SEPARATION AND PRECONCENTRATION OF COPPER (II) ION BY FATTY HYDROXAMIC ACIDS IMMOBILIZED ONTO AMBERLITE XAD – 4 RESIN

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ABSTRACT

A method of copper (II) ion preconcentration and separation from other ions by using a column containing fatty hydroxamic acids – loaded Amberlite XAD 4 resin (FHA-Amb) is described. Several factors, which affect the separation and preconcentration efficiency such as pH, sample volume, and concentration of eluent and flow rate, have been investigated. A quantitative recovery of copper (II) ion from FHA-Amb resin column was obtained using 10% HNO₃ solutions as eluent with a preconcentration factor of 60. A method for separation of Cu(II) from Zn(II) and Cd(II) is proposed. A rapid sample throughput, a clean separation, a high preconcentration factor and simplicity are the main advantages in these analytical procedures.

INTRODUCTION

Separation and preconcentration techniques are of great importance owing to the limited sensitivity of an analytical instrument for trace analysis. Over the past ten years a large amount of data has been accumulated on chelating sorbents. Among them, sorbents obtained by immobilization of chelating agents on solid supports have gained much attention [1-6].

Copper is an essential element not only for life in animals but also plants and lower form of organisms [7]. In natural water and biological samples its level is low, and various steps of separation and preconcentration or enrichment are usually required [5]. Flame and graphite furnace atomic absorption spectrometry [4,6] and spectrophotometric methods [8,9] are the most common methods for determination of copper. However, there are many difficulties to determine low concentration of copper due to in sufficient sensitivity of the instrument. Thus a preconcentration and/or separation step is necessary. Preconcentration is necessary to bring the concentration of the analytes into the dynamic range of the flame atomic absorption detector used, while separation is employed to eliminate potential interfering matrix constituents.

Various separation-preconcentration techniques have been used for the trace copper such as liquid-liquid extraction by using complexing agents [10,11], co-precipitation through partial precipitation [12], ion-selective imprinted polymer microbeads [13], adsorbent containing antimony oxide and barium sulfate [14], enrichment on an silica-immobilised cationic polyelectrolyte [15], 2-o-vanillinthiosemicarbazone

loaded Amberlite XAD-2 [6] and microporous polypropylene film supported liquid membrane [16].

Liquid-liquid solvent extraction of metal chelating complexes has been used as a separation method for a long time. However, this method leads to many disadvantages. Among them are, usually, time consuming and labor intensive. The other main disadvantages of liquid-liquid solvent extraction are the use of large amounts of organic solvents for extraction and subsequent disposal of the solvent, which creates another environmental problem [6]. The liquid-liquid solvent extraction cannot be combines with atomic absorption spectrometry (AAS) or inductive couple plasma–atomic emission spectrometry (ICP-AES) due to the difficulties of introducing organic solvents into nebulizer of AAS or plasma of ICP-AES [17].

A very efficient system for separation and preconcentration of trace metal ions is immobilization of chelating agent on various supports. This method has several advantages over liquid-liquid extraction. The advantage include preconcentration from a larger sample volume and establishing higher concentration factors [18]. Amberlite XAD-4 resin is one of the polystyrene-based adsorbent with a high surface area. Therefore, Amberlite XAD-4 resin has been utilized as a support for several neutral complexing agents, such as *n,n*-bis(2-hydroxyethyl) glycine [19], sodium diethyldithiocarbamate [20] and *o*-vanillinsemi carbazone [6].

Hydroxamic acids are superior reagents for extraction and spectrometric determination of metal ions [18]. In recent years, the short chain, cyclic [19] and macro-cyclic ligands (crown ether) [20] hydroxamic acids have been reported for metal complexation. In

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this paper, we report the results of our investigations on fatty hydroxamic acids (FHA), synthesized from commercial palm olein, to be used as an extractant for Cu (II) ion. Although the FHA is a mixture of fatty hydroxamic acid, separation into individual components is not required for an effective copper ion separation.

EXPERIMENTAL SECTION

Material

Analytical-grade of hydroxylamine hydrochloride, sodium acetate, sodium hydroxide (all from Fluka, Switzerland), acetic acid, vanadium pentoxide and nitrate salts of copper, zinc, cobalt and nickel (all from Merck, Germany) were of the highest purity available and used without any further purification. The commercial palm olein was obtained from Ngo Chew Hong Oils and Fats (M) Sdn. Bhd. Malaysia. The standard solutions of metal ions for AAS measurement were prepared by diluting the spectrosol stock solution from BDH Chemical (England). All the solutions were prepared with distilled water.

Synthesis and Characterization of FHA

The FHA was prepared as described in our previous publication [21]. Qualitative analysis of hydroxamic acid groups on FHA was carried out by observes the colored complex formed after the methanolic solution of the FHA was reacted with iron (III), copper (II) and vanadium (V) in a dilute hydrochloric acid solution. The amount of the hydroxamic acid group was estimated based on nitrogen content of the dry FHA determined by Elemental analyzer model 932 (LECO, USA). FTIR spectra of FHA were recorded with Fourier Transform Infrared Spectrophotometer (Perkin Elmer FTIR-Spectrum BX, USA) using KBr disk.

Procedures

Preparation of the FHA loaded Amberlite XAD-4 resin (FHA-Amb)

The Amberlite XAD-4 resin was moistened with methanol for 12 h, then wash with hydrochloric acid 6M, distilled water, 2M sodium hydroxide and distilled water again. After filtration, the resin was shaken with 2000 ppm of FHA solution in methanol at 35 rpm for 12 h. The resin was then filtered and kept in refrigerator.

Effect of FHA concentrations on the impregnation of Amberlite XAD-4

A 0.5 g portion of Amberlite XAD-4 resin was shaken with 20 mL of FHA dissolved in methanol at 35 rpm for 12 h. The concentration of FHA was in the range 250 – 2000 ppm. The sorption of FHA on Amberlite XAD-4 was measured spectrophotometrically. One mL of FHA, before (initial) and after (final) shaken with

Amberlite XAD-4, was then added with 10 mL methanol and 0.1 mL of 0.02 M vanadium (V) dissolved in 0.1 M HCl. Then, the absorbance was measured using UV-Visible spectrophotometer at 475 nm for the calculation of resin sorption capacity.

Effect of pH on metal ions uptake by FHA-Amb

The effect of pH on metal ions uptake by FHA-Amb was determined by batch equilibrium techniques. The metal ion (20 mL, 0.001 M) was shaken with 100 mg of FHA-Amb for 12 h to ensure the equilibrium is attained in all cases. The pH of the metal solutions was adjusted to 1-6 with 0.01 M acetate buffer solutions before shaken. After the equilibration, the concentration of ion in solution was determined by AAS for the calculation of sorption capacity.

General extraction and desorption procedures on copper (II) ion uptake by column technique

FHA-Amb (4g) was packed into a column with an internal diameter 1 cm to 10 cm height. A 1000 mL solution containing the desired concentration of copper (II) ion at pH 6, adjusted with 0.01 M of acetate buffer was passed trough the column at space velocity of 0.3 mL.min^{-1} (except in the case of space velocity study) using a pump model P-50 (Pharmacia Biotech, Sweden). The concentration of copper (II) ion before and after passing the column was determined using AAS for the calculation of percentage sorption of copper (II) ion. The columnar stripping of copper (II) ion was performed using nitric acid (except in the case of effect of acid study) solution as eluent. The acid was passed trough the column containing FHA-Amb-Cu at the desired of space velocity. The successive fractions of effluent (3 mL) were collected automatically using a fraction collector (GradiFrac Phamacia Biotech, Sweden) The concentration of copper after stripping was determined using AAS for the calculation of percentage recovery.

RESULT AND DISCUSSION

Characterization of the FHA

Complexes of the FHA with vanadium (V), iron (III) and copper (II) are purple, dark red and green, respectively. These are the common color of the complexes observed when these metal ions are reacted with hydroxamic acids [22]. FTIR spectrum of the FHA (Fig 1) shows the characteristic absorption bands of monosubstituent amides at 3050 - 3400 cm^{-1} (medium peak), 1650 - 1750 cm^{-1} (sharp peak) and 1450 – 1600 cm^{-1} (medium peak), which indicate the presence of O-H and N-H stretching and bending modes. Absorption bands that appear at 2800 – 3000 cm^{-1} (sharp and medium peaks) and 1024 cm^{-1} are due
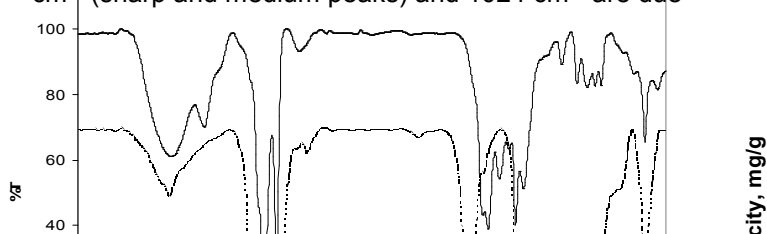
Fig 1. FTIR spectra of FHA (1) and commercial palm olein (2)

Table 1. The metal ions capacity (mg/g) on sorption of metal ions by FHA-Amb

Metal Ion	pH					
	1	2	3	4	5	6
Cu (II)	0.00	0.00	0.01	2.14	3.74	5.08
Zn (II)	0.00	0.00	0.03	0.31	0.33	0.40
Cd (II)	0.01	0.03	0.03	0.09	0.13	0.25

to C-H stretching and bending respectively. Both qualitative tests support that the FHA is successfully produced from the commercial palm olein. The nitrogen content of the dry FHA analyzed by the elemental analysis is found to be 4.93%. This indicates that there is 3.52 mmol/g of hydroxamic acid groups in one gram of the FHA. The FHA produced from this synthesis is actually a mixture of lauryl-, myristyl-, palmityl-, stearyl-, oleyl- and linoleyl- hydroxamic acid, as palm olein consist of lauric-(0.5%), myristic-(1.2%), palmitic-(38.5%), stearic-(4.4%), oleic-(41%) and linoleic acids (12.1%) [23].

Effect of FHA concentration on immobilization of FHA onto Amberlite XAD-4 resin

The amount of FHA immobilization onto Amberlite XAD-4 as a function of concentration of FHA is shown in Fig 2. It can be seen that at the concentration of 1000 ppm FHA, the resin reaches the maximum sorption. The maximum capacity of FHA in the Amberlite XAD-4 resin is 10.10 mg/g resin.

Effect of pH on sorption of Cu (II), Cd (II) and Zn (II) by FHA-Amb

The sorption behavior of copper (II), Cd (II) and Zn (II) on FHA-Amb at different pH values was examined by the batch method and the results are presented in Table 1. The results indicate that all the metal ions show the maximum capacity at pH 6. However, the highest capacity is shows by Amberlite XAD-4 – FHA – copper

Fig 2. Immobilization of FHA onto Amberlite XAD-4 resin as function of concentration of FHA
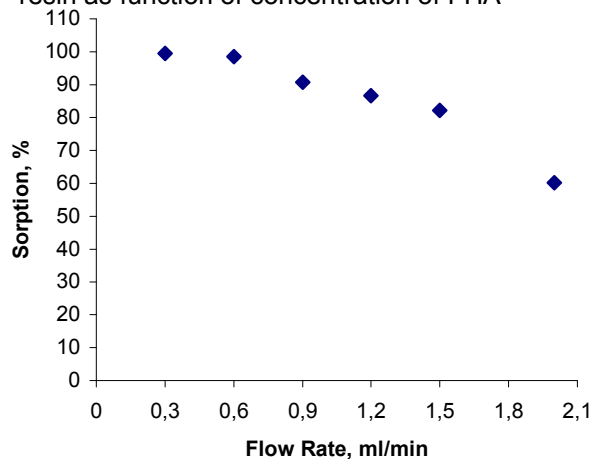

Fig 3. Effect of flow rate on sorption of copper (II) on FHA loaded Amberlite XAD-4 resin. Copper: 20 ppm. pH: 6.

(II). The capacity of the resin is an important factor to determine the amount of resin is required to quantitatively remove a specific metal ion from a solution.

Effect of flow rate and aqueous volume on sorption of copper (II) ion

The effect of flow rate on the copper sorption using column method was studied by varying the flow rate from 0.3 – 2 mL.min^{-1} under optimum pH (pH 6) (as determined by the batch method). The results (Fig 3) shows that the sorption of copper (II) on the resin was higher than 98% at the flow rate equal or lower than 0.6 mL.min^{-1}. The sorption decreases with the increase of the flow rate In order to achieve the maximum sorption, the flow rate of 0.3 mL.min^{-1} was chosen for subsequent experiments. The effect of sample volume on copper sorption was also investigated by passing 25 – 500 mL solution, containing 20 ppm of copper (II) ion, through the column at a constant flow rate of 0.3 mL.min^{-1}. In all
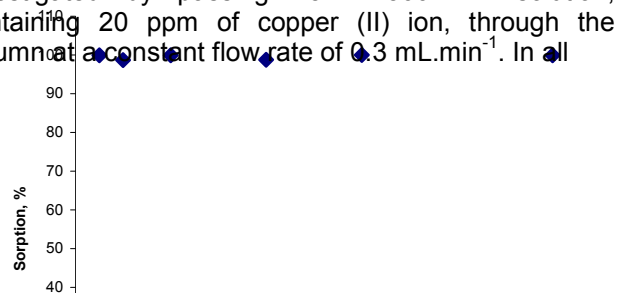
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Fig 4. Effect of volume of aqueous on sorption of copper (II) on FHA loaded Amberlite XAD-4 resin. Copper: 20 ppm. pH: 6. Flow rate: 0.3 mL.min^{-1}
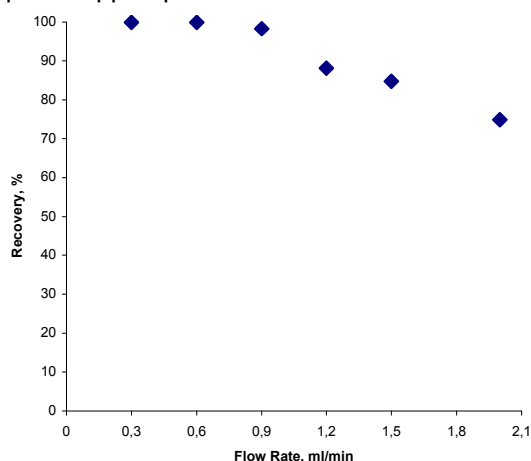

Fig 6. Effect of eluent flow rate on desorption of copper (II) from FHA loaded Amberlite XAD-4 resin. Copper: 20 ppm. pH: 6. Acid volume: 20 mL

cases, the percent of sorption were higher than 98 (Fig 4).

Effect of nitric acid concentration on desorption of copper (II) ion

The elution of copper (II) from the column was studied by using nitric acid solution of different concentration (5 – 25%) as stripping agent. The volume of acid used was 20 mL at 1 mL.min^{-1} of flow rate. The results (Fig 5) show that the total elution was reached at concentrations of acid equal or more than 10%. Accordingly, 10% of HNO$_3$ was chosen as eluent for subsequent experiment.

Effect of HNO$_3$ flow rate on desorption of copper (II)

The influence of the nitric acid flow rate on desorption of copper (II) from the column was also studied. The results (Fig 6) showed that the percentage of recoveries were decreased as the flow rate increased within the range 0.3 – 2 mL.min^{-1} for 20 mL of HNO$_3$ 10%. As shown in Fig 6, the percentage of recoveries
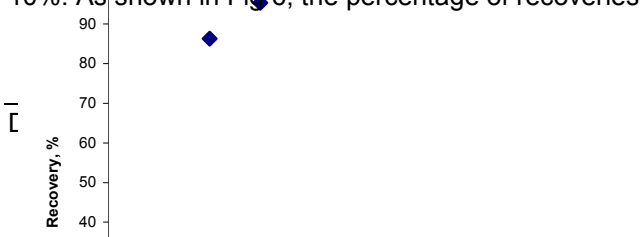

Fig 5. Effect of HNO$_3$ concentrations on desorption of copper (II) from FHA loaded Amberlite XAD-4 resin. Copper: 20 ppm. pH: 6. Acid volume: 20 mL. Flow rate: 1 mL.min^{-1}.

Table 2. Preconcentration factor for copper (II) on FHA loaded Amberlite XAD-4

Vol. of Solution Passed (mL)	Concentration (ppm)	Final Elution Vol. (mL)	Recovery (%)	Pre concent. Factor
1000	0.01	15	99.86	66.67
1000	0.01	20	100	50
1000	0.01	25	100	40

Table 3. Metal ions sorption on column FHA-Amb

Metal Ion	Concentration (ppm)	Sorption (%)
Cu	20	100
Zn	20	8.98
Cd	20	6.78

was over 99 at flow rate equal or lower than 0.6 mL.min^{-1}. Accordingly, 0.6 mL min^{-1} of flow rate was chosen for subsequence studies.

Preconcentration and separation of copper (II) from Zn (II) and Cd (II)

Preconcentration of 1000 mL of aqueous solution containing 0.01 ppm of copper (II) ion at pH 6 was carried out. The sorption of copper was performed at aqueous flow rate of 0.3 mL.min^{-1}. While, the elution of copper from column was performed using 10% of nitric acid as eluent, at flow rate of 0.6 mL.min^{-1}. The results, as shown in Table 2, show that the percentage recoveries for all preconcentration factors are more than 99%. This is indicates that the FHA-Amb can be applied for the preconcentration of copper (II) ion in aqueous media.

Separation of copper (II) from Zn (II) and Cd (II) was carried out on the FHA-Amb column. The sorption of metal ions on the resin was performed by passing
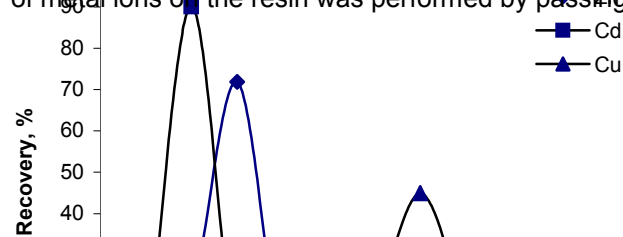
Fig 7. Separation of Copper (II) from Zn (II) and Cd (II). Cu extracted 20 ppm, total desorption 99.87%. Zn extracted 1.8 ppm, total desorption 98.94%. Cd extracted 1.4 ppm, total desorption 99.93%.

trough to the column 100 mL solution containing 20 ppm of copper (II), Zn (II) and Cd (II) ions at pH 6 and flow rate of 0.3 mL.min^{-1}. The results are shown in Table 3. It can be seen that the sorption for both Zn (II) and Cd (II) was lower than 10%. Meanwhile, the sorption of copper (II) was 100%. This indicates that complex of copper (II)-FHA on the resin is more stable than complexes of Zn (II)- and Cd (II)-FHA. The difference will affect to the retention of metal ions during elution. Fig 7 shows the results of desorption of metal ions from the column. It can be seen that copper is separated well from both Zn (II) and Cd (II), while Zn (II) and Cd (II) were not separated. This is probably because the stability of these two complexes is very similar.

CONCLUSION

The fatty hydroxamic acids, synthesized from commercial palm olein, were loaded onto Amberlite XAD-4 resin and use for the separation and recovery of copper from aqueous media. The separations of Cu (II) from Cd (II) and Zn (II) at pH 6 are conveniently achieved.

A preconcentration process has been proposed for the determination of Cu (II) in water samples, which contain trace concentrations of Cu (II) that they cannot be measured directly by FAAS. It has been shown that the preconcentration factor is up to 60.

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