Chapter-III

**Synthesis and characterization of Potassium
2-benzoyl hydrazine carbodithioate (PBHCD) and its
application in separation and preconcentration of trace
metals in water and leafy vegetables and determination
by ICP–AES**

The strong metal binding property of dithiocarbamates combined with the insolubility of metal complexes in water and the capacity of molecules to form chelate complexes are the advantages for the wide application of dithiocarbamate compounds as ligands in heavy metal determination. The applications of this class of compounds in medicine, agriculture, industry, analytical and organic chemistry, as well as their physicochemical properties are summarized in several review articles [1-10]. Dithiocarbarmates (DTCs) have attracted interest as chelating agents because of their thermodynamically stable metal complexes and selectivity against alkali and alkaline earth metals [11], hence are suitable for trace metal preconcentration as well as for sample cleanup.

Review of literature revealed that several dithiocarbamates are used as ligands in trace metal analysis. An extraction preconcentration of trace metals from sea water usuing dithiocarbametes and determination by inductively coupled plasma-atomic emission spectrometry (ICP-AES) was reported by Sugimae [12]. In this method Cu, Mn and Zn along with other elements were complexed with sodium diethyldithiocarbamate and the complexes were extracted with chloroform. Preconcentration of trace metals, Cd, Cu, Fe, Mn and Zn in river water using hexamethylene-ammonium hexamethylene dithiocarbamate (HMAHMDC) reagent and ammonium pyrrolidine dithiocarbamate (APDC) reagent followed by xylene extraction was reported by Tao et al. [13]. Ramesh et al. [14] developed a method for preconcentration of trace metals Cd(II), Cu(II), Mn(II), Ni(II), Pb(II) and Zn(II) in saline water using Amberlite XAD-4 resin coated with dithiocarbamates and determination by inductively coupled plasma-atomic emission spectrometry. Ramesh et al. [15] developed a solvent extraction mehod using piperidine dithiocarbamate for the preconcentration and determination of Cd(II), Cd(II), Cu(II), Mn(II), Ni(II), Pb(II) and Zn(II). Smith et al. [16] studied the application of sodium dibenzyldithiocarbamate as a precipitating agent for preconcentration of trace metals in water. A preconcentration method using ammonium pyrrolidinedithiocarbamate as reagent for determination of trace metals in seawater and natural water was studied by Shah et al. [17]. Application of poly (dithiocarbamate) for preconcentration of trace metals in natural waters and determination by hydride generation-inductively coupled argon plasma was reported by Van Berkel et al. [18]. Flow injection preconcentration method coupled with direct sample insertion for ICP-AES analysis was studied by Moss

and Salin [19]. Lopez-Artiquez [20] developed an activated charcoal-ammonium pyrrolodine-dithiocarbamate separation and preconcentration method for determination of Co, Ni, Cu, Cd and Pb by ICP–AES. Alexandrova and Arpadjan [21] studied column solid-phase extraction using solid ammonium hexamethylenedithiocarbamate (HMDC) mixed with polyurethane foam for the preconcentration of trace amounts of Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni and Pb from analytical reagent grade sodium salts prior to their determination by ICP-AES or AAS. On-line flow injection cobalt-ammonium pyrrolidinethiocarbamate co-precipitation for preconcentration of Cd, Cu, Fe, Ni, Pb and Zn in rain water samples was reported by Zhuang et al. [22]. Atanasova et al. [23] described column solid-phase extraction method for the preconcentration of As, Co, Se, Cr, Pb, Zn, Cu, Mn, Cd, Sb and Sn in water using sodium diethyldithiocarbamate supported polyurethane foam and subsequent determination by ICP-AES. Sodium diethyldithiocarbamate in presence of weak oxidizing agent, as a co-precipitative agent for the preconcentration of Se, Cu, Pb, Zn, Fe, Co, Ni, Mn, Cr and Cd was reported by Atanasova et al. [24]. Abollino et al. [25] developed a solid-phase extraction/slurry-sampling procedure using dithiocarbamate–Amberlite XAD-2 resin for preconcentration of the metals in highly saline matrices and determination by ICP-AES. Preconcentration of Cd(II), Cu(II), Mn(II), Ni(II), Pb(II) and Zn(II) in saline matrices using Amberlite XAD-4 resins coated with ammonium pyrrolidine dithiocarbamate (APDC) and piperidine dithiocarbamate (pipDTC) and subsequent determination by inductively coupled plasma atomic emission spectrometry was studied by Ramesh et al. [26]. A column solid-phase extraction procedure for separation and preconcentration of bismuth in natural water samples using sodium diethyldithiocarbamate (NaDTTC) or piperidene dithiocarbamate (pipDTC)-coated Amberlite XAD-7 resin prior to their determination by inductively coupled plasma atomic emission spectrometry (ICP-AES) was reported by Rao et al. [27].

Study of aforesaid preconcentration methods revealed that the dithiocarbamates were used as solid sorbents by embedding between inert resin particles without any chemical bonds between inert solid support and dithiocarbamate. Hitherto to no attempt has been made in the functionalization of resin with dithiocarbamates. In view of this we have prepared an aromatic dithiocarbamate, which is suitable for fucntionalization of Amberlite XAD resins by covalently coupling of aromatic dithiocabamate with polymer back bone through azo (-N = N-) spacer group that provide stable chelating resins. These

functionalized resins 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.

Amberlite XAD series resins have several advantages over other supports because of their good physical properties such as their porosity, uniform pore size distribution, high surface area as chemical homogeneous non-ionic structure, and good adsorbent properties for great amounts of uncharged compounds [28]. The most widely used support materials for this purpose are XAD-2, XAD-4 and XAD-16 in the Amberlite XAD series. Amberlite XAD-16 has an edge over these resins due to the high surface area in comparison to the XAD-2 and XAD-4 resins [29]. The large surface area also makes it possible to increase the number of chelating sites and to make them more accessible towards the enrichment of metal ions. This can be achieved by selecting a ligand of small size and a polymeric support of moderate cross-linking agent such as Amberlite XAD-16. Generally, resins having largest surface area are preferred. Due to these properties, Amberlite XAD-16 has been selected as a solid-phase for Functionalization with ligand.

In the present study we have synthesized an aromatic dithiocarbamate namely potassium 2-benzoylhydrazinecarbodithioate, characterized by IR and used for the functionalization of Amberlite XAD-16 by covalent coupling of ligand with polymer backbone through an azo spacer. The functionalized resin was applied for the solid phase extraction of Cu(II), Mn(II) and Zn(II) and determination by ICP-AES.

3.1   Potassium 2-benzoylhydrazinecarbodithioate (PBHCD)
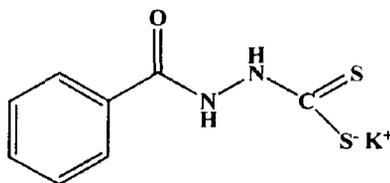
The reagent Potassium 2-benzoylhydrazinecarbodithioate (PBHCD) has R_2N-group which is electron releasing tendency along with the sulphur atoms which increase their electron donor capacity permitting the formation of strong complex with the metal ions. It makes it a good reagent for metal ion enrichment in SPE studies. In addition the reagent can be easily synthesized in the laboratory and can be used for functionalization of amberlite.

3.2   RESULTS AND DISCUSSION

3.2.1   Characterization of potassium 2-benzoylhydrazinecarbodithioate (PBHCD)

The detailed procedure of synthesis of potassium 2-benzoylhydrazine-carbodithioate (PBHCD) and functionalization of Amberlite XAD-16 with the reagent, along with the schemes are reported in sections 2.5.1, 2.7.1 and Figs. 2.2, 2.5. The FT-IR spectrum of PBHCD and functionalized Amberlite XAD-16 with PBHCD are shown in Figs. 3.1 and 3.2 respectively. The FT-IR spectrum of PBHCD (Fig 3.1) showed characteristic IR bands were at 3313 cm^{-1} for N-H stretching, 3110 cm^{-1} for Ar-H stretching, 1622 cm^{-1} for C=O stretching, 1273 cm^{-1} for C=S stretching and 1069 cm^{-1} for C-N stretching.

3.2.2   Characterization of AXAD-16 with PBHCD

The FT-IR spectrum of PBHCD (Fig 3.1) showed characteristic IR bands were at 3313 cm^{-1} for N-H stretching, 3110 cm^{-1} for Ar-H stretching, 1622 cm^{-1} for C=O stretching, 1273 cm^{-1} for C=S stretching and 1069 cm^{-1} for C-N stretching respectively. The FT-IR spectrum of XAD-16-PBHCD presented in Fig. 3.2 exhibited characteristic bands were at 3399 cm^{-1} for N-H stretching, 2924 cm^{-1} for Ar-H stretching, 1659 cm^{-1} for C=O stretching, 1545 cm^{-1} for N=N stretching, 1278 cm^{-1} for C=S stretching, and 1114 cm^{-1} for C-N stretching. These similarities between the spectra of ligand (PBHCD) and the functionalized resin support the functionalization of Amberlite XAD-16 with PBHCD.
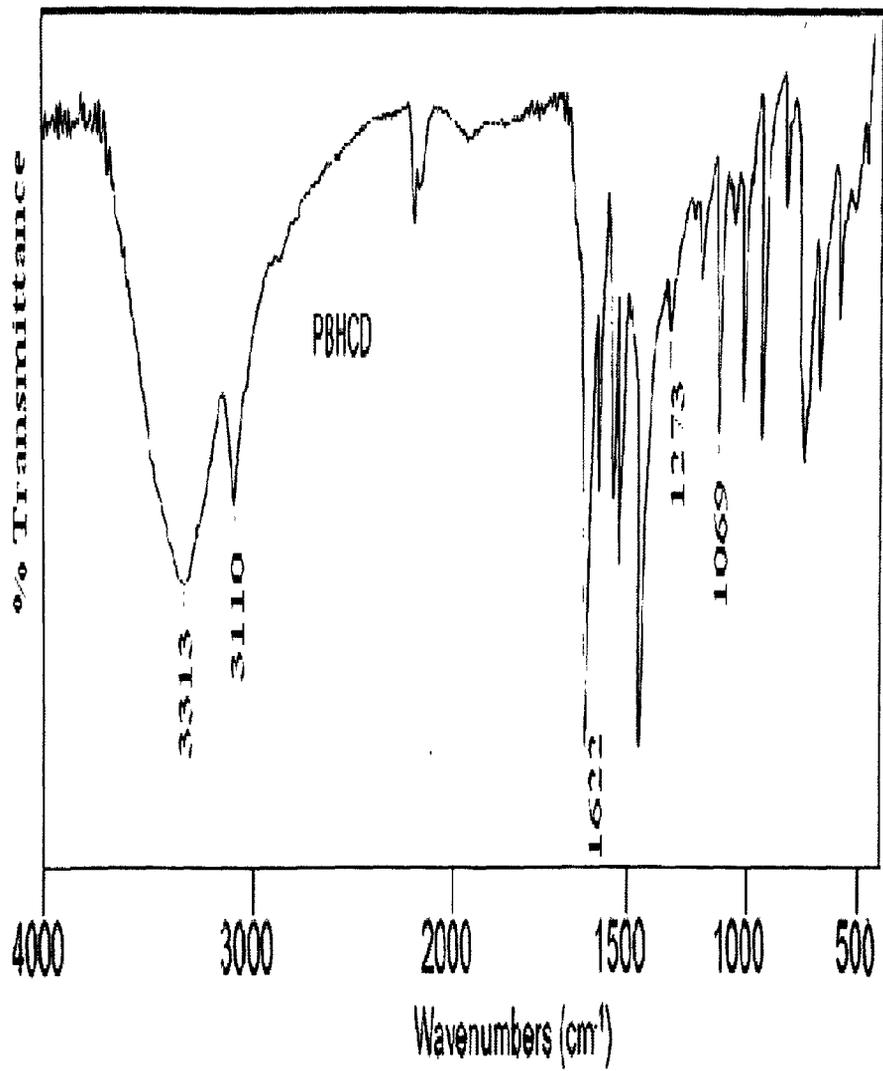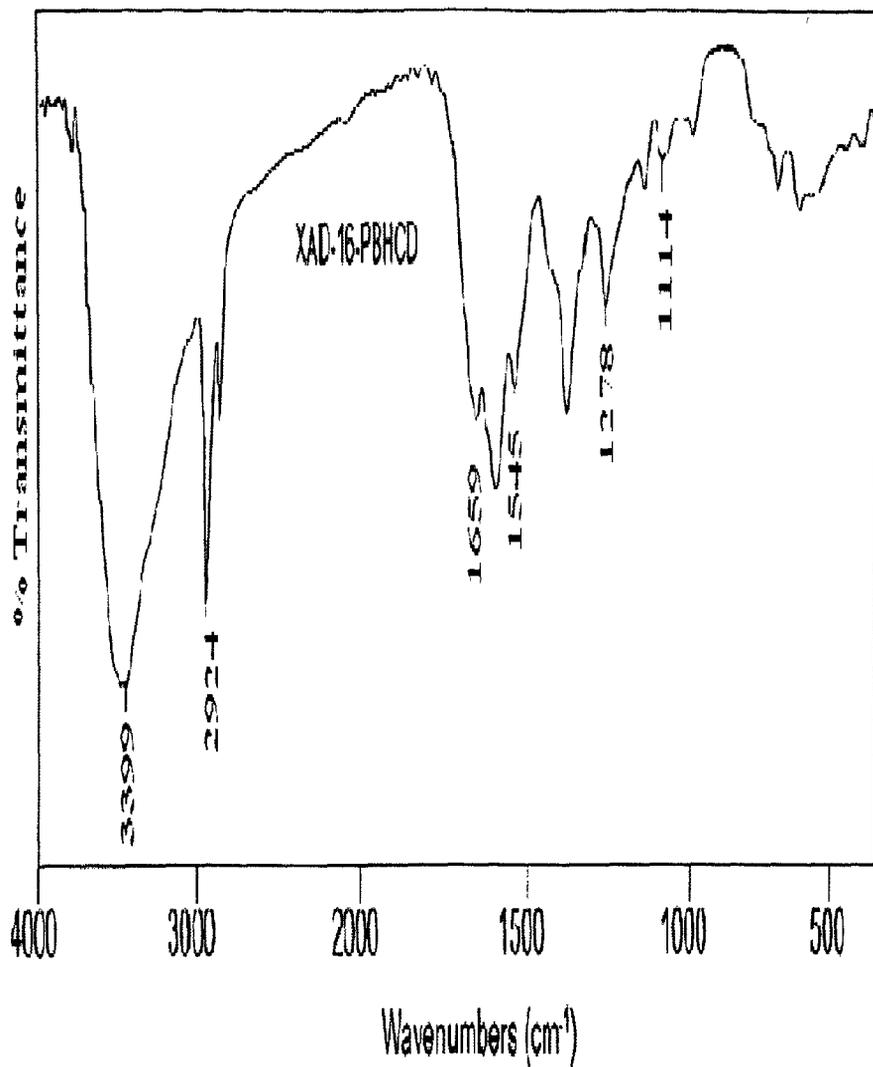
Fig. 3.1: FT-IR spectrum of PBHCD

Fig. 3.2: FT-IR spectrum of Amberlite XAD-16-PBHCD

3.2.3   Effect of pH on metal preconcentration

The pH of the working solution is a critical parameter for the quantitative recoveries of metal ions by solid phase extraction [30]. The influence of the pH was investigated in the pH range of 2.0–9.0 with spiked solutions while keeping the other parameters constant. The data corresponding to each element were shown in Table 3.1. The metal ions were eluted from the solid phase and their determination by ICP-AES gave the recovery efficiency of the eluted metal ions at different pH. The recovery values for the analyte metals as a function of pH are shown in Fig.3.3. The results demonstrate that the sorption was maximum and quantitative (>98%) in pH range 4.0-6.0 for Cu(II), 4.0-6.0 for Mn(II) and 5.0-7.0 range for Zn(II). Hence, pH 5.0 was chosen as the optimum pH for solid-phase extraction of the three metal ions. At higher pH values the recovery efficiency was probably reduced due to the formation of $M(OH)_n$ or $M(OH)^+$.

Table 3.1: Effect of pH on the complexation of metals from Amberlite XAD-16 coated with PBHCD

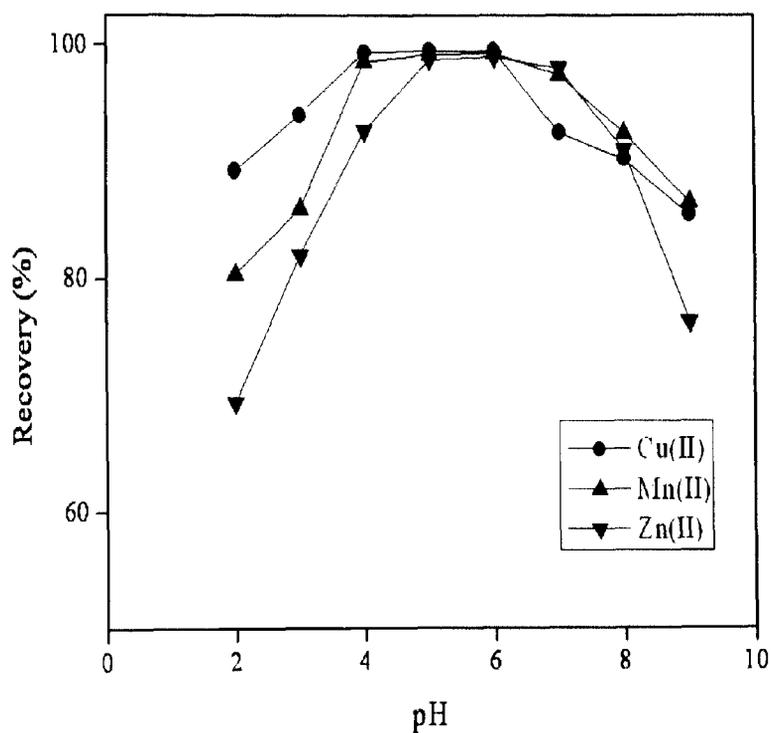| pH	% Recovery		
	Cu(II)	Mn(II)	Zn(II)
2.0	69.3 ± 2.11	62.4 ± 2.23	64.5 ± 2.15
3.0	70.5 ± 1.95	71.5 ± 1.91	75.2 ± 1.85
4.0	78.7 ± 1.63	78.6 ± 1.71	82.6 ± 1.42
5.0	86.5 ± 1.15	88.6 ± 0.94	90.4 ± 0.86
6.0	99.1 ± 0.31	99.4 ± 0.36	99.5 ± 0.29
7.0	99.1 ± 0.31	99.4 ± 0.29	99.5 ± 0.26
8.0	99.0 ± 0.43	98.6 ± 0.52	99.4 ± 0.34
9.0	99.5 ± 0.36	96.7 ± 0.72	96.7 ± 0.72

Fig. 3.3: Effect of pH on recovery (%) of metal ions

3.2.4   Effect of amount of resin on preconcentration of metals

For the maximum recovery of metals in environmental and biological samples there must be sufficient quantity of resin that ensures total retention of metals onto its surface. The quantity of Amberlite XAD-16-PBHCD resin that required for retention of total analytes Cu(II), Mn(II) and Zn(II) in samples was tested by taking varying amounts (100-800 mg) of XAD-16-PBHCD resin filled in the column. It was found that maximum recoveries of all the examined analytes were observed when 400 mg of resin was used in the column. Therefore 400 mg of Amberlite XAD-16-PBHCD resin was used for subsequent determination.

3.2.5   Sample and eluent flow rates

The effect of flow rate of the sample solution on the retention of the metal ions onto Amberlite XAD-16-PBHCD resin was studied by the column packed with 400 mg resin. Sample solutions were passed through the column at varying the flow rates (1.0 mL min^{-1}– 4.0 mL min^{-1}) maintained by peristaltic pump at their optimum pH. 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 2.5 mL min^{-1} and further increase in flow rate caused a gradual decrease in sorption due to insufficient contact time between the resin and metal ions. Therefore, the flow rate was chosen as 2.5 mL min^{-1}.

Elution of metal ions from the column was studied by using different concentrations (0.5-3.0 M) of eluent solutions such as nitric acid and hydrochloric acid. The results are presented in Table 3.2 and graphically presented in Fig. 3.4. It was observed that the recovery of metal ions with HCl was less and quantitative elution of Cu(II), Mn(II) and Zn(II) ions was possible with 2.0 M HNO$_3$. Hence, 2.0 M HNO$_3$ was selected as the eluent for the analysis of the metals.

Table 3.2: Effect of acid concentration on elution of metals

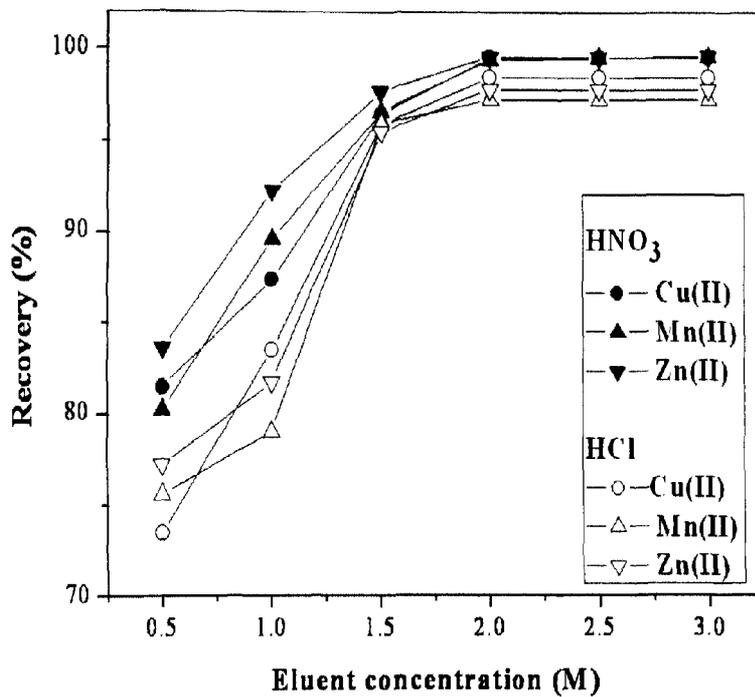| HNO$_3$	% Recovery			HCl	% Recovery		
	Cu(II)	Mn(II)	Zn(II)		Cu(II)	Mn(II)	Zn(II)
0.5	81.48	80.25	83.62	0.5	73.43	75.56	77.18
1.0	87.37	89.58	92.24	1.0	83.52	79.02	81.75
1.5	96.42	96.56	97.65	1.5	95.84	95.91	95.47
2.0	99.51	99.38	99.55	2.0	98.42	97.21	97.76
2.5	99.53	99.51	99.53	2.5	98.42	97.21	97.79
3.0	99.54	99.56	99.56	3.0	98.43	97.21	97.79

Fig. 3.4: Effect of acid concentration on elution of metal ions

3.2.6 Effect of the sample volume

The effect of sample volume on the elution of Cu(II), Mn(II) and Zn(II) was studied by taking different volumes of the water samples in the range of 100, 250, 500, 750 and 1000 mL. The results are presented in Table 3.3. It was observed that the extraction was almost constant up to 500mL of aqueous phase (preconcentration factor ~50) in the case of Cu(II), Mn(II) and Zn(II). However, the efficiency of the recovery slightly decreased and time taking was high when sample volume was more than 500 mL. Hence, 500 mL water sample was chosen for the present study.

3.2.7 Sorption capacity and detection limits

The sorption capacity of Amberlite XAD-16-PBHCD (maximum amount of metal sorbed per gram) of each metal ion was determined by batch method. The resin (1g) was saturated with Cu(II), Mn(II) and Zn(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 was desorbed with 10 mL of 2.0 M HNO$_3$ and determined by ICP-AES. The sorption capacities in mg g^{-1} are 5.6, 4.2 and 5.4 for Cu(II), Mn(II) and Zn(II), respectively. The detection limits for this method were determined based on blank signals (n = 10) plus three times the standard deviation of the blank signals. The detection limits were 5.6, 4.5 and 1.8 μg L^{-1} for Cu (II), Mn (II) and Zn (II) respectively.

Table 3.3: Effect of sample volume on elution of metal ions

Volume of sample(mL)	Recovery (%)		
	Cu(II)	Mn (II)	Zn(II)
100	96.1 ± 0.39	96.2 ± 0.36	98.8 ± 0.28
250	97.1 ± 0.54	96.4 ± 0.69	98.2 ± 0.32
500	99.2 ± 0.33	99.5 ± 0.72	99.6 ± 0.21
750	98.1 ± 0.43	98.1 ± 0.38	98.5 ± 0.37
1000	97.9 ± 0.61	98.1 ± 0.42	97.6 ± 0.41

3.2.8 Kinetics of sorption

The rate of uptake of metal ions on Amberlite XAD-16-PBHCD 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 ($30\pm0.1°C$). The metal ions on the resin surface were eluted with 2 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. 3.5. 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(Cu(II), 4.4; Mn(II), 3.1; and Zn(II) 4.3 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-16-PBHCD reflects a good accessibility of the chelating sites of the resin to metal ions.

3.2.8 Resin stability and reusability

The stability of Amberlite XAD-16-PBHCD was studied in acid (1.0-6.0 M HNO_3). It was shaken with acid solutions of varying concentrations for 4h and filtered. The solid was washed with distilled water until free from acid and air-dried, and its sorption capacity was determined using a batch method. The sorption capacity of the acid-treated resin was found to be similar (variation, <2.8%) to that of the untreated one. This shows that the resin can resist an acid concentration up to 6.0 mol L^{-1}. It can also be reused for more than 10 cycles of sorption-desorption without any significant change in the sorption capacity (<1.4%).
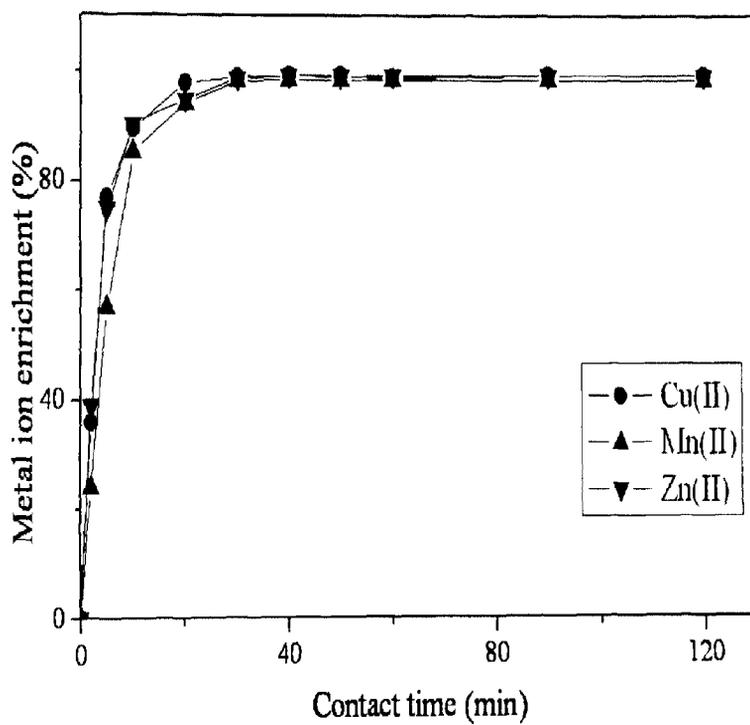
Fig. 3.5: Kinetics of metal ion sorption on Amberlite XAD-16-PBHCD resin

3.2.10 Effect of foreign ions

The effect of cations and anions such as sodium, potassium, calcium, magnesium, chloride, nitrate sulphate and phosphate anions that are commonly present in natural water and food samples like leafy vegetables, on the preconcentration of Cu(II), Mn(II) and Zn(II) by Amberlite XAD-16-PBHCD functionalized resin with optimized conditions has been investigated. The tolerance limits of various foreign species on the sorption of the metal ions are given in Table 3.4. The tolerance limit of foreign ions was taken as that value which caused an error of not more than 5 % in the emission reading. The results in Table 3.4 demonstrate that the anions and cations do not affect the sorption of Cu(II), Mn(II) and Zn(II) under reported conditions. The alkaline and alkaline earth metals were almost not retained through the column due to low solubility constant of their chelates and the small amounts of retained matrix ions were removed by washing with 10-15 ml of buffer solutions as reported by Uzun el al. [31].

Table 3.4: Tolerance limits of matrix ions for Determination of Cu(II), Mn(II) and Zn(II) by the Proposed Method

Matrix ion	Tolerance limit (mg L^{-1})	Recovery (%)
Na^+	35000	97.26 ± 0.11[a]
K^+	30000	96.61 ± 0.16
Ca^{2+}	30000	98.34 ± 0.14
Mg^{2+}	25000	95.25 ± 0.17
Cl^-	30000	98.26 ± 0.13
NO_3^-	20000	97.16 ± 0.19
HCO_3^-	23000	96.32 ± 0.15
CH_3COO^-	30000	98.17 ± 0.19
PO_4^{3-}	3000	95.24 ± 0.16
SO_4^{2-}	30000	97.28 ± 0.14
Fe^{3+}	50	96.14 ± 0.17
Co^{2+}	40	96.74 ± 0.13
Pb^{2+}	40	95.91 ± 0.16

[a]Mean ± standard deviation

3.2.11 Analytical characteristics

The accuracy of the developed procedure was evaluated by determining the metal ions in the standard reference material NIST 1643e natural water. According to results in Table 3.5, concentrations of the three metal ions determined by the proposed method are in good agreement with the certified values. Results indicate the applicability of the developed procedure in metal ions determination free of interference.

Table 3.5: Determination of trace metal ions in Standard Reference Materials (NIST 1643e water) by the proposed method ($n = 5$)

Metal ion	NIST 1643e water ($\mu g\ L^{-1}$)	
	Certified value	Proposed method
Cu(II)	22.76	22.74 ± 0.11
Mn(II)	38.97	38.91 ± 0.05
Zn(II)	78.5	78.4 ± 0.46

3.2.12 Determination of trace metal ions in natural water samples

Water samples were collected from bore well (Tirupati), river water (Penner river, Nellore) and sea water (Bay of Bengal, Nellore) and determined the Cu(II), Mn(II) and Zn(II) metal ions. The results are presented in Table 3.6. The values revealed that the concentration of copper is in the range of 16.80-27.82 μg L^{-1}, manganese is in the range of 5.14-17.61 μg L^{-1} and Zinc is in the range of 80.29-140.18 μg L^{-1}. The detection limits were 5.6, 4.5 and 1.8 μg L^{-1} for Cu(II), Mn(II) and Zn(II), respectively.

Table 3.6: Determination of Cu(II), Mn(II) and Zn(II) in natural water samples ($n = 5$)

Sample	ICP-AES method (μg L^{-1})					
	Cu(II)	RSD (%)	Mn(II)	RSD (%)	Zn(II)	RSD (%)
Bore well water[b]	27.82 ± 0.16	0.56	15.61 ± 0.21	1.35	140.18 ± 0.14	0.09
River water[c]	16.80 ± 0.33	1.96	17.61 ± 0.29	1.65	80.29 ± 0.25	0.31
Sea water[d]	18.59 ± 0.24	1.29	5.14 ± 0.17	1.75	116.11 ± 0.19	0.16

[a] Mean standard deaviation ($n = 5$), [b]Collected in our laboratotry, [c]Collected from Penner river (Nellore), [d]Collected from Bay of Bengal (Nellore, A.P, India).

3.2.13 Determination of trace metal ions in leafy vegetable samples

Leafy vegetable samples namely, Cabbage (*B. oleracea var. capitata*), Thotakura (*A. tricolor*), Palakura (*I. frutescens*) and Chukkaku (*R. vesicarius*), 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), Mn(II) and Zn(II) metal ions, the results are presented in Table 3.7. The concentrations of three metals in leafy vegetables collected from the agricultural fields of the areas irrigated by Kalyani river water were found in the range of 11.45-24.64 μg g^{-1} for Copper, 12.62-27.80 μg g^{-1} for Manganese and 12.45-28.22 μg g^{-1} for Zinc. The high concentration of metal ions copper, manganese and zinc 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 leafy vegetables.

Table 3.7: Determination of Cu(II), Mn(II) and Zn(II) in leafy vegetable samples

leafy sample	ICP-AES method (μg g^{-1})					
	Cu(II)	RSD (%)	Mn(II)	RSD (%)	Zn(II)	RSD (%)
Cabage (*B. oleracea var. captala*)	18.65 ± 0.18	0.96	13.95 ± 0.11	0.79	12.45 ± 0.14	1.12
Thotakura (*A. tricolor*)	11.45 ± 0.14	1.22	27.80 ± 0.29	1.04	25.90 ± 0.23	0.89
Palakura (*I. frutescens*)	24.64 ± 0.23	0.93	12.62 ± 0.14	1.11	28.22 ± 0.31	1.09
Chukkaku (*R. vesicarius*)	30.85 ± 0.32	1.03	16.80 ± 0.18	1.07	30.26 ± 0.33	1.09

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

3.3   Conclusions

The results of the present study showed that, PBHCD is a good reagent that can be used for funtionalisaton of amberlite. The amberlite XAD-16-PBHCD has a good potential for separation and preconcentration of metal ions like Cu(II), Mn(II) and Zn(II) from natural water and leafy vegetables and can be determined by ICP-AES. The new chelating resin functionalized with PBHCD through polymer back bone azo (-N = N-) spacer group is a stable chelating resins in acidic medium. Reliability, sensitivity, selectivity and eco-friendly approach of the XAD-16 resin are some of the additional factors. This developed method has high tolerance limits from the matrix ions and is useful for the preconcentration and determination of metal ions in the leafy vegetable and natural water samples.

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