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2-Mercaptobenzimidazole Immobilized with Amberlite Xad-2 Using as Solid Phase Extractor for the Determination of Fe(II), Cu(II), and Cd(II) in Sewage and Waste Water Samples by Flame Atomic Absorption Spectrometry

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ABSTRACT

A method for solid phase extraction of Fe(II), Cu(II), and Cd(II) metal ions using Amberlite XAD-2 immobilized with 2-mercaptobezimidazole has been developed. The optimal experimental conditions for quantitative sorption of three metals, pH, and effect of amount of ligand, effect of sample volume, effect of flow rate, concentration of eluent and effect of diverse ions were investigated. The adsorbed metal ions on the adsorbent were quantitatively eluted by 5ml of 3N HCl. The detection limits were 0.42, 0.61 and 0.95µg. L^{-1} for Fe(II), Cu(II) and Cd(II) respectively. The method was successfully applied for the determination of Fe(II), Cu(II), and Cd(II) metal ions in sewage water and industrial waste waters samples.

Key words: solid phase extraction, heavy metals, Amberlite Xad-2

INTRODUCTION

Heavy metal analysis is necessary in environmental samples including water samples and soil samples today, because they are sensitive indicators of environmental pollutions, due to traffic and anthropogenic activities [1-3]. Flame atomic absorption spectrometry (FAAS), is among the most widely used method for the determination of the heavy metals at trace levels, but the sensitivity and selectivity of FAAS is usually insufficient for the determination of heavy metals at trace concentration in complex matrix environmental samples [4-7].

Therefore, Separation–preconcentration systems including liquid–liquid extraction [8], copricipitation [9], cloud point extraction [10], membrane filtration [11] and solid phase extraction [12,13] are used to solve this problem. Among this methods solid phase extraction method has found increasing applications for the preconcentration of trace metal ions and elimination of matrix interference prior to FAAS analysis. Different solid phase extractors such as Amberlite XAD resins [14-16], silica gel [17-19], alumina [20,21] and activated carbon [22] have been used for the solid phase extraction of metal ions from different matrices.

The use of Amberlite XAD resins with large surface area and macroporous structure convenient for preconcentration, isolation and chromatographic separation of various compounds is an improvement over activated carbon because they are more suitable for elution and are free from contamination risks. In addition XAD resins present greater adsorption capacities and easier elution than alumina, silica gel etc [23].

Therefore the present study 2-mercaptobenzimidazole-Amberlite XAD-2 sorbent was prepared and its utilization in solid phase extraction procedure for preconcentration and determination of Fe(II), Cu(II), and Cd(II) in sewage water and industrial waste water samples by flame atomic absorption spectrometry (FAAS). The parameters including pH of the sample, sample volume, amount of resin, type and volume of eluents and effect of foreign ions were studied. The principle interest of using this chelating resin in trace analysis is based on the simplicity of the method for separation and preconcentration of the studied metal ions. The main advantages of the proposed method are the low detection limit, high preconcentration factor, short analysis time and high selectivity.

MATERIALS AND METHODS

Apparatus

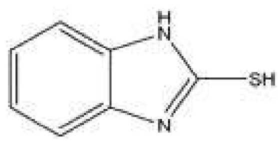
Flame Atomic absorption spectrometer {Perkin-Elmer model 2380, USA} equipped with single element hallow cathode lamp and air-acetylene burner, used for the determination of metals. ELICO deluxe pH meter used for preparation of buffer solution.

Reagents and Materials

All chemicals were used Analytical Grade (Merk, India). Deionised double distilled water used for through out experimental study. Stock solution of the studied metal ions were prepared by dissolving appropriate amounts of ferrous sulphate for Fe(II), copper sulphate pentahydrate for Cu(II) and cadmium chloride for Cd(II). Acetate buffer solution was prepared by dissolving of sodium acetate trihydrate in water and adjusting with pH with acetic acid.

Preparation of 2-mercaptobenzimidazole immobilized with Amberlite XAD-2

5 g of Amberlite XAd-2 was added to 50ml of 0.1% of 2-mercaptobenzimidazole (50 mg of 2-mercaptobenzimidazole dissolved in acetone). The mixture was stirred 2hrs. The resin coated reagent was filtered off, washed with water and dried at room temperature.



2-mercaptobezimidazole

Column preparation
A column of 30 cm long and 10 mm inner diameter containing 500 mg of 2-mercaptobenzimidazole immobilized with Amberlite XAD-2 packed with small amount of glass wool because of to prevent the loss of adsorbent during the sample passed through the column. The column was conditioned by passing through 10 ml of acetate buffer (at pH 3).

Preconcentration Procedure
The standard solution containing 0.1µg of Fe, 0.1µg Cu of and 0.05 µg of Cd metal ions, then the pH adjusted with acetate buffer at pH 3. The sample solution passed through the mini column at a flow rate of 5ml / min. Then the column washed with 2ml of distilled water, the adsorbed metal ions eluted by the using 5ml of 3N HCl at a flow rate of 2 ml/ min. The concentration of metal ions was determined by FAAS.

Collection and preparation of real samples
Sewage water sample collected from Tirupati municipal corporation and industrial waste waters were collected from Gajulamandyam industrial area, near Tirupati. Before the analysis, the samples were filtered through a cellulose membrane filter (Millipore) of pore size 0.45µm. The organic content of the water samples was oxidized in the presence of 1% H_2O_2 and an addition of concentrated nitric acid[10]. After acidification to 1% with concentrated nitric acid, they were stored in polyethylene bottles.

RESULT AND DISCUSSION

Effect of pH
The effect of pH plays a major role in the preconcentration studies, due to this the influence of pH was investigate at the pH ranges 2-8 with model solutions keeping other parameters were constant. Fe(II), Cu(II) and Cd(II) metal ions were tested in different pH values with 100ml of model solution. The results are presented in Fig 1. The results of this study showed that metal ions were completely adsorbed on the adsorbent over the pH range of 2.0-3.0. Therefore, pH 3 was selected as the optimum pH for further studies.

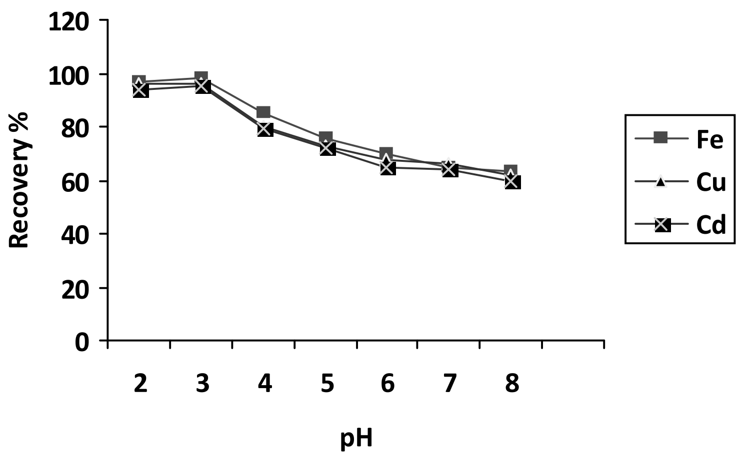


Fig: 1 Effect of pH on recovery of metal ions (amount of analytes 0.1µg Fe, 0.1µg Cu and 0.05µg Cd; eluent: 3N HCl).

Effect of amount of ligand

For proper modification of Amberlite XAD-2 adsorbent, the effect of the amount of 2-mercaptobenzimidazole on the retention of Fe(II), Cu(II), Zn(II) and Cd(II) ions were studied. Various amounts (25-250) of 2-mercaptobenzimidazole were added to 5g of Amberlite XAD-2 and 500mg of mixture was used as a mini column. The results are presented in Table Fig 2, the quantitative recoveries of the working elements were obtained by using 50mg of 2-mercaptobenzimidazole modified Amberlite XAD-2 resin. Therefore, 50mg of the ligand was used for further studies.

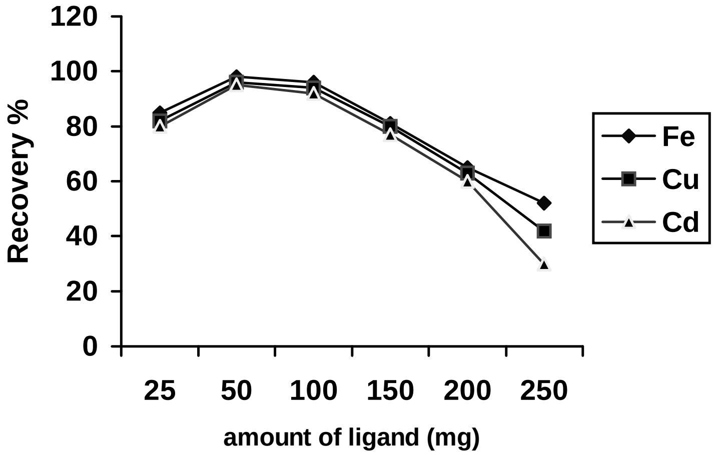


Fig: 2 Effect of amount of 2-mercaptobezimidazole on recovery of metal ions (pH: 3; amount of analytes 0.1µg Fe, 0.1µg Cu and 0.05µg Cd; eluent: 3N HCl).

Effect of choice of eluent and Flow rate

Different concentrations of eluents were tested to elute the adsorbed metal ions complex in the column. In order to choose most effective different concentrations eluents such as 3N HNO_3, 2N HNO_3, 1N HNO_3, 3N HCl, 2N HCl, 1N HCl, were studied. The elution studies were carried out maintaining the concentration of 0.1µg.ml^{-1}, 0.1 µg.ml^{-1}and 0.05 µg.ml^{-1}of Fe(II), Cu(II) and Cd(II) in 100 ml volume of sample. The quantitative recoveries were obtained by using of 5 ml of 3N HCl at the flow rate of a 2ml/min, the results are presented in Table 1.

Table 1. Effect of type and concentration on the recoveries of metal ions

Eluent type	Volume (ml)	Recovery (%)		
		Fe	Cu	Cd
3 N HNO_3	10	85	87	83
3 N HNO_3	5	88	89	85
3 N HCl	10	96	95	95
3 N HCl	5	98	96	95
2N HCl	10	92	90	93
2N HCl	5	93	92	94
1 N HCl	10	90	87	90
1 N HCl	5	89	90	91

As the retention of analytes on the adsorbent was depends up on the flow rate of the samples solution and eluent. The effect of flow rate was examined under the pH 3 by the passed sample solution through the mini column with the flow rate carrying in the range of 2-5ml /min. The quantitative recoveries of metal ions were obtained with a flow rate of 5ml/min was observed in sample and 2 mi/min for eluent. Table 2 illustrated Optimum experimental conditions for preconcentration of each metal ion.

Table 2. Specification of present method at optimum condition for eachmetal ion

Parameters	Fe	Cu	Cd
PH	3	3	3
Amount of adsorbent (mg)	500	500	500
Volume eluent	5 ml 3N HCl	5 ml 3N HCl	5 ml 3N HCl
Detection limit(μg.L^{-1})	0.42	0.61	0.95
Recovery (%)	95	97	98

Effect of sample volume

Effect of sample the sample solution volume on Fe(II), Cu(II) and Cd(II) sorption was studied by passing 50-300ml of sample solution containing same 0.1μg.ml^{-1}, 0.1 μg.ml^{-1}, and 0.05 μg.ml^{-1}of Fe(II), Cu(II) and Cd(II) ions were passed through the mini column at a flow rate of 5ml/min. The quantitative recoveries were obtained by using of 100ml of sample solution and increasing the volume of sample recoveries of metal ions was gradually decreased. Therefore 100ml volume of sample was selected for further studies.

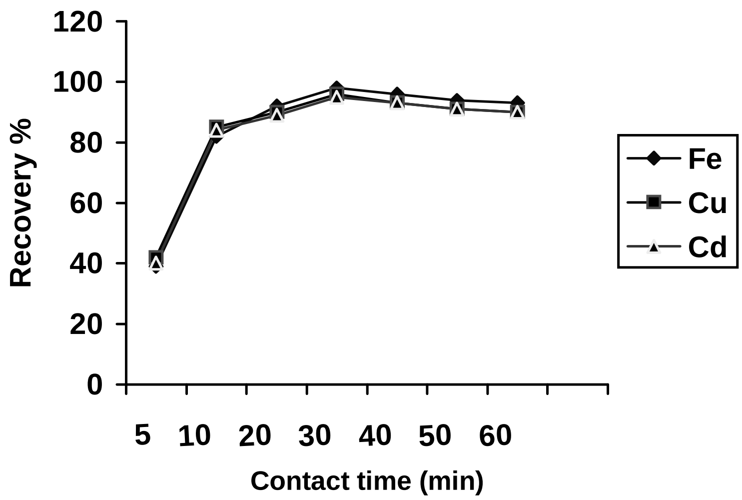


Fig 3 Extraction time on recovery of metal ions (pH: 3; amount of analytes 0.1μg Fe, 0.1μg Cu and 0.05μg Cd, eluent: 3N HCl).

Time of sorption

The rate of uptake of metal ions on Amberlite XAD-2 -2-mercaptobezimidazole was studied by batch method. Standard solution containing 0.1µg.ml^{-1}, 0.1 µg.ml^{-1}, and 0.05 µg.ml^{-1}of Fe(II), Cu(II) and Cd(II) individual metal ion was added to 500mg of resin and stirred for 2-60 min at room temperature. The adsorbed metal ions on the resin were eluted with 5ml of 3N HCl and determined by FAAS. The saturation of the resin with the time is presented in Fig 3. The absorption of metal ions on resin to loaded 50% at the time of above 6 min for each metal ion (Fe, 6; Cu, 10; Cd, 8.4). The resin-metal interaction is sufficiently rapid for all metal ions at optimum pH.

Effect of Foreign Ions

Preconcentration procedures for trace elements in the high salt content samples can be strongly affected by the matrix constituents of the sample. This is known as matrix effect. Before the application of the preconcentration method for the determination of analyte ions in samples with complicated matrix, the influences of some alkaline and alkaline earth ions on the recoveries of the analyte ions were also investigated. The results are presented in Table 3. Metal ions were quantitatively recovered at large amounts for alkaline and earth alkaline ions and some anions. The matrix ion contents in the eluent solutions were found to be significantly lower and suitable for atomic absorption spectrometric determinations.

Table 3 Effects of the matrix ions on the recoveries of the examined metal ions

Ion	Added As	Tolerance Limit Ion (mg L^{-1})
Na^+	NaCl	1000
K^+	KCl	1000
Cl^-	NaCl	1000
SO_4^{2-}	Na_2SO_4	8500
Mg^{+2}	$MgCl_2$	800
HCO_3^-	$NaHCO_3$	800
PO4 $^{3-}$	Na3PO4	900
Zn^{+2}, Ba^{+2}, Ca^{+2},	As Nitrates	1000
Ag^+, Al^{+3}, Cr^{+3}	As Nitrates	250

Detection limits of the method

The method detection limits were calculated by three times the standard deviation of the solutions (with out samples or standards). The values were 0.42, 0.61 and 0.95µg. L^{-1} for Fe(II), Cu(II) and Cd(II) respectively. These limits were based on 25 ml of blank solution undergoing the preconcentration. They can be improved by increasing the sample volume.

Analytical applications

To check the applicability of the proposed method for the separation and preconcentraon of Fe(II), Cu(II) and Cd(II) ions using modified resin Amberlite XAD-2- 2-mercpatobezimidazole was subjected to analysis of sewage water and industrial waste water samples.

The levels of the trace metals concentration slightly increased in waste water sample owing to this waste water collected from near Gajulamandyam industrial area, most of the discharges waste water directly entering in to the environment. So this reason the levels of trace metals was increased in waste waters, the results were shown in Table 4. Sewage water sample were collected in Tirupati municipal corporation area, the levels of trace metals were slight increased due to contamination followed by house-hold waste waters and washing industries water may be responsible to increasing levels of heavy metals (Table 5).

Table 4. Determination of Fe(II), Cu(II) and Cd(II) in Waste water samples

Element	Added ($\mu g.L^{-1}$)	Found ($\mu g.L^{-1}$)	Recovery (%)
Fe	0	112.2±2.1	
	100	114.5±1.7	102.0
Cu	0	92.4±3.1	
	100	194.8±1.2	101.2
Cd	0	14.5±1.68	
	100	116.3±1.32	101.6

Table 5. Determination of Fe(II), Cu(II) and Cd(II) in Sewage water samples

Element	Added ($\mu g.L^{-1}$)	Found ($\mu g.L^{-1}$)	Recovery (%)
Fe	0	345±3.6	
	100	447±3.2	100.4
Cu	0	680±3.61	
	100	785±2.1	100.6
Cd	0	7.3±1.47	
	100	108.6±1.68	101.2

CONCLUSION

This separation and preconcentration procedure were developed for determination Fe(II), Cu(II) and Cd(II) metal ions in real samples by FAAS. Amberlite XAD-2 2-mercpatobezimidazole resin has good loading capacity, the absorption time of resin is also very fast and good reusability. The advantages of the method are simple, time saving and with high enrichment factors. The proposed method was successfully applied for the determination of trace metals in municipal sewage water and industrial waste water samples. Table 6 shown some reported studies for preconcentration of metals ions with modified Amberlite XAD resins.

Table 6. Some recent reported studies for preconcentration of metals ions with modified Amberlite XAD resins.

Element	System	Detection limit(µg.L^{-1})	Detected	Samples	References
Mn(II), Fe(II), Co(II), Cu(II), Cd(II), Zn(II), Pb(II), Ni(II)	Amberlite XAD-2000/diethyldithiocarbamate	0.20,0.35, 0.25, 0.20,0.20, 0.15, 0.45, 0.25	FAAS	natural waters, vegetables	24
Cr(VI)	Amberlite XAD-4/diphenylcarbazide	6	visible spectrophotometer	Water samples	25
Fe(III), Pb(II), Cr(III)	Amberlite XAD-2000/	0.32,0.51, 0.81	AAS	water samples.	26
Zn(II), Mn(II), Ni(II), Pb(II), Cd(II), Cu(II), Fe(III), Co(II)	Amberlite XAD-16/ 4-{[(2-hydroxyphenyl)imino] methyl}-1,2-benzenediol (HIMB)	1.72,1.30, 2.56, 2.10,0.44, 2.93, 2.45, 3.23	FAAS	Water, milk samples	27
Cu(II), Ni(II), Co(II), Cd(II)	Amberlite XAD-4/ 2,3-dihydroxynaphthalene	1.9, 0.9, 1.2 µg, 1.4	ICP-AES	natural water samples	28
Cu(II),Zn(II), Mn(II)	Amberlite XAD-16/3-((2,6-dichlorophenyl)(1H-indol-3-yl)methyl)-1H-indole (DCPIMI)	1.9, 1.5, 2.6	FAAS	Food samples	29
Cd(II), Ni(II)	Amberlite XAD-4/G.stromboliensis (species)	0.24, 0.3	FAAS	natural water, food samples	30
Fe(II), Cu(II), Cd(II)	Amberlite XAD-2/ 2-mercaptobenzimidazole	0.42,0.61,0.95	FAAS	sewage water, waste water samples	Present work

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