Chapter-V

Synthesis and characterization of 3-(2-hydroxyphenyl)-1H-1,2,4-triazole-5(4H)-thione(HPTT) and its application in solid phase extraction of trace metals Cu(II), Fe(II), Co(II) and Mn(II) in environmental and food samples

The review of literature on the determination of Cu(II), Fe(II), Co(II) and Mn(II) metal ions in environmental samples showed that several methods employing thiosemicarbazide derivative (Triazole) are used to separate and preconcentrate the elements according to the nature of the samples, the concentrations of the analytes and measurement techniques.

Gao, et al. [1] used chemically modified activated carbon with 1-acylthio-semicarbazide for selective solid-phase extraction and preconcentration of traces of Cu(II) along with other elements from water samples. Application of molecular modeling of 4-ethyl-1-(pyridin-2-yl)thiosemicarbazide and its Cu(II) complex for separation of Cu(II) from water samples was reported by Hassanien et al. [2]. Rao et al. [3] reported a solid phase extraction of Cd, Cu and Ni from leafy vegetables and plant leaves using Amberlite XAD-2 functionalized with 2-hydroxy-acetophenone-thiosemicarbazone (HAPTSC) and determination by inductively coupled plasma atomic emission spectroscopy. Liu et al. [4] described a solid phase spectrophotometric determination method for determination of nickel in water and vegetable samples at sub-$\mu g \ l^{-1}$ level with o-carboxylphenyldiazoaminoazobenzene loaded XAD-4. Solid phase extraction method for trace metals from environmental samples using Amberlite XAD-7 loaded with 2-hydroxy-propiophenone-4-phenyl-3-thiosemicarbazone and determination by inductively coupled plasma–atomic emission spectrometry was reported by Veni et al. [5]. Uchida et al. [6] reported determination of 12 elements in biological samples using ICP-AES after extracting with tetramethyl ammonium hydroxide and ethylene diaminotetraacetic acid.

Alonso et al. [7] described a flow injection ICP-AES method for the sequential determination of trace amounts of heavy metals (Cd, Co, Cu and Zn) in biological samples. A method based on the complexation of the metal ions with 1,5-bis (di-2-pyridyl) methylene thiocarbohydrazide and its subsequent on-line extraction into isobutyl methyl ketone was reported by Cordero et al. [8]. Nobrega et al. [9] studied determination of elements in biological and botanical materials by ICP-AES and mass spectrometry after extraction with a tertiary amine reagent.

Narin et al. [10] synthesized a chelating resin by immobilizing 1-(2-pyridylazo)-2-naphtol on Amberlite XAD-16 and studied its application for solid phase extraction of Co(II), Cu(II) along with metals in natural water samples. Wuilloud et al. [11]

determined the lead in drinking water by ICP-AES with ultrasonic nebulization and flow-injection on-line preconcentration using an Amberlite XAD-16 Resin. Tokalioglu et al. [12] described atomic absorption spectrometric method after sorption on amberlite XAD-16 resin for the determination of heavy metals in lake water. Elci et al. [13] described the determination of trace impurities in some nickel compounds by flame atomic absorption spectrometry after solid phase extraction using Amberlite XAD-16 resin. Venkatesh et al [14] synthesized a reagent 2-{[1(3,4 Dihydroxyphenyl) methylidene]amino}benzoic acid, immobilized on Amberlite XAD-16 as metal extractant. Sharma et al. [15] studied the solid phase extraction and determination of metal ions in aqueous samples using Quercetin modified Amberlite XAD-16 chelating polymer as metal extractant. Ghaedi et al. [16] described a flame atomic absorption spectrometric method for the determination of copper, zinc and manganese after solid-phase extraction using 2,6-dichlorophenyl-3,3-bis(indolyl)methane loaded on Amberlite XAD-16. Sharma et al. [17] described a preconcentration method for the determination of trace metal ions from aqueous samples using newly developed gallic acid modified Amberlite XAD-16 chelating resin.

In view of this, we have developed a new thiosemicarbazide derivative and used for the separation and preconcentration of Cu(II), Fe(II), Co(II) and Mn(II) in water and vegetable samples based on the coupling of ligand 3-(2-nitrophenyl)-1*H*-1,2,4-triazole-5(4*H*)-thione (NPTT) with polymer back bone through azo spacer. The established method was applied for the preconcentration and determination of analytes in water and food samples.

5.1 Structure of 3-(2-hydroxyphenyl)-1*H*-1,2,4-triazole-5(4*H*)-thione
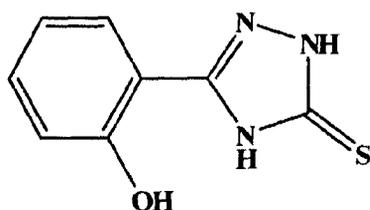
The reagent, 3-(2-hydroxyphenyl)-1*H*-1,2,4-triazole-5(4*H*)-thione (HPTT) form stable complexes with many transition metal ions. The reagent can be easily synthesized in the laboratory and is suitable for functionalization of solid support like Amberlite XAD-16, which is a good requirement in solid phase extraction techniques.

5.2   RESULTS AND DISCUSSION

5.2.1   Characterization of 3-(2-hydroxyyphenyl)-1*H*-1,2,4-triazole-5(4*H*)-thione (HPTT)

The detailed procedure of synthesis of 3-(2-hydroxyphenyl)-1*H*-1,2,4-triazole-5(4*H*)-thione (HPTT) and functionalization of Amberlite XAD-16 with the reagent, along with the schemes are reported in sections 2.5.3, 2.7.3 and Figs. 2.3, 2.7. The FT-IR and ^{1}H NMR spectrum of HPTT and FT-IR spectrum of functionalized Amberlite XAD-16 with HPTT are showed in Figs. 5.1, 5.2 and 5.3 respectively.

IR (KBr) ($\ddot{u}_{max}$, cm^{-1}): 3396 (N-H), 3158 (O-H), 2985 (Ar-H), 1604 (C=N), 1226 (C=S) and 1168 (C-N); ^{1}H NMR (DMSO-d_6): δ 11.43 (1H, s, NH), 9.89 (1H, s, OH), 7.34-7.31 (m, 2H, Ar), 6.83-6.81 (d, 2H, Ar), 3.86 (1H, s, NH),; ^{13}C NMR (DMSO-d_6): δ 177.5, 156.3, 139.4, 131.1, 126.6, 120.2, 119.2, 115.9. APCI-MS (*m/z*) 194 [M+H], Anal. calcd for $C_8H_7N_3OS$: C, 49.73; H, 3.65; N, 21.75; Found:C, 49.68; H, 3.61; N, 20.71.
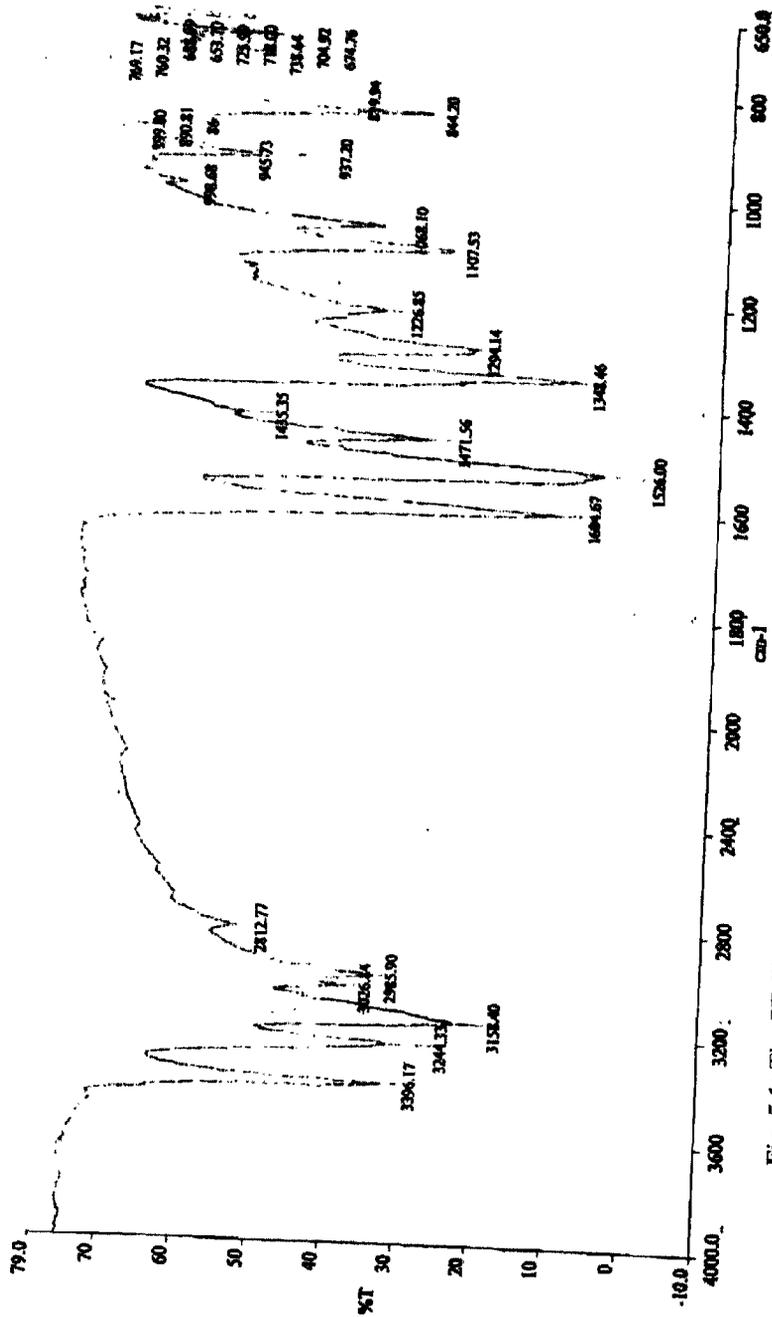
Fig. 5.1: The FT-IR spectrum of 3-(2-hydroxyyphenyl)-1*H*-1,2,4-triazole-5(4*H*)-thione (HPTT)

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Fig. 5.2: The ^{1}H NMR spectrum of 3-(2-hydroxyyphenyl)-1H-1,2,4-triazole-5(4H)-thione (HPTT)

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5.2.2 Characterization of AXAD-16 with HPTT

The FT-IR spectrum (Fig. 5.1) of HPTT showed bands at 3394, 2986, 1646, 1247 and 1168 cm^{-1} due to N-H stretching, Ar-H stretching, C=S stretching, C=N and C-N stretching, respectively. The FT-IR spectrum of XAD-16-HPTT presented in Fig. 5.3 showed bands at 3356, 2979, 1628, 1546, 1233, 1147 cm^{-1} due to N-H stretching, Ar-H stretching, N=N stretching, C=S stretching, C=N and C-N stretching respectively. These similarities between the spectra of ligand (HPTT) and the functionalized resin support the functionalization of Amberlite XAD-16 with HPTT.
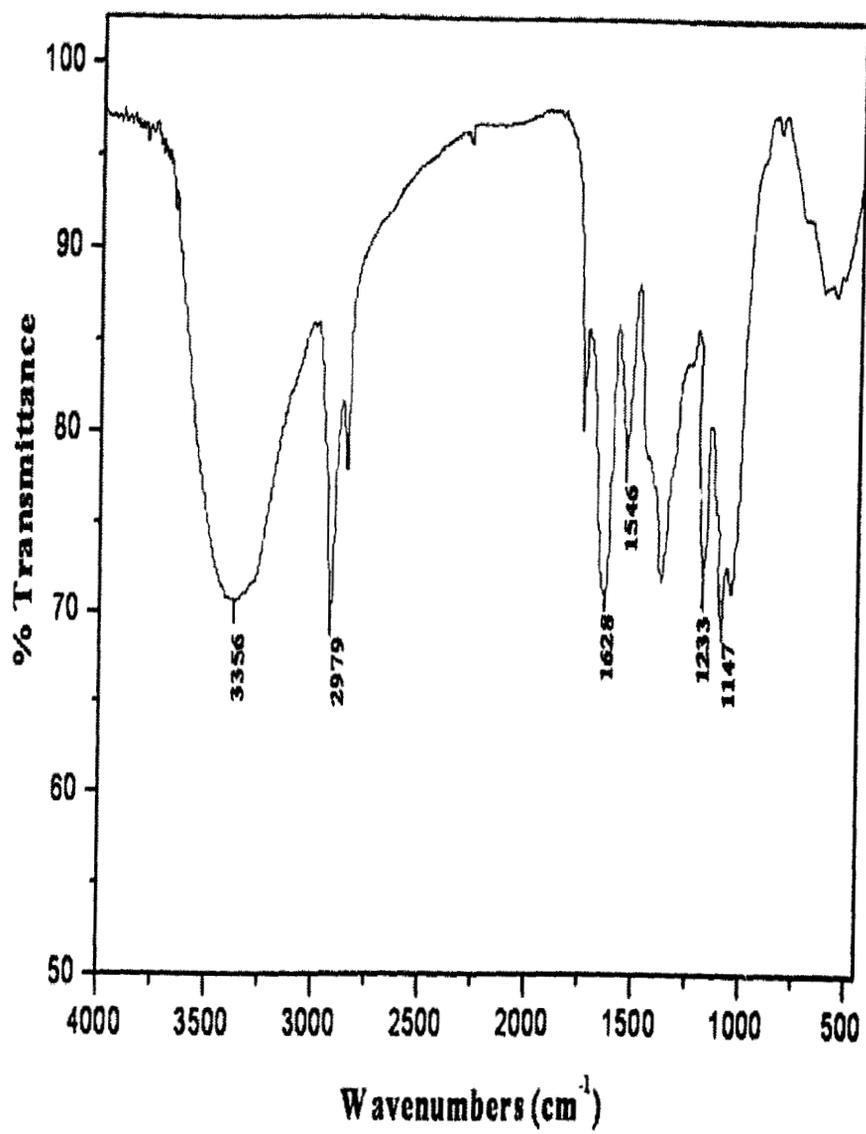
Fig. 5.3: FT-IR spectrum of Amberlite XAD-16-HPTT

5.2.3 Effect of pH on metal preconcentration

In the solid-phase extraction studies, the influence of pH of the aqueous solution is one of the most important factors for quantitative recoveries of metal ions. The influence of pH on uptake of metal ions Cu(II), Fe(II), Co(II), and Mn(II) onto the resin functionalized with HPTT was studied using the column procedure. An amount of 500 mg of functionalized resin was placed in a column and a suitable aliquot of metal ion solution containing Cu(II), Fe(II), Co(II), and Mn(II) was passed through the column at optimum flow rate by changing the pH of aqueous solution from 2.0 to 8.0 using appropriate buffers. The experiments were carried in triplicate for the metal ions. The data corresponding to metal ion recovery is presented in Fig. 5.4 and the optimum pH range for metal ion is given in Table 5.1. The optimum pH range for maximum recoveries are 3.0-6.0 for Cu, 5.0-6.0 for Fe, 4.0-6.0 for Co and 4.0-7.0 for Mn. The results revealed that at pH 5.0 the quantitative sorption of four metals was achieved. Hence, this pH was selected as optimum pH for SPE of metal ions.

5.2.4 Effect of amount of resin on preconcentration of metals

The amount of solid phase in the column is a main parameter for the quantitative recovery of analyte ions. For the maximum recovery of metals in environmental and food samples, there must be sufficient quantity of resin that ensures total retention of metals onto its surface. The quantity of Amberlite XAD-16-HPTT resin that required for retention of total analytes, Cu(II), Fe(II), Co(II), and Mn(II) in samples was studied by taking varying amounts (100-800 mg) of Amberlite XAD-16-HPTT resin filled in the column. It was found that maximum recoveries of all the examined analytes were observed when 500 mg of resin was used in the column. Therefore 500 mg of Amberlite XAD-16-HPTT resin was used for subsequent determinations.

Table 5.1: Effect of pH on the complexation of metals from Amberlite XAD-16 coated with HPTT

pH	% Recovery			
	Cu(II)	Fe(II)	Co(II)	Mn(II)
2	90.2 ± 0.71	70.7 ± 1.62	74.9 ± 1.46	80.4 ± 1.24
3	99.0 ± 0.42	81.2 ± 1.11	88.2 ± 0.76	88.9 ± 0.93
4	98.8 ± 0.53	92.4 ± 0.84	95.0 ± 0.92	97.9 ± 0.92
5	99.6 ± 0.36	96.0 ± 0.75	95.7 ± 0.84	98.3 ± 0.71
6	99.5 ± 0.42	96.7 ± 0.52	95.8 ± 0.76	98.7 ± 0.64
7	92.4 ± 0.81	94.6 ± 0.68	90.7 ± 0.71	98.2 ± 0.74
8	90.2 ± 0.93	89.2 ± 0.72	88.9 ± 0.91	92.4 ± 1.11
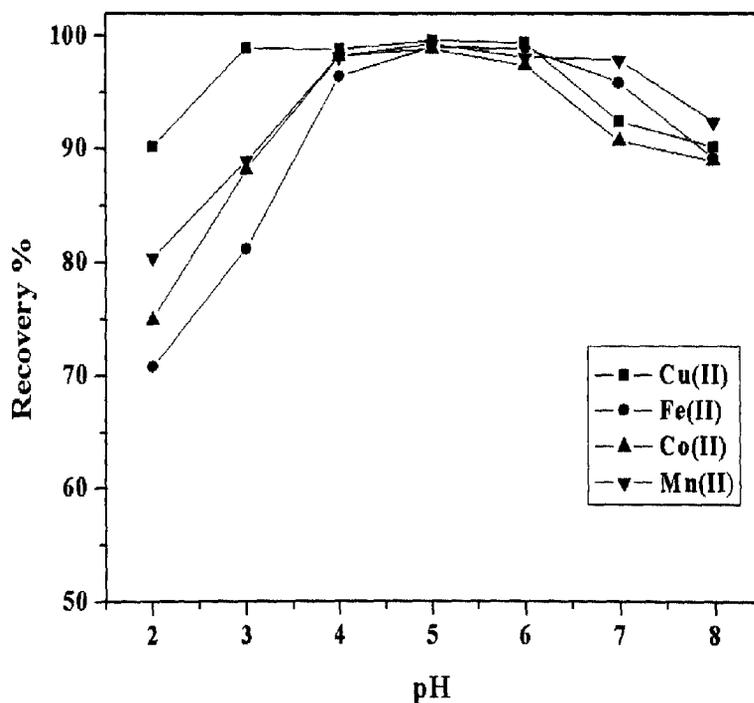
Fig. 5.4: Effect of pH on recovery (%) of metal ions

5.2.5 Effect of flow rate

The rate of the flow of metal solutions through the column is one of the factors affecting the duration of the determination and directly related to the contact of the solution with the resin thereby providing good retention of the metal ions on the resin. The influence of the sample flow rate on the retention and recoveries of the analyte ions on Amberlite XAD-16-HPTT resin were examined. It was found that the optimum flow rate for loading these metal ions on resin bed was between 1.5 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 increased flow rate more than 2.5 mL min^{-1} causes a gradual decrease in sorption due to insufficient contact time between analytes and adsorbent, thus, a flow rate of 2.5 mL min^{-1} was selected in this work for elution of these metals from resin.

5.2.6 Selection of the best eluent and its optimization of concentration

Various acids were used to identify the best eluent for the sorbed metal ions from Amberlite XAD-16-HPTT. Eluent solutions such as hydrochloric acid, nitric acid and sulphuric acid were used for desorbing the adsorbed cobalt, nickel, copper and iron ions. For each sample, the recovery percents of Cu(II), Fe(II), Co(II), and Mn(II) ions were calculated and the results are showed in Table 5.2. From the observed result of the experiments, 1.0 M HNO_3 solution was found to be suitable for all of the analytes. Hence 1.0 M HNO_3 was selected as the eluent for the analysis of the metals.

Table 5.2: Recovery of trace metals Cu(II), Fe(II), Co(II), and Mn(II) using various eluents

Eluents	Recovery (%)[a]			
	Cu(II)	Fe(II)	Co(II)	Mn(II)
0.05 M HCl	48.4 ± 3.5	48.1 ± 3.6	39.3 ± 4.1	46.1 ± 3.9
0.1 M HCl	83.5 ± 2.4	81.7 ± 2.7	79.8 ± 2.6	75.6 ± 2.5
0.5 M HCl	95.8 ± 1.7	95.4 ± 1.8	96.4 ± 1.3	95.9 ± 1.2
1.0 M HCl	98.9 ± 0.8	97.5 ± 0.7	98.7 ± 0.8	96.9 ± 1.1
0.05 M HNO_3	52.4 ± 3.5	51.6 ± 3.6	49.4 ± 3.7	52.1 ± 3.4
0.1 M HNO_3	87.5 ± 2.4	86.1 ± 2.5	83.4 ± 2.6	85.3 ± 2.6
0.5 M HNO_3	99.4 ± 0.5	99.1 ± 0.6	97.3 ± 0.9	98.9 ± 0.8
1.0 M HNO_3	99.7 ± 0.4	99.6 ± 0.3	99.6 ± 0.3	99.3 ± 0.4
0.05 M H_2SO_4	42.9 ± 3.7	45.1 ± 3.4	40.8 ± 3.6	43.2 ± 3.8
0.1 M H_2SO_4	82.1 ± 2.1	76.5 ± 2.4	75.7 ± 2.6	75.4 ± 2.8
0.5 M H_2SO_4	97.8 ± 1.2	97.6 ± 1.2	95.4 ± 1.3	96.9 ± 1.2
1.0 M H_2SO_4	98.7 ± 0.7	97.3 ± 1.1	98.3 ± 0.6	97.1 ± 1.1

5.2.7 Effect of sample volume

In order to obtain high preconcentration factor, the solid phase extraction technique is a common procedure for extraction and separation of metal ions from large sample volumes [18-20]. The effect of the sample solution volume on the metal sorption was also studied at pH 5 by passing 100–1000 mL volumes through the column and the results are shown in the Table 5.3. It was observed that the recoveries was almost same up to 500 mL of aqueous phase (preconcentration factor ~50) in the case of Cu(II), Fe(II), Co(II), and Mn(II). However, there was no change in the efficiency of the recovery when sample volume was more than 500 mL and use of higher volumes taking longer analysis time. Hence, 500 mL water sample was chosen as the appropriate volume.

5.2.8 Sorption capacity

The sorption capacity of Amberlite XAD-16-HPTT resin was determined by batch method. The resin (1.0 g) was saturated with Cu(II), Fe(II), Co(II), and Mn(II) solutions (concentration 50 μg mL^{-1}) by equilibrating on a mechanical shaker under optimum conditions. The solid matrix was filtered and washed with distilled water. The remaining metals in supernatant liquid were determined by ICP-AES, after appropriate dilution. The amounts of metals sorbed onto Amberlite XAD-16-HPTT resin were obtained by mass balance. The sorption capacity values of resin were   5.46 mg g^{-1} for Cu(II), 5.21 mg g^{-1} for Fe(II), 4.62 mg g^{-1} for Co(II) and 4.73 mg g^{-1} for Mn(II).

Table 5.3: Effect of sample volume on elution of metal ions

Volume of sample(mL)	Recovery (%)[a]			
	Cu(II)	Fe(II)	Co(II)	Mn(II)
100	95.5 ± 0.37	95.4 ± 0.29	95.7 ± 0.39	95.6 ± 0.28
200	96.7 ± 0.43	96.2 ± 0.36	95.9 ± 0.29	95.8 ± 0.37
300	98.6 ± 0.49	97.9 ± 0.39	96.3 ± 0.28	96.9 ± 0.32
400	99.1 ± 1.59	98.9 ± 1.23	98.9 ± 1.23	98.8 ± 1.18
500	99.6 ± 0.57	99.5 ± 0.48	99.3 ± 0.38	99.1 ± 0.32
600	98.4 ± 0.42	94.6 ± 0.28	96.3 ± 0.31	97.2 ± 0.35
700	94.2 ± 0.25	92.4 ± 0.27	90.7 ± 0.21	94.3 ± 0.18
800	92.6 ± 0.21	89.9 ± 0.18	87.4 ± 0.16	91.5 ± 0.24
900	88.2 ± 2.98	84.4 ± 2.89	84.7 ± 2.83	86.1 ± 2.86
1000	86.4 ± 2. 82	83.2 ± 2.56	82.8 ± 2.32	82.3 ± 2.42

Table 5.4: Optimum experimental conditions for the sorption and desorption of metal
ions on Amberlite XAD-16-HPTT resin

Experimental parameters	Metal ion			
	Cu(II)	Fe(II)	Co(II)	Mn(II)
pH	3.0-6.0	5.0-6.0	4.0-6.0	5.0-7.0
Flow rate (mL min^{-1})	2.5	2.5	2.5	2.5
HNO$_3$ conc. for desorption (M)	1.0	1.0	1.0	1.0
t$_{1/2}$ (min)	3.6	3.4	4.0	2.9
Sorption capacity (mg/g)	5.46	5.21	4.62	4.73
Average recovery (%)	99.6	99.1	98.9	99.3

5.2.10 Effect of foreign ions

Various cations and anions that are commonly present in real samples like natural
water and vegetables along with heavy metals, may interfere in the latter's determination
through by competing complexation reactions. Common chemical species such as
chloride, nitrate, sulphate and phosphate anions along with cations such as Na$^+$, K$^+$, Ca^{2+}
and Mg^{2+} in natural water and food samples have been studied on the sorption of metal
ions Cu(II), Fe(II), Co(II) and Mn(II) by Amberlite XAD-16-HPTT functionalized resin
with optimized conditions. The tolerance limits of various foreign species on the sorption
of the metal ions are given in Table 5.5. The tolerance limit of foreign ions was taken as
that value 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).

Table 5.5: Tolerance limits of matrix ions for determination of Cu(II), Fe(II), Co(II) and Mn(II) by the proposed method ($n=5$)

Matrix ion	Tolerance limit (mg L^{-1})	Recovery (%)
Na$^+$	42000	98.1 ± 1.5^a
K$^+$	40000	97.2 ± 1.2
Ca^{2+}	38000	97.5 ± 1.4
Mg^{2+}	33000	96.6 ± 1.2
Cl$^-$	40000	98.3 ± 1.6
NO$_3^-$	30000	97.1 ± 1.8
HCO$_3^-$	26000	95.7 ± 1.5
CH$_3$COO$^-$	29000	97.4 ± 1.1
PO$_4^{3-}$	3300	95.1 ± 1.4
SO$_4^{2-}$	33000	96.9 ± 1.6
Al^{3+}	150	95.7 ± 1.3
Cr^{6+}	60	95.4 ± 1.1
Zn^{2+}	45	95.6 ± 0.9
Pb^{2+}	42	97.4 ± 1.4
Cd^{2+}	42	96.1 ± 1.3

^{a}Mean ± standard deviation

5.2.11 Column reuse

A series of sorption/desorption experiments were performed to understand the reusability of the sorbent (functionalized Amberlite XAD-16-HPTT resin), After sorption, the sorbent was treated with 10 mL nitric acid (1 mol L^{-1}) to desorb Cu(II), Fe(II), Co(II) and Mn(II) and this sorption/desorption procedure was repeated 10 times, by passing 500 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 10 runs, the recoveries of all of the analytes slightly decreased to below 95 %. The functionalized Amberlite XAD-16-HPTT resin can be regenerated fully up to 10 cycles. On storing for six months under dark and dry conditions, the stability of sorbent was excellent and adsorption capacity did not change significantly. Therefore, multiple use of the functionalized Amberlite XAD-16-HPTT resin is feasible.

5.2.12 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 5.6, concentrations of the four 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 5.6: Recovery of trace metals from standard reference materials after preconcentration on Amberlite XAD-16-HPTT resin

Element	NIST 1643e Water ($\mu g \ l^{-1}$)	
	Certified value	Proposed method
Cu	22.76 ± 0.31	22.71 ± 0.31
Fe	98.10 ± 1.40	97.73 ± 1.48
Co	27.06 ± 0.32	26.83 ± 0.36
Mn	38.97 ± 0.69	38.91 ± 0.81

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

5.2.13 Determination of trace metal ions in water samples

Water samples were collected from tap water (Tirupati) and river water (Penner river, Nellore) and determined the Cu(II), Fe(II), Co(II) and Mn(II) metal ions, the results are presented in Table 5.7. The results revealed that the concentration of Copper is in the range of 15.86-18.32 μg L^{-1}, Iron is in the range of 11.81-14.36 μg L^{-1}, Cobalt is in the range of 1.84-2.93 μg L^{-1} and Manganese is in the range of 3.96-12.42 μg L^{-1}.

Table 5.7: Determination of trace metal ions in various water samples ($n = 5$)

Sample	ICP- AES method (μg L^{-1})			
	Cu(II)	Fe(II)	Co(II)	Mn(II)
Tap water	15.86 ± 0.36[a]	11.81 ± 0.21	1.84 ± 0.46	3.96 ± 0.16
River water	18.32 ± 0.56	14.36 ± 0.21	2.93 ± 0.35	12.42 ± 0.26

[a]Mean±standard deaviation ($n = 5$)

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5.2.14 Determination of trace metal ions in vegetable samples

Vegetable samples namely, Cauliflower *(Brassica olera. var. Botrytis)* and Sweet Potato *(Ipomoea)*, were collected from two different places (Mallamgunta area and Renigunta area) from the near by agricultural fields of Tirupati town, and determined the Cu(II), Fe(II), Co(II) and Mn(II) metal ions, the results are presented in Table 5.8. The concentrations of four metals in vegetables collected from the agricultural fields of the areas were found in the range of 0.71-2.71 μg g^{-1} for Copper, 5.69-78.23 μg g^{-1} for Iron and 0.19-0.46 μg g^{-}l for Cobalt and 0.32-1.24 μg g^{-}l for Manganese. The high concentration of metal ions copper, iron, cobalt and manganese 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.

Table 5.8: Determination of Cu(II), Fe(II), Co(II) and Mn(II) in vegetable samples

Vegetable sample	ICP-AES method (μg g^{-1})			
	Cu(II)	Fe(II)	Co(II)	Mn(II)
Brassica olera. var. Botrytis (Cauliflower)	2.71 ± 0.26[a]	78.23 ± 0.18	0.46 ± 0.14	1.24 ± 0.26
Ipomoea (Sweet Potato)	0.71 ± 0.12	5.69 ± 0.34	0.19 ± 0.26	0.32 ± 0.21

[a] Mean ± standard deviation ($n = 5$)

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5.3   Conclusions

It can be concluded that the SPE method based on the fucntionalization of Amberlite XAD-16-HPTT is applicable for the separation and preconcentration of Cu(II), Fe(II), Co(II) and Mn(II) in water and vegetable samples and determination by ICP-AES. The optimum experimental conditions for the quantitative sorption of four metals, effect of pH, sample volume, flow rate, concentration of eluent, sorption capacity, kinetics of sorption, and the effect of diverse ions on the sorption of analytes have been investigated. All the metal ions were quantitatively retained by the functionalized resin at pH 5.0 and sorbed metals could be eluted with 1.0 M HNO_3. The functionalized chelating resin Amberlite XAD-16-HPTT is stable in acidic medium, has good resin-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 10 times without affecting its sorption capacity. The developed solid phase extraction method has 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 Cu(II), Fe(II), Co(II) and Mn(II) in water and food samples. This proposed method has high tolerance limits from the matrix ions and is useful for the preconcentration and determination of metal ions from the natural water and food samples.

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