

Chapter-IV

**Synthesis and Characterization of 3-(2-nitrophenyl)-1*H*-
1,2,4-triazole-5(4*H*)-thione (NPTT) and its application
for preconcentration of Pb(II), Ni(II), Cu(II) and Cd(II)
in water and food samples and determination by
ICP-AES**

The use of chelating ligands containing sulphur and nitrogen has generated much interest in the last few years in analytical studies as well as in structural studies of metal complexes. Sulphur containing ligands have the remarkable property of the sulphur atom as a potential donor to form stable complexes in which the back bonding from the metal ion is possible under favourable conditions. In addition presence of nitrogen along with sulphur tends to lower the solubility of the complexes, making the isolation of these complexes easier. Triazoles are a group of compounds obtained by condensing thiosemicarbazide with aromatic acid chlorides. These reagents function as good chelating agents and form complexes with several metal ions by bonding through thioketo sulphur atom and hydrazino nitrogen atom. Triazoles usually bind to a metal ion as bidentate N,S-donor ligands while can function as tridentate species if third donor site is present in the remaining part of ligating system. Such tridentate ligands will show good complexing potential towards ions of trace metals like Pb, Ni, Cu, Cd, Fe, Co and Mn. Apart from good complexing ability, these aromatic ligands can easily be coupled to Amberlite XAD-2, XAD-4 or XAD-16 through functionalization by means of an -N = N-spacer. They provide good stability high sorption capacity for metal ions, good flexibility in working conditions, good metal ion enrichment capacity and can be used for many cycles of extraction.

The review of literature showed that there are several preconcentration methods employing thiosemicarbazide derivative (Triazole) that are used to separate and preconcentrate trace elements according to the nature of the samples, the concentrations of the analytes and measurement techniques.

Liu et al. [1] described a solid phase spectrophotometric determination method for determination of nickel in water and vegetable samples at sub $\mu\text{g L}^{-1}$ level with *o*-carboxylphenyldiazoaminoazobenzene loaded XAD-4. Porta et al. [2] developed quinoline-8-ol loaded Amberlite XAD-2 resin on-line preconcentration method for the determination of manganese and nickel in water samples by inductively coupled plasma-atomic emission spectrometry. This system improved the detection limits of Cd, Cu, Fe, Mn, Ni and Zn compared with ICP-AES alone. The method was applied for the determination of metals in Antarctic sea water. Determination of Pb in sea water after sample preconcentration using chelex-100 resin by a combination of hydride generation with ICP-AES was reported by Reimer and Miyazaki [3]. Application of on-line flow

injection anionic exchange resin (resin L 296) for preconcentration of trace metals was reported by Liu et al. [4]. Peng et al. [5] developed 8-hydroxyquinoline-5-sulphonic acid immobilized active carbon-silica gel for on-line microcolumn preconcentration and determination of Al, Cu, Cr, Cu, Fe, Hg, Mn, Ni and Pb. Peng et al. [6] developed column preconcentration method for the determination of trace metals by flow injection ICP-AES. In this method, meso-tetrakis-(4-sulphophenyl) porphyrin immobilized silica gel was used for several reference standards and satisfactory results were obtained.

Guo et al. [7] established a preconcentration procedure using PAN loaded with polyurethane foam for the determination of Co and Pb in natural waters. Lan and Yang [8] developed silica gel immobilized 8-quinoline on-line column preconcentration method for the determination of Cu, Ni and Cd in sea water by flow injection ICP-AES. The procedure was in good agreement with the certified values. Gomez et al. [9] used 1, 5, bis (di-2-pyridylmethylene) thiocarbonylhydrazide as a reagent for the determination of cobalt in biological samples by solvent extraction ICP-AES. Guo et al. [10] reported 8-hydroxyquinoline-5-sulphonic acid-cellulose microcolumn method coupled to ICP-AES for trace elemental determination. Manickum and Verbeek [11] developed slurry sampling method for the determination of traces of Al, Ba and Mn by ICP-AES. Application of tributyl phosphate and back-extraction with ammonium acetate and ammonium carbonate for preconcentration of trace metals was reported by Manzoori and Shemirani [12]. Li et al. [13] analysed Sb, Pb and Ti in water samples using diantipyrylmethane-iodide solid phase extraction method and determination by ICP-AES. Malakova and Mateva [14] developed preconcentration method using sodium di-*n*-propyldithiophosphinate for determination of bismuth by ICP-AES. Ji et al. [15] reported pg/g level determination of major, minor and trace elements by ICP-AES after chelex-100 resin preconcentration. Zhang et al. [16] developed ion-pair solvent extraction method for the determination of Bi, Cd, Cu, Fe, Hg, Mo, Pb, Sn, V and Zn in natural water samples. The method was applied to standard reference materials and the results obtained were highly satisfactory. Millward and Kluckner [17] studied the determination of low levels of cadmium in marine and fresh water sediments by graphite furnace atomic absorption spectrometry employing a reduced palladium chloride modifier and by ICP-AES. Alonso et al. [18] reported the determination of nickel in biological samples by ICP-AES after extraction with 1, 5-bis (di-2-pyridylmethylene) thiocarbonylhydrazide. Uchida et al. [19] reported determination of 12 elements in biological samples using

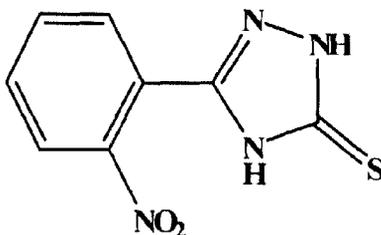
ICP-AES after extracting with tetraethyl ammonium hydroxide and ethylene diaminetetraacetic acid. Gomez et al. [20] used 1,5-bis (di-2-pyridylmethylene) thiocarbonylhydrazide as a reagent for the determination of cobalt in biological samples by solvent extraction ICP-AES. Separation and determination of cadmium in biological materials by continuous-flow fluid extraction coupled to flow injection ICP-AES was reported by Alonso et al. [21]. A flow injection ICP-AES method for the sequential determination of trace amounts of heavy metals (Cd, Co, Cu and Zn) in biological samples based on the complexation of the metal ions with 1,5-bis (di-2-pyridyl) methylene thiocarbonylhydrazide and its subsequent on-line extraction into isobutyl methyl ketone was reported by Cordero et al. [22]. Nóbrega et al. [23] studied determination of elements in biological and botanical materials by ICP-AES and mass spectrometry after extraction with a tertiary amine reagent. Preconcentration of Cd, Co, Cu, Ni and Zn using different off-line ion exchange procedures followed by the ICP-AES detection was reported by Prusisz and Zurnicki [24].

The review of above preconcentration methods revealed that methods based on solvent extraction and solid phase extraction are used for the preconcentration of metals such as Pb(II), Ni(II), Cu(II) and Cd(II) in order to determine by ICP-AES in various environmental matrices. The process based on solid phase extraction has advantages over solvent extraction. Different procedures like loading/coating of the solid support with chelating reagents or functionalization of resin with suitable chelating compound have been used in the development of solid phase extraction methods. A variety of supports and chelating ligands have been used in the design of solid supports in the development of solid-phase extraction methods. The most prominent among the supports used are activated carbon, silica gel, polyurethane foam and Amberlite XAD series. Thus the thiosemicarbazide and their derivatives that were used in SPE for the determination of metal ions include benzildithiosemicarbazone [25], o-carboxylbenzenediazoaminoazobenzene [26], 1-acylthiosemicarbazide [27], dimethylglyoxal bis(4-phenyl-3-thiosemicarbazone) [28] and pyridoxal-4-phenyl-3-thiosemicarbazone [29]. Thus, there is a continued interest in the development/application of chelating reagents that can provide good stability, high sorption capacity for metal ions and good flexibility in working conditions. In view of this, we have synthesized a new thiosemicarbazide derivative (3-(2-nitrophenyl)-1*H*-1,2,4-triazole-5(4*H*)-thione) and used for

functionalization of XAD-2 for preconcentration of trace metals viz., Cd, Cu, Ni, and Pb and determination by ICP-AES.

The established method was applied for the preconcentration and determination of analytes in water and vegetable food samples. Optimum experimental conditions were investigated with respect to a standard solution of the matrix, in order to examine the possibility of obtaining the maximum extraction efficiency with minor sample treatment and minimal experimental conditions.

4.1 Structure of 3-(2-nitrophenyl)-1*H*-1,2,4-triazole-5(4*H*)-thione (NPPT)



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

The reagent 3-(2-nitrophenyl)-1*H*-1,2,4-triazole-5(4*H*)-thione (NPPT) has three binding sites, nitrogen, oxygen and sulphur and is thus capable of forming chelate rings, which makes it a good reagent for metal ion enrichment. In addition, the reagent can be easily synthesized in the laboratory and is suitable for functionalization of solid support like Amberlite XAD-2, which is a good requirement in solid phase extraction techniques.

4.2 RESULTS AND DISCUSSION

4.2.1 Characterization of 3-(2-nitrophenyl)-1*H*-1,2,4-triazole-5(4*H*)-thione (NPPT)

The detailed procedure of synthesis of 3-(2-nitrophenyl)-1*H*-1,2,4-triazole-5(4*H*)-thione (NPPT) and functionalization of Amberlite XAD-2 with the reagent, along with the schemes are reported in sections 2.5.1, 2.7.1 and Figs. 2.3, 2.6. The FT-IR and ¹H NMR spectrum of NPPT and FT-IR spectrum of functionalized Amberlite XAD-2 with NPPT are showed in Figs. 4.1, 4.2 and 4.3 respectively.

IR (KBr) (ν_{\max} , cm^{-1}): 3417 (N-H), 3051 (Ar-H), 1616 (C=N), 1258 (C=S) and 1152 (C-N); ¹H 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),. ¹³C 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 C₈H₆N₄O₂S: C, 43.24; H, 2.72; N, 25.21; Found: C, 43.18; H, 2.69; N, 25.17.

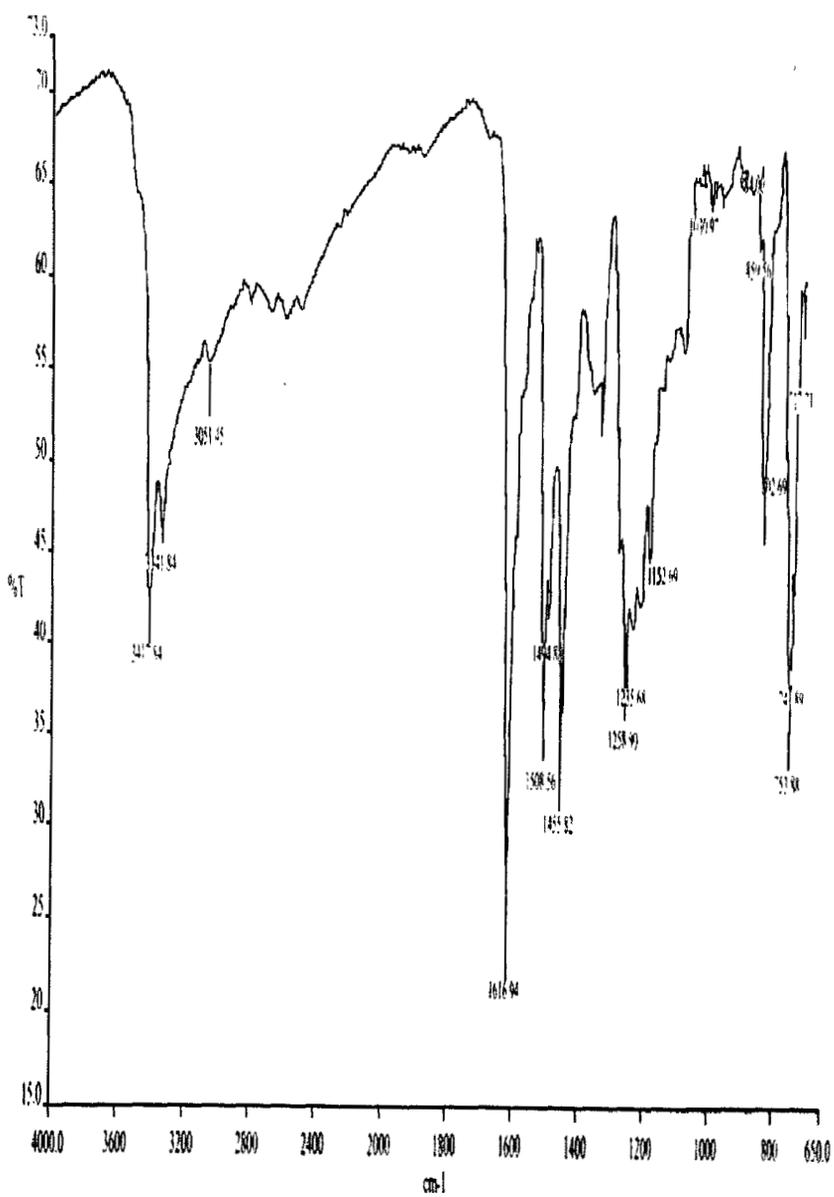


Fig. 4.1: The FT-IR spectrum of 3-(2-nitrophenyl)-1H-1,2,4-triazole-5(4H)-thione (NPTT)

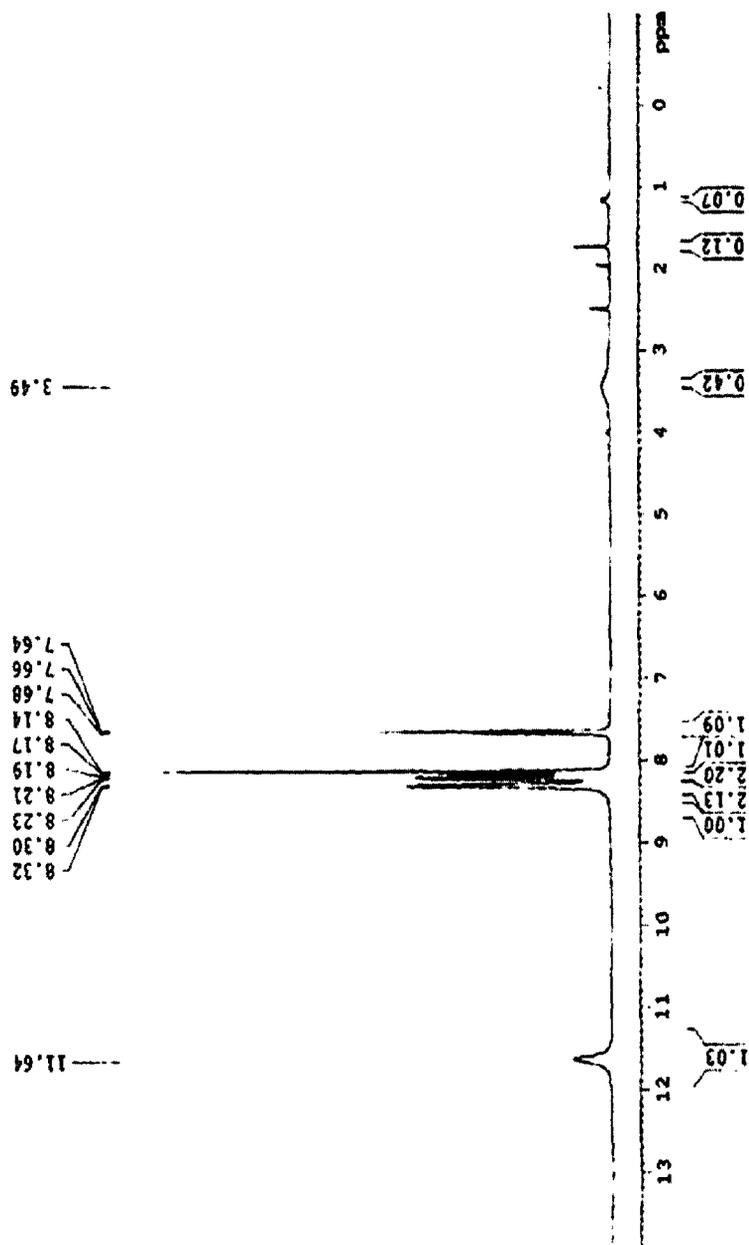


Fig. 4.2: The ¹H NMR spectrum of 3-(2-nitrophenyl)-1H-1,2,4-triazole-5(4H)-thione (NPTT)

4.2.2 Characterization of Amberlite XAD-2-NPTT

The FT-IR spectrum of NPTT (Fig 4.1) showed characteristic IR bands at 3417 cm^{-1} for N-H stretching, 3051 cm^{-1} for Ar-H stretching, 1616 cm^{-1} for C=N stretching, 1258 cm^{-1} for C=S stretching and 1152 cm^{-1} for C-N stretching, respectively. The FT-IR spectrum of XAD-2-NPTT presented in Fig. 4.3 exhibited characteristic bands at 3394 cm^{-1} for N-H stretching, 2948 cm^{-1} for Ar-H stretching, 1659 cm^{-1} for C=O stretching, 1592 cm^{-1} for C=N stretching, 1523 cm^{-1} for N=N stretching, 1228 cm^{-1} for C=S stretching and 1149 cm^{-1} for C-N stretching. These similarities between the spectra of ligand (NPTT) and the functionalized resin support the functionalization of Amberlite XAD-2 with NPTT.

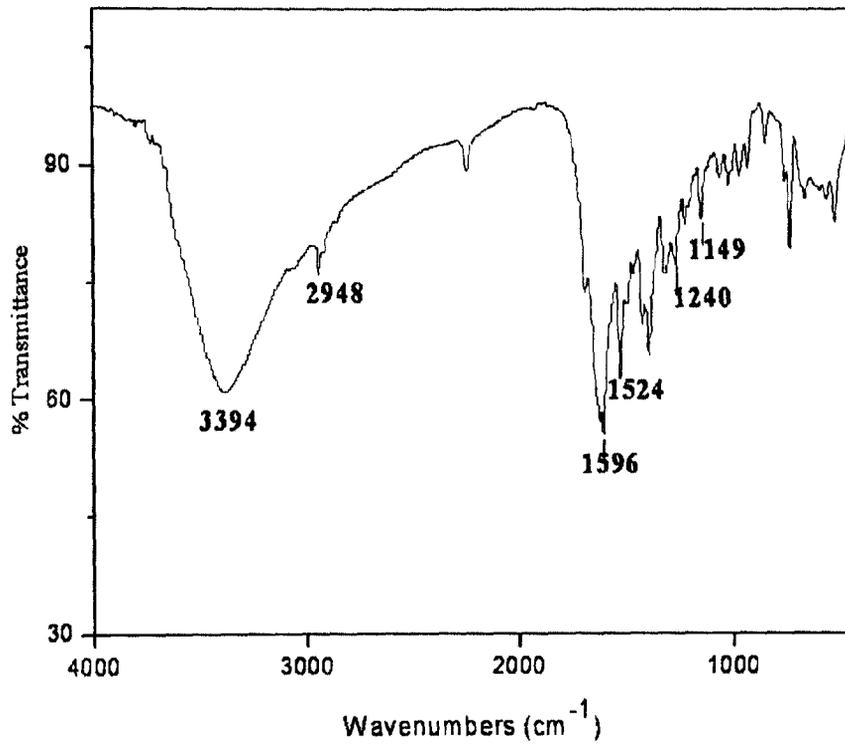


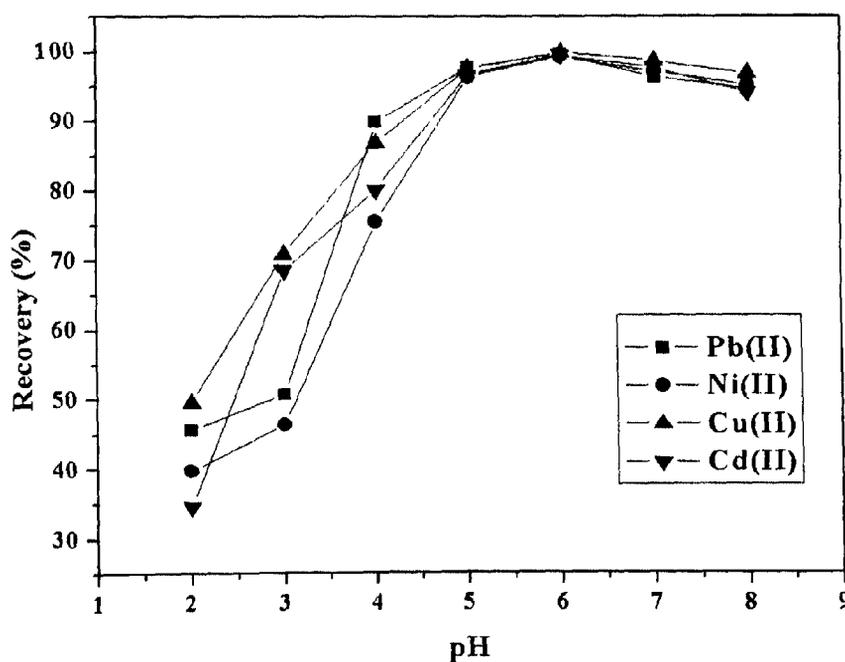
Fig. 4.3: FT-IR spectrum of Amberlite XAD-2-NPTT

4.2.3 Effect of pH

pH is one of the important factors affecting the efficiency of retention/elution of metal ions by solid phase extraction [30]. 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 pH in the range of 2.0–9.0. To evaluate the effect of pH on the extraction efficiency, the pH of the 600 mL sample solutions containing 50 µg each of Pb(II), Ni(II), Cu(II) and Cd(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 were then eluted by an appropriate eluent and determined by ICP-AES. The data corresponding to metal ion recovery is presented in Fig. 4.4 and the optimum pH range for metal ions is given in Table 4.1. In all 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 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 schiff base. 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 for the further studies.

Table 4.1: Effect of pH on the complexation of metals from Amberlite XAD-2 coated with NPTT

pH	% Recovery			
	Pb(II)	Ni(II)	Cu(II)	Cd(II)
2	45.6 ± 2.81	39.8 ± 4.24	49.4 ± 2.42	34.6 ± 4.52
3	50.7 ± 2.33	46.4 ± 2.91	70.8 ± 1.82	68.6 ± 2.14
4	89.8 ± 1.64	75.4 ± 2.12	86.8 ± 1.82	80.1 ± 1.91
5	91.9 ± 1.51	89.3 ± 2.94	92.6 ± 2.34	93.6 ± 2.12
6	99.9 ± 0.72	99.7 ± 0.51	99.8 ± 0.63	99.4 ± 0.43
7	95.2 ± 1.13	96.1 ± 1.92	96.3 ± 2.21	95.9 ± 1.53
8	92.2 ± 1.53	93.6 ± 1.34	94.2 ± 1.14	92.4 ± 1.92

**Fig. 4.4:** Effect of pH on recovery (%) of metal ions

4.2.4 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 upto 500 mg, the metal ions Pb(II), Ni(II), Cu(II) and Cd(II) recoveries were increased. Further, increasing the amount of solid phase at a fixed value of eluting solution (10 mL of 1.0 M HNO₃), there was no increase in the recoveries. Hence, in the proposed procedure, 500 mg of Amberlite XAD-2-NPTT resin was used.

4.2.5 Effect of flow rate

The effect of flow rate of the sample solution on the retention of the metal ions Pb(II), Ni(II), Cu(II), and Cd(II) on the Amberlite XAD-2-NPTT resin was studied in the column packed with 500 mg resin. Sample solutions were passed through the column at various flow rates (1.0 mL min⁻¹ – 5.0 mL min⁻¹) maintained by peristaltic pump at their optimum pH 6.0. 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 on the resin was between 1.0 - 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 metal ions, hence, 2.5 mL min⁻¹ flow rate was chosen as optimum flow rate for elution of these metals from resin.

4.2.6 Selection of the best eluent and its optimization of concentration

For the analytical performance of solid phase preconcentration system, the type and concentration of eluent is also important. A series of selected eluent solutions such as hydrochloric acid, nitric acid and sulphuric acid were used for desorbing the adsorbed lead, nickel, copper and cadmium ions. For each sample the recovery percents of Pb(II), Ni(II), Cu(II) and Cd(II) ions were calculated and the results are showed in Table 4.2. As a result of the experiments, 1.0 M HNO₃ solution was found to be satisfactory for all of

the analytes. Hence 1.0 M HNO₃ was selected as the eluent for the analysis of the metals ions.

4.2.7 Effect of the sample volume

To obtain high preconcentration factor, volume of the sample solution is an important parameter [31]. The effect of sample volume on the elution of Pb(II), Ni(II), Cu(II), and Cd(II) was studied. Different volumes of the water samples were taken in the range of 100-1000 mL and the results were shown in the Table 4.3. It was observed that the recovery was almost same up to 600 mL of aqueous phase (preconcentration factor ~60) in the case of Pb(II), Ni(II), Cu(II), and Cd(II). However, the efficiency of the recovery slightly decreased when sample volume was more than 600 mL. Hence, 600 mL water sample was chosen for the present study.

4.2.8 Sorption capacity

The sorption capacity of Amberlite XAD-2-NPTT (maximum amount of metal sorbed per gram) of each metal ion was determined by batch method. The resin (1g) was saturated with Pb(II), Ni(II), Cu(II) and Cd(II) ion solutions (concentration, 50 µg mL⁻¹) by equilibrating the solutions using a mechanical shaker under optimum conditions. The solid matrix was filtered and washed with distilled water. The sorbed metal ions on the resin was desorbed with 10 mL of 1.0 M HNO₃ and determined by ICP-AES. The sorption capacities in mg g⁻¹ were 4.8 for Pb(II), 3.9 for Ni(II), 4.4 for Cu(II) and 4.2 for Cd(II).

Table 4.2: Recovery of trace metals Pb(II), Ni(II), Cu(II) and Cd(II) using various eluents

Eluents	Recovery (%) ^a			
	Pb(II)	Ni(II)	Cu(II)	Cd(II)
0.05 M HCl	48.6 ± 2.73	48.1 ± 2.83	53.4 ± 2.36	48.6 ± 2.84
0.1 M HCl	82.3 ± 1.72	78.9 ± 2.14	84.5 ± 1.62	82.4 ± 1.74
0.5 M HCl	97.5 ± 1.24	95.9 ± 1.52	95.7 ± 1.62	95.2 ± 1.67
1.0 M HCl	97.7 ± 1.16	96.4 ± 1.65	97.9 ± 1.17	97.3 ± 1.26
0.05 M HNO ₃	51.4 ± 2.14	51.2 ± 1.94	54.6 ± 2.95	51.1 ± 3.16
0.1 M HNO ₃	84.4 ± 1.82	84.6 ± 1.72	86.1 ± 1.56	84.3 ± 1.92
0.5 M HNO ₃	99.3 ± 0.63	98.8 ± 0.46	99.6 ± 0.48	99.2 ± 0.57
1.0 M HNO ₃	99.8 ± 0.47	99.3 ± 0.33	99.8 ± 0.32	99.5 ± 0.43
0.05 M H ₂ SO ₄	46.8 ± 2.92	46.6 ± 2.87	46.8 ± 2.62	45.4 ± 3.12
0.1 M H ₂ SO ₄	79.7 ± 1.95	74.9 ± 2.15	80.6 ± 1.95	73.5 ± 2.26
0.5 M H ₂ SO ₄	96.7 ± 1.53	96.9 ± 1.42	97.3 ± 1.46	97.2 ± 1.54
1.0 M H ₂ SO ₄	97.2 ± 1.16	97.61 ± 1.24	98.6 ± 1.23	95.7 ± 1.92

^aMean ± standard deviation (n=5)

Table 4.3: Effect of sample volume on elution of metal ions

Volume of sample(mL)	Recovery (%)			
	Pb(II)	Ni(II)	Cu(II)	Cd(II)
100	96.2 ± 0.96	95.9 ± 1.15	96.5 ± 0.81	96.4 ± 0.71
200	96.7 ± 1.92	95.9 ± 1.13	96.4 ± 0.74	96.2 ± 0.94
300	97.3 ± 1.94	97.9 ± 1.83	97.4 ± 1.62	97.8 ± 1.82
400	98.8 ± 2.82	98.2 ± 1.75	99.2 ± 0.45	98.6 ± 1.96
500	99.1 ± 0.63	98.9 ± 1.56	99.4 ± 0.42	99.3 ± 0.53
600	99.3 ± 0.47	99.1 ± 0.64	99.6 ± 0.61	99.5 ± 0.42
700	94.3 ± 1.28	95.1 ± 1.35	95.7 ± 1.16	94.1 ± 1.42
800	91.4 ± 0.56	91.5 ± 0.52	93.6 ± 0.84	90.9 ± 0.91
900	86.7 ± 1.63	85.3 ± 1.46	85.2 ± 1.36	84.4 ± 1.42
1000	82.3 ± 1.94	80.3 ± 2.34	81.4 ± 2.12	81.2 ± 1.83

4.2.9 Kinetics of sorption

Sorption kinetics is one of the important parameter that are being studied in solid phase extraction methods because it provides the rate of sorption of metals onto resin functionalized with a reagent in the dynamic column mode for routine analysis of water. The rate of uptake of metal ions on Amberlite XAD-2-NPTT was studied by batch method. Fifty micrograms of individual metal ion solutions was added to 1 g of resin and stirred for 2, 5, 10, 20, 30, 40, 50, 60, 90 and 120 min at a fixed temperature ($30 \pm 0.1^\circ\text{C}$). The metal ions on the resin surface were eluted with 1.0 M HNO_3 and analyzed by ICP-AES as described in the recommended procedure. The saturation of resin with time is graphically presented in Fig. 4.5. 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 (Pb(II), 4.2; Ni(II), 3.6; Cu(II), 3.9 and Cd(II), 4.0 min, respectively). The kinetics of the resin-metal interaction is sufficiently rapid for all 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.

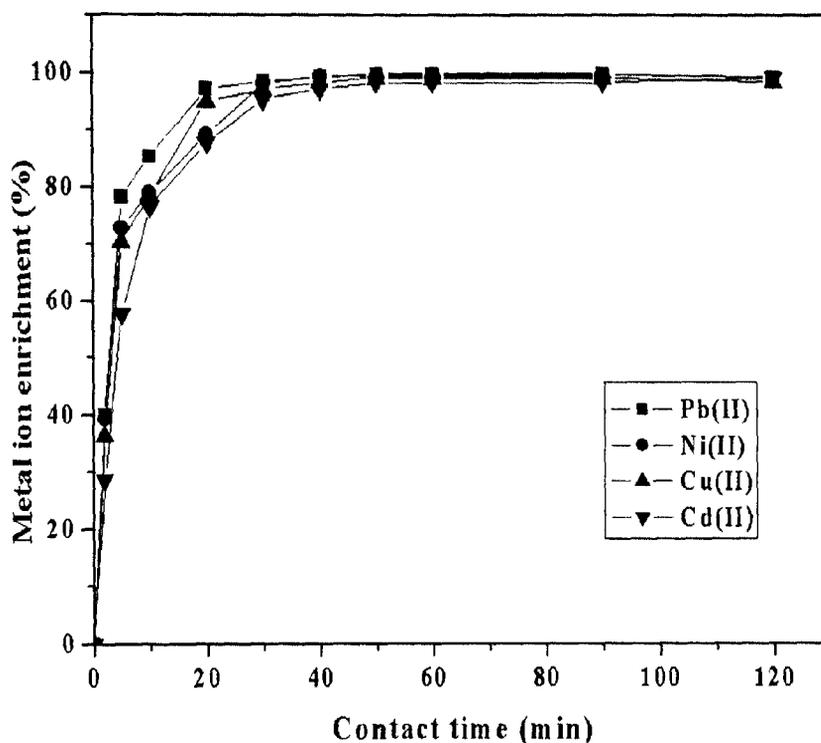


Fig. 4.5: Kinetics of metal ion sorption on Amberlite XAD-2-NPTT resin

4.2.10 Effect of foreign ions

The effect of commonly occurring cations such as sodium, potassium, calcium, magnesium along with the anions like chloride, nitrate, sulphate and phosphate in water and food samples have been studied on the sorption of metal ions, Pb(II), Ni(II), Cu(II) and Cd(II) by Amberlite XAD-2-NPTT functionalized resin with optimized conditions. The tolerance limits of various foreign species on the sorption of the metal ions are given in Table 4.4. The tolerance limit of foreign ions was taken as that value which caused an error of not more than 5 % in the emission reading. Due to good sorption capacity of the resin, all the four metal ions can be preconcentrated simultaneously at a reasonable concentration level (total amount does not exceed sorption capacity).

4.2.11 Column reusability

In order to examine the long-term stability of the reagent, it was subjected to successive concentration and elution cycles (10 runs in a day and the next 10 runs one-day later, and so on, total 20 runs) by passing 600 mL of metal solutions through the column. The stability and potential recyclability of the column-containing reagent were assessed by monitoring the change in the recoveries of the analytes. After 20 runs, the recoveries of all of the analytes slightly decreased to below 95 %.

Table 4.4: Tolerance limits of matrix ions for determination of Pb(II), Ni(II), Cu(II) and Cd(II) by the proposed method ($n=5$)

Matrix ion	Tolerance limit (mg L ⁻¹)	Recovery (%)
Na ⁺	28000	98.1 ± 1.1 ^a
K ⁺	24000	97.2 ± 1.4
Ca ²⁺	20000	96.8 ± 0.9
Mg ²⁺	18000	96.3 ± 0.8
Cl ⁻	23000	98.5 ± 1.6
NO ₃ ⁻	14000	97.3 ± 1.8
HCO ₃ ⁻	10000	95.2 ± 1.3
CH ₃ COO ⁻	10000	95.4 ± 1.2
PO ₄ ³⁻	2500	95.1 ± 1.7
SO ₄ ²⁻	16000	96.4 ± 1.5
Al ³⁺	100	95.4 ± 1.2
Cr ⁶⁺	51	95.1 ± 1.4
Zn ²⁺	40	95.6 ± 0.9
Co ²⁺	44	97.4 ± 1.2

^aMean ± standard deviation

4.2.12 Accuracy of the method

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 4.5, concentrations of the seven metal ions determined by the proposed method are in good agreement with the certified values. Results indicate the applicability of developed procedure in metal ions determination free of interference.

Table 4.5: Recovery of trace metals from standard reference materials after preconcentration on Amberlite XAD-2-NPTT resin

Element	NIST 1643e Water ($\mu\text{g l}^{-1}$)	
	Certified value	Proposed method
Pb	19.58 ± 0.25	19.56 ± 0.24
Ni	62.41 ± 0.29	62.38 ± 0.42
Cu	22.76 ± 0.31	22.73 ± 0.34
Cd	6.51 ± 0.42	6.47 ± 0.26

The values reported are a mean of five readings \pm S.D

4.2.13 Determination of trace metal ions in water samples

Water samples were collected from Penner river (Nellore) and sea water (Bay of Bengal, Nellore) and determined Pb(II), Ni(II), Cu(II) and Cd(II) metal ions, the results are presented in Table 4.6. The values revealed that the concentration of Lead is in the range of 7.42-15.42 $\mu\text{g L}^{-1}$, Nickel is in the range of 14.32-17.31 $\mu\text{g L}^{-1}$, Copper is in the range of 16.27-17.10 $\mu\text{g L}^{-1}$ and Cadmium is in the range of 0.72-1.92 $\mu\text{g L}^{-1}$.

Table 4.6: Determination of trace metal ions in various water samples ($n = 5$)

Sample	ICP- AES method ($\mu\text{g L}^{-1}$)			
	Pb(II)	Ni(II)	Cu(II)	Cd(II)
River water	15.42 \pm 0.56	14.32 \pm 0.27	17.10 \pm 0.31	1.92 \pm 0.28
Sea water	7.42 \pm 0.21	17.31 \pm 0.24	16.27 \pm 0.46	0.72 \pm 0.16

^a Mean \pm standard deviation ($n = 5$).

4.2.14 Determination of trace metal ions in vegetable samples

Vegetable samples namely, Lady's Finger (*Abelmoschus esculentus*), Onion (*Allium sepa*), Cucumber (*Cucumis sativus*), Tomato (*Lycopersicum esculentum*) and Drumstick (*Moringa oleifera*), were collected from two different places (Mallamgunta area and Renigunta area) from the near by agricultural fields of Tirupati town, and determined the Pb(II), Ni(II), Cu(II) and Cd(II) metal ions, the results are presented in Table 4.7. The concentrations of four metals in vegetables collected from the agricultural fields of the areas irrigated by Kalyani river water were found in the range of 0.047-0.138 mg g⁻¹ for Lead, 1.632-3.045 mg g⁻¹ for Nickel, 0.183-0.602 mg g⁻¹ for Copper and 0.021-0.028 mg g⁻¹ for Cadmium. The high concentration of metal ions lead, nickel, copper and cadmium found from the samples collected from the Renigunta area could possibly reflect the influence of effluents entering the irrigated water in that region. This indicates the great impact of irrigation water on the elemental concentrations in vegetables.

4.2.15 Analytical features

The analytical features of the proposed method such as recovery, precision were estimated by applying successive retention and elution cycles with 600 mL of a sample solution containing 50 µg of Pb(II), Ni(II), Cu(II) and Cd(II) under the optimum conditions, mentioned above. The recoveries of Pb(II), Ni(II), Cu(II) and Cd(II) were quantitative (>99%) and the precision of the method was very good (S.D<2.5%) with functionalized Amberlite XAD-2-NPTT. The detection limits based on three-times the standard deviation of the blank solution were found to be 0.16, 0.20, 0.18 and 0.22 µg L⁻¹ detection limit for Pb(II), Ni(II), Cu(II) and Cd(II) respectively.

Table 4.7: Determination of trace metal ions in various food samples (mg g⁻¹)

Botanical Name	Added	Metal ions ^a											
		Pb(II)			Ni(II)			Cu(II)			Cd(II)		
		Found	Recovery (%)	RSD (%)	Found	Recovery (%)	RSD (%)	Found	Recovery (%)	RSD (%)	Found	Recovery (%)	RSD (%)
<i>Abelmoschus esculentus</i> (Lady's Finger)	0.0	0.058	-	2.3	3.045	-	1.9	0.183	-	1.6	0.021	-	3.4
	5.0	5.057	99.6	1.1	8.033	99.6	1.2	5.181	99.1	0.9	5.020	98.7	1.1
	10.0	10.057	99.5	1.0	13.012	98.9	1.0	10.180	98.9	0.8	10.020	97.8	0.8
<i>Allium sepa</i> (Onion)	0.0	0.138	-	2.3	2.043	-	1.6	0.378	-	1.9	0.026	-	3.2
	5.0	5.137	99.2	1.2	7.029	99.3	0.9	5.377	99.8	1.1	5.025	96.2	1.2
	10.0	10.135	98.2	0.9	12.025	99.1	0.7	10.374	99.2	0.8	10.024	94.8	0.9
<i>Cucumis sativus</i> (Cucumber)	0.0	0.129	-	1.2	2.147	-	1.8	0.598	-	1.8	0.027	-	3.1
	5.0	5.127	98.4	0.9	7.121	98.8	0.9	5.591	98.8	1.2	5.026	98.3	1.1
	10.0	10.128	99.2	0.8	12.116	98.6	0.6	10.589	98.6	1.1	10.025	94.9	0.8
<i>Lycopersicum esculentum</i> (Tomato)	0.0	0.047	-	3.4	1.263	-	2.8	0.602	-	1.7	0.024	-	3.3
	5.0	5.046	97.8	1.6	6.253	99.2	1.2	5.598	99.5	1.1	5.023	97.3	0.8
	10.0	10.045	96.4	1.4	11.249	98.9	1.0	10.595	98.9	0.8	10.022	95.4	0.7
<i>Moringa oleifera</i> (Drumstick)	0.0	0.096	-	1.7	1.632	-	2.9	0.576	-	1.7	0.028	-	3.1
	5.0	5.094	98.5	0.8	6.601	98.1	1.5	5.568	98.7	1.3	5.027	96.4	1.0
	10.0	10.093	97.8	0.6	11.598	97.9	1.4	10.565	98.1	1.2	10.026	94.8	0.8

^aMean standard deviation (n=5)

4.3 Conclusions

The newly developed method can be successfully used for separation and preconcentration of Pb(II), Ni(II), Cu(II), and Cd(II) in water and food samples and can be determined 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 reusability of the resin is more than 20 times without affecting its sorption capacity. The method has high tolerance limits from the matrix ions. The proposed solid phase extraction 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 Pb(II), Ni(II), Cu(II), and Cd(II) in water and food samples.

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