 0.61 for Cu(II)	15
Amberlite XAD-2-NPTT	Cd(II), Cu(II), Ni(II) and Pb(II)	ICP-AES	2.5	60	0.16−0.22	present method

presented in Table 3. The results revealed that the concentration of cadmium is in the range of 0.72−1.92 μg L^{-1}, copper is in the range of 16.27−17.10 μg L^{-1}, nickel is in the range of 14.32−17.31 μg L^{-1}, and lead is in the range of 7.42−15.42 μg L^{-1}.

Determination of Trace Metal Ions in Vegetable Samples. Vegetable samples, namely, Lady's Finger (*A. esculentus*), onion (*A. sepa*), cucumber (*C. sativus*), tomato (*L. esculentum*), and drumstick (*M. oleifera*), were collected from nearby agricultural fields of Tirupati town; the concentrations of Cd(II), Cu(II), Ni(II), and Pb(II) ions were determined, and the results are presented in Table 4. The concentrations of four metals in vegetables were in the range of 0.021−0.028 mg g^{-1} for cadmium, 0.183−0.602 mg g^{-1} for copper, 1.632−3.045 mg g^{-1} for nickel, and 0.047−0.138 mg g^{-1} for lead.

Comparative with Other Methods. A comparison of the proposed method with other SPE methods in terms of detection limit was evaluated, and results are summarized in Table 5. The SPE method developed by using Amberlite XAD-2 functionalized with NPTT showed low DL when compared to other methods reported in the literature. These results indicate that the proposed method is suitable for the determination of Cd(II), Cu(II), Ni(II), and Pb(II) in environmental and biological samples at low concentrations.

■ CONCLUSION

The newly developed method can be successfully used for separation and preconcentration of Cd(II), Cu(II), Ni(II), and Pb(II) in water and food samples for determination by ICP-AES. Amberlite XAD-2-NPTT has a good metal loading capacity, the half loading time ($t_{1/2}$) of this chelating resin is also very short, and the kinetic studies ensure faster exchange kinetics in the process of metal ion uptake. The resin can be reused for 10 times without affecting its sorption capacity. The method has high tolerance limits from the matrix ions. The proposed SPE method has the advantages such as high enrichment factor high tolerance limits of foreign ions and low detection limit. The present method is highly useful for the determination of Cd(II), Cu(II), Ni(II), and Pb(II) in water and food samples.

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