



Preconcentration and determination of copper and cadmium ions with 1,6-bis(2-carboxy aldehyde phenoxy)butane functionalized Amberlite XAD-16 by flame atomic absorption spectrometry

Elif V. Oral^{a,*}, Ibrahim Dolak^a, Hamdi Temel^b, Berrin Ziyadanogullari^a

^a University of Dicle, Faculty of Science, Department of Chemistry, 21280 Diyarbakır, Turkey

^b University of Dicle, Faculty of Education, Department of Chemistry, 21280 Diyarbakır, Turkey

ARTICLE INFO

Article history:

Received 8 July 2010

Received in revised form

11 November 2010

Accepted 12 November 2010

Available online 19 November 2010

Keywords:

Solid phase extraction

Amberlite XAD 16

Preconcentration

Copper

Cadmium

ABSTRACT

A new chelating resin, covalently linked 1,6-bis(2-carboxy aldehyde phenoxy)butane with the Amberlite XAD-16 was synthesized and used for preconcentration of Cu(II) and Cd(II) prior to their determination by flame atomic absorption spectrometry (FAAS). It was characterized by elemental analyses and Fourier Transform Infrared Spectroscopy (FT-IR). Cu(II) and Cd(II) ions were quantitatively preconcentrated on minicolumn loaded with synthesised resin at pH 4.00 and 6.00, respectively. They were eluated with 5 mL of 0.5 mol L⁻¹ HCl. Recoveries of Cu(II) and Cd(II) were found to be 100 ± 2.15, 100 ± 1.40 (N=5), the limits of detection of Cu(II) and Cd(II) in the determination by FAAS (3s, N=20) were found to be 0.33 and 1.19 µg L⁻¹, respectively. The effect of foreign ions on the recovery has been investigated. The proposed method has been applied for the determination of Cu(II) and Cd(II) ions to the real samples collected from Tigris river water in Diyarbakır and Elazığ cities in Turkey. Standard addition method and analysis of the certified reference material (NCS-DC 73350) was employed to check the accuracy of the method.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

The environmental exposure to the heavy metals is a well known risk factor for human health and they are too harmful to plants and animals [1–5]. Heavy metals used in the present study include Cu and Cd: copper is an essential element not only for mammals but also for plants and lower forms of organisms. It has various and many biological effects as an essential and as a toxic element. Cadmium is a natural element from the earth's crust that is taken in by plants and then passed on to animals through food chain. Exposure to abnormal levels of cadmium can result in its accumulation capabilities in living organisms beside its high toxic potential. For this reasons cadmium and copper determination in water and biological matrices is a good tool for environmental and toxicological monitoring [6].

The determination of metal ions at trace level is also very important in the context of environmental protection, food and agriculture chemistry and high purity materials. FAAS has been widely used for the determination of the heavy metals at trace levels because of the relatively simple and inexpensive equipment required. But the sensitivity of FAAS was insufficient for trace analysis. In the trace analysis, the preconcentration and separa-

tion method of analytes from the matrix is frequently necessary to enhance the sensitivity and the precision of their determination prior to FAAS analysis [7]. Several preconcentration techniques have been extensively developed for this purpose. But the solid phase extraction (SPE) has been increasingly used for preconcentration and separation of trace and ultra trace amounts of inorganic and organic species from complex matrices [8–12]. Various researchers have emphasized the advantages of SPE over other preconcentration techniques such as liquid–liquid extraction, ion exchange techniques, coprecipitation, cloud point extraction, chemical and biosorption [9–13]. The basic principle of SPE is the transfer of metals from the aqueous phase to the active sites of the adjacent solid phase; it can also be termed as solid–liquid extraction [14,15]. Chelating resins have been frequently used SPE's as they provide good stability, high sorption capacity for metal ions and good flexibility in working conditions [9]. Amberlite XAD resins are widely used to develop several chelating materials for preconcentration procedures due to its good chemical and physical properties such as porosity, high surface area, durability and purity [16–18].

In the presented work, 1,6-bis(2-carboxy aldehyde phenoxy)butane has been covalently bonded with commercially available polystyrene-divinyl benzene co-polymer, Amberlite XAD-16 through a –C=N– group resulting chelating resin. This resin was packed in a mini column and used for the separation and preconcentration of Cu(II) and Cd(II) prior to their determination by FAAS. Effect of several parameters such as pH, sorption capacity,

* Corresponding author. Tel.: +90 412 248 85 50x3174; fax: +90 412 248 83 00.
E-mail address: evarahan@dicle.edu.tr (E.V. Oral).

the type, volume and the flow rate of the elution solutions, the flow rate and volume of the sample solution on the preconcentration efficiency have been investigated. The proposed method has been applied for the determination of Cu(II) and Cd(II) ions to the real samples such as two parts of Tigris river water in Diyarbakır and Elazığ cities in Turkey, automobile exhaust particles obtained from the places where crowded traffic exist, romaine lettuce and parsley grown up in Diyarbakır. The method was validated by standard addition method and analysing leaves of poplar (NCS-DC 73350) certified reference material.

2. Experimental

2.1. Apparatus

For SPE, 1.0 cm i.d. × 10.0 cm filtration columns equipped with polypropylene frits were used. The measurements were performed with a Perkin Elmer AA 400 model FAAS. The pHs of the solutions were measured with a Mettler Toledo pH-meter equipped with a glass electrode. The functional groups of synthesized resin (for Amberlite XAD-16 and Amberlite XAD-16-1,6-bis(2-carboxy aldehyde phenoxy)butane) were analyzed in KBr tablets by using a Mattson 1000 model (Fourier transform infrared spectrometry) FT-IR and the elemental analyses were conducted on EA1108 CHNS-O, FISONs instrument. Temperature and pressure controlled microwave oven was used to digest the samples (Berghof MWS2).

2.2. Reagents

Deionized water was used to prepare all solutions. All solvents and reagents used were analytical grade. A stock solutions of Cu(II) and Cd(II) were prepared by dissolving appropriate amount of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in deionized water. A hydrochloric acid solution of 0.5 mol L^{-1} were prepared by diluting concentrated HCl solution (Merck) and used as a carrier for elution of the analyte from the column. The pHs were adjusted with in the range of 0.01 – 0.5 mol L^{-1} HNO_3 or NaOH. The pipettes and vessels were kept in dilute nitric acid at least over night, and subsequently washed with distilled water. Afterwards, they were dried.

2.2.1. Preparation of Amberlite XAD-16

Adsorber resin Amberlite XAD-16 (polystyrene divinyl benzene) of surface area $800 \text{ m}^2/\text{g}$ and pore diameter 10 nm was supplied from Sigma. It was treated with 4 mol L^{-1} HCl to remove the contaminants before using. After the resin was purified with deionized water until its pH was neutral, with an ethanol:water (1:1) solution and finally with deionized water again. Then it was stored in a polyethylene bottle [19,20].

2.3. Synthesis of Amberlite XAD-16-1,6-bis(2-carboxy aldehyde phenoxy)butane

2 g of Amberlite XAD-16 (2) bead were treated with 10 mL of concentrated HNO_3 and 4 mL of concentrated H_2SO_4 and the mixture stirred at 60°C for 1 h on the oil bath. Thereafter, the reaction mixture was poured into an ice-water mixture. The nitrated resin (3) was filtered, washed repeatedly with water until free from acid and thereafter treated with a reducing mixture of 16 g of SnCl_2 18 mL of concentrated HCl and 20 mL of ethanol. The mixture was refluxed for 12 h at 90°C . The solid precipitate was filtered and washed with water and 2 mol L^{-1} NaOH which released amino resin (R-NH₂) from (R-NH₃)₂ SnCl_6 (R resin matrix) [21–23]. The amino resin (4) was first washed with 2 mol L^{-1} HCl and finally with deionized water. The amino resin and 1,6-bis(2-carboxy aldehyde phenoxy)butane (1) which was synthesised by İlhan et al. [24]

were poured into an 50 mL ethanol and the mixture was refluxed for 24 h at 90°C . The resulting brown coloured beads (5) (Schiff base) were filtered, washed with ethanol and dried in air. The reaction sequence is shown in Fig. 1.

2.4. Recommended procedure for preconcentration and determinations of metal ions

The column method was used to concentrate the trace metal ions. 250 mg of Amberlite XAD-16-1,6-bis(2-carboxy aldehyde phenoxy)butane was wetted with 10 mL deionized water and shaken for 2 h. Afterwards $1.00 \text{ cm} \times 10.00 \text{ cm}$ polyethylene column was packed with the mixture. Before using the column, a 1 mol L^{-1} HCl solution and deionized water were passed through the column in order to condition and clean column. The pH of Cu(II) and Cd(II) solutions were adjusted to pH 4.00 and 6.00, respectively, by adding NaOH and HNO_3 solutions. The sample solutions were passed through the column at a flow rate of 4 mL min^{-1} . The elution was made with 5 mL of 0.5 mol L^{-1} HCl for each ions with a flow rate of 1 mL min^{-1} . The analyte ions in the eluent were determined by FAAS.

2.5. Procedure for certified reference materials

Leaves of poplar (NCS-DC 73350) certified reference materials (100 mg) were digested with 6 mL of concentrated HNO_3 , 2 mL of concentrated H_2O_2 in temperature and pressure controlled microwave digestion system for 31 min and diluted to 50 mL with deionized water. The solution was passed through the column under the optimum experimental conditions. The preconcentration procedure was applied to these solutions. The concentrations of analyte ions in the final solution were determined by FAAS.

2.6. Analysis of real samples

2.6.1. Analysis of water samples

River water samples were collected from two parts of Tigris river water in Diyarbakır and Elazığ cities, before the analysis, the samples were filtered through a $0.45 \mu\text{m}$ cellulose membrane filter. They were stored in polyethylene bottles at 4°C . Prior to application of method, pH of the samples were adjusted to pH 4.00 and 6.00, respectively, for Cu(II) and Cd(II). The elution were made with 5 mL of 0.5 mol L^{-1} HCl for each metal ions. The levels of the investigated analyte ions in the final solutions were determined by FAAS.

2.6.2. Procedures for automobile exhaust particles, romaine lettuce and parsley samples

Automobile exhaust particles obtained from the places where crowded traffic exist in Diyarbakır city. For the digestion of automobile exhaust particles samples, 0.25 g of automobile exhaust particles was mixed with $\text{HF-HNO}_3\text{-H}_2\text{O}_2$ (0.2–3–1) in microwave oven. After digestion, the volume was made up to 50 mL with distilled water. Prior to trace metal analysis, the samples solutions were adjusted to pH 4.00 and 6.00 for Cu(II) and Cd(II), respectively. Then the procedure given above was applied to the digested sample solution.

The romaine lettuce sample was collected from urban vegetable garden in Diyarbakır. The parsley sample was purchased from the local markets in Diyarbakır. The romaine lettuce and parsley samples were washed thoroughly with tap water followed by deionized water, dried at 110°C , and ground to pass a 200 mesh sieve [25,26]. 0.25 g of romaine lettuce and parsley samples were digested with 4 mL of concentrated HNO_3 and 2 mL of concentrated H_2O_2 in microwave system. After digestion, the volume was made up to 50 mL with distilled water. Prior to trace metal analysis, sample solutions were adjusted to pH 4.00 and 6.00 for Cu(II) and

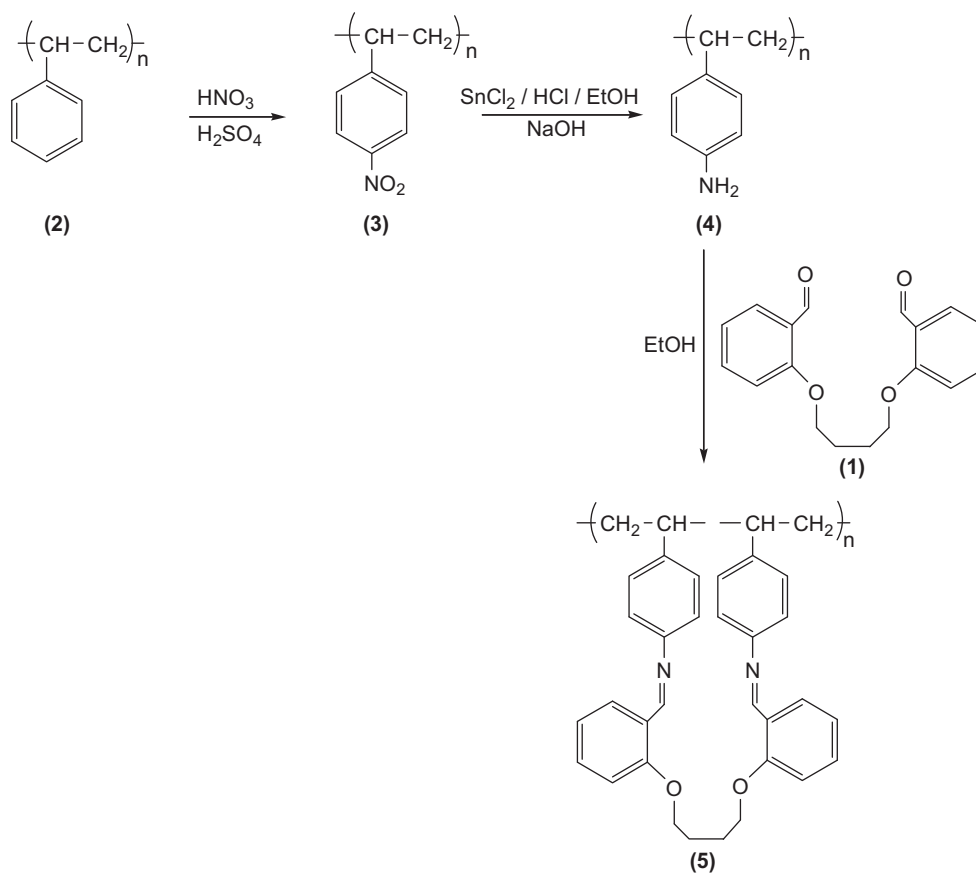


Fig. 1. Reaction sequence for various stages of the preparation of the Amberlite XAD-16 resin modified with 1,6-bis(2-carboxy aldehyde phenoxy)butane.

Cd(II), respectively. Then the reformed preconcentration method was applied to the samples.

3. Results and discussions

3.1. Characterization studies

FT-IR spectra of Amberlite XAD-16 and Amberlite XAD-16-1,6-bis(2-carboxy aldehyde phenoxy)butane resin were received by using the potassium bromide technique. Additional peaks in the FT-IR spectrum of the Amberlite XAD-16-1,6-bis(2-carboxy aldehyde phenoxy)butane resin that do not appear in the spectrum of free Amberlite XAD-16 are at, $\nu(\text{C}=\text{N})$: 1631, $\nu(\text{C}-\text{N})$: 1368, $\nu(\text{C}-\text{O})_{\text{arom.}}$: 1291, 1247, $\nu(\text{C}-\text{O})_{\text{alif.}}$: 1170, 1041 which appear to originate due to modification of resin by the ligand and are characteristic vibrations, respectively (Fig. 2a and b).

Comparative analysis of the FT-IR spectra of Amberlite XAD-16-1,6-bis(2-carboxy aldehyde phenoxy)butane before and after copper and cadmium sorption showed that azometin group ($>\text{C}=\text{N}$) of Amberlite XAD-16-1,6-bis(2-carboxy aldehyde phenoxy)butane at 1631 cm^{-1} vibrations were shifted at $5\text{--}10\text{ cm}^{-1}$ [21,27]. These observations suggest that chelation involving azometin group is at least partly responsible for the sorption of copper and cadmium. Chelation of copper and cadmium through C–O–C group also seems to play a role. After copper and cadmium sorption $1291, 1247, 1170\text{ cm}^{-1}$ C–O–C vibrations were shifted to $1292, 1170, 1047\text{ cm}^{-1}$ [28]. Conclusive evidence of the bonding is also shown by the observation that new bands in the FT-IR spectra of the Cu(II) and Cd(II) metal complexes appear at $521, 463\text{ cm}^{-1}$ and $518, 436\text{ cm}^{-1}$ assigned to $\nu(\text{Cu}-\text{O})$, $\nu(\text{Cu}-\text{N})$ and $\nu(\text{Cd}-\text{O})$, $\nu(\text{Cd}-\text{N})$, respectively, stretching vibrations [24,29] (Fig. 2c and d).

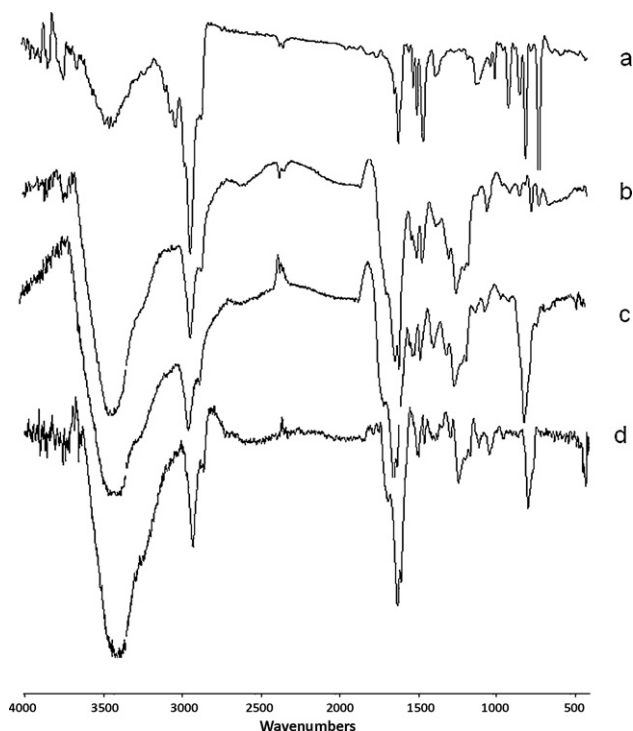


Fig. 2. FT-IR Spectrum of (a) Amberlite XAD-16, (b) Amberlite XAD-16 resin modified by 1,6-bis(2-carboxy aldehyde phenoxy)butane, (c) Amberlite XAD-16-1,6-bis(2-carboxy aldehyde phenoxy)butane after sorption of copper, and (d) Amberlite XAD-16-1,6-bis(2-carboxy aldehyde phenoxy)butane after sorption of cadmium.

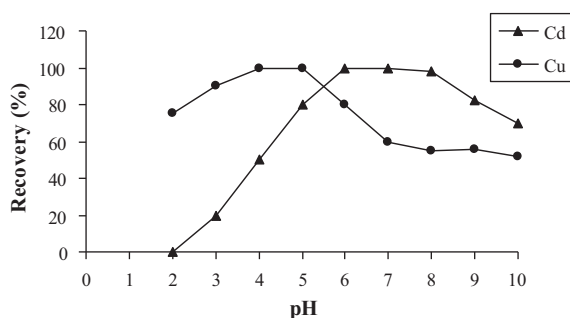


Fig. 3. Effect of pH on the sorption Cu(II) and Cd(II) on Amberlite XAD-16-1,6-bis(2-carboxy aldehyde phenoxy)butane. Cu(II) and Cd(II) concentration $1 \mu\text{g mL}^{-1}$; volume of solution 50 mL; amount of adsorbent 0.25 g; eluted with 5 mL of 0.5 mol L^{-1} HCl.

Data obtained from CHN elemental analysis were C 76.12%, H 5.97%, N 5.22% and they were comparable with the theoretically calculated values C 75.98%, H 6.01%, N 5.13%

3.2. Effect of pH on method

pH is an important parameter to obtain quantitative recoveries for metal ions. The influences of pH of the sample were investigated in the pH range of 2–10. The pH values of element solutions were adjusted to a range of 2–10 with HNO_3 or NaOH . For this purpose 250 mg Amberlite XAD-16-1,6-bis(2-carboxy aldehyde phenoxy)butane was packed in a column and 50 mL of metal solutions containing $1 \mu\text{g mL}^{-1}$ Cu(II) and Cd(II) were passed at optimum flow rate and find the effect of pH on the degree of metal sorption. The degree or percentage of metal sorbed was determined by FAAS in supernatant liquid in desorbed resin. According to these studies, the optimum pH range is 4.00–5.00 for Cu(II) and 6.00–8.00 for Cd(II) as shown in Fig. 3. All further works were performed at pH 4.00 for Cu(II) and 6.00 for Cd(II).

3.3. Eluent type and volume

In order to elute the adsorbed Cu(II) and Cd(II) ions on the Amberlite XAD-16-1,6-bis(2-carboxy aldehyde phenoxy)butane, 0.25, 0.5 and 1.0 mol L^{-1} nitric and hydrochloric acid solutions have been tested as eluent. The eluate volumes were 3, 5 and 10 mL. As can be seen from Table 1, 0.5 mol L^{-1} 5 mL HCl solution was found to be satisfactory results (>98%) for Cu(II) and Cd(II).

Table 1
Effect of the type and volume of elution solutions on the recovery of Cu(II) and Cd(II).

Type of Elution solution	Concentration (mol L^{-1})	Volume (mL)	Cu(II) recovery (%)	Cd(II) recovery (%)	
HCl	0.25	3	67	74	
		5	80	86	
		10	85	88	
	0.5	3	83	86	
		5	100	100	
		10	100	100	
	1.0	3	78	88	
		5	100	100	
		10	100	100	
	HNO ₃	0.25	3	58	55
			5	70	75
			10	77	80
0.5		3	79	78	
		5	90	90	
		10	99	98	
1		3	84	85	
		5	100	100	
		10	100	100	

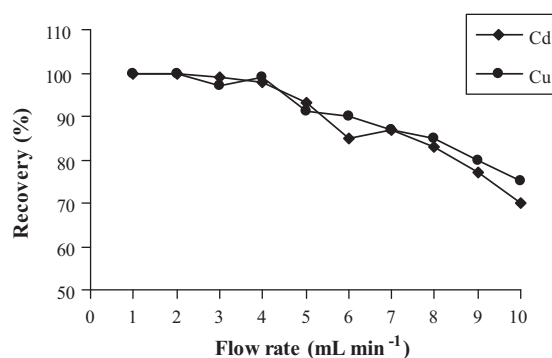


Fig. 4. Effect of sample solution flow rate on sorption. Cu(II) and Cd(II) concentration $1 \mu\text{g mL}^{-1}$; volume of solution 50 mL; amount of adsorbent 0.25 g; pH values 4.00 and 6.00, respectively; eluted with 5 mL of 0.5 mol L^{-1} HCl.

3.4. Effect of flow rate of sample solution

In the column procedure, the degree of metal ion retention on the adsorbent was studied at various flow rates of the solutions. Therefore, the effect of the flow rate of the sample solution was studied by using peristaltic pump. For each metal ion, a set of 50 mL solutions each contains $50 \mu\text{g}$ analyte were adjusted to the optimum pH value. Thereafter they were passed through the column at a flow rate between 1 and 10 mL min^{-1} . The studies showed that the flow rate had more influence on the sorption of metal ions. Two metal ions can be sorbed quantitatively by the resin at a flow rate of $1.0\text{--}4.0 \text{ mL min}^{-1}$ as shown in Fig. 4. For sorption, the flow rate slower than 1.0 mL min^{-1} was not studied to avoid long time of analysis. Above 4.0 mL min^{-1} , the recoveries of metal ions were decreased, as the metal ions probably could not equilibrate properly with the resin bed. So, all further studies the sample flow rates were chosen as 4.0 mL min^{-1} for both metal ions.

The effect of the eluent flow rate in the step of desorption of the metals from the minicolumn was also investigated by using peristaltic pump. The influences of the flow rates of the eluent solutions (HNO_3 and HCl) were investigated in the flow rate ranges of $1\text{--}3 \text{ mL min}^{-1}$. It was observed that a flow rate of 1 mL min^{-1} was most effective for stripping the metal ions from the matrix.

3.5. Effect of amount of adsorbent

The retention of Cu(II) and Cd(II) ions were examined in relation to the amount of adsorbent. The amount of adsorbent was varied from 100 to 500 mg. And results show that Cu(II) and Cd(II) ions were quantitatively retained in the range of 250–500 mg of adsorbent. So, in order to obtain maximum recovery with minimum amount of adsorbent, 250 mg of the adsorbent was used for Cu(II) and Cd(II) in subsequent experiments.

3.6. Effect of sample volume

The solid phase extraction technique is a common procedure for extraction and separation from large sample volumes to obtain high preconcentration factor. For this purpose the effect of sample solution volume on the metal sorption was studied by passing 50, 100, 250, 500, 750 and 1000 mL volume solution containing 0.25, 0.125, 0.05, 0.025, 0.017, $0.0125 \mu\text{g mL}^{-1}$ of Cu(II) and Cd(II) ions through the column under the optimum conditions. The adsorption of the metal ions was not affected by sample volume below 500 mL. Above this, the percent of sorption decreased for the analytes as shown in Fig. 5. In this study, eluent volume was 5 mL for both ions, therefore the preconcentration factors were 100 for the analytes. These result showed that Cu(II) and Cd(II) could be determined in

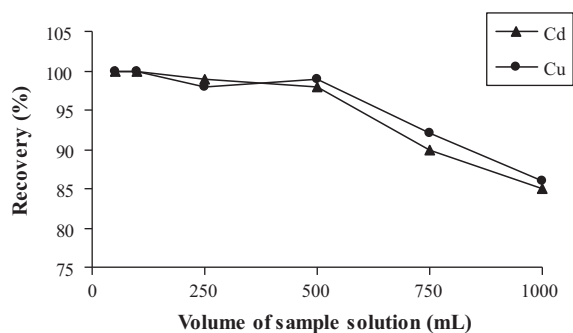


Fig. 5. Effect of volume of sample solution. Volume on the metal sorption was studied by passing 50, 100, 250, 500, 750 and 1000 mL volume solution containing 0.25, 0.125, 0.05, 0.025, 0.017, 0.0125 $\mu\text{g mL}^{-1}$ of Cu(II) and Cd(II) ions through the column. Amount of adsorbent 0.25 g; pH values 4.00 and 6.00 for Cu(II) and Cd(II) ions, respectively; eluted with 5 mL of 0.5 mol L⁻¹ HCl.

the concentration of 0.025 $\mu\text{g mL}^{-1}$ by the proposed method, which could not be determined directly by FAAS.

3.7. Reusability of the resin

In the present study, the metal ions were sorbed and desorbed on 250 mg of the Amberlite XAD-16-1,6-bis(2-carboxy aldehyde phenoxy)butane) several times by using a solution (50 mL) having a concentration of 5–50 $\mu\text{g mL}^{-1}$ under optimum experimental conditions. It was found that the sorption capacity after 10 cycles of sorption and desorption does not vary more than 2.0%. Therefore it can be said that repeated use of the resin is possible.

3.8. Effect of electrolytes

The effect of various electrolytes like NaCl, KCl, CaCl₂ and MgSO₄, which are known as interferic ions in the AAS determination, on the sorption of Cu(II) and Cd(II) with Amberlite XAD-16-1,6-bis(2-carboxy aldehyde phenoxy)butane resin matrix was studied (Table 2).

3.9. Total sorption capacity

The resin capacity for the sorption of metal ions was determined by the following procedure. Firstly, 0.25 g Amberlite XAD-16-1,6-bis(2-carboxy aldehyde phenoxy)butane was packed in a column,

Table 2
Effect of electrolytes and foreign ions.

Ion	Added concentration (mg L ⁻¹)	Recovery (%)	
		Cu(II)	Cd(II)
Na ⁺	1000	100.8	99.2
	10,000	99.6	100.2
	20,000	95.2	98.2
K ⁺	500	99.3	100.9
	1000	101.5	99.2
	2000	100.6	102.1
Ca ²⁺	500	100.8	102.3
	1000	98.5	100.8
	2000	96.9	96.0
Mg ²⁺	250	100.5	100.9
	500	90.2	91.2
	1000	80.5	84.2
Cl ⁻	1540	100.8	99.2
	15,400	99.6	100.2
	30,800	95.2	98.2
SO ₄ ²⁻	995	100.5	100.9
	1990	90.2	91.2
	3980	80.5	84.2

Table 3

Total sorption capacity of the resin for metal ions on Amberlite XAD-16-1,6-bis(2-carboxy aldehyde phenoxy)butane.

Metal ion	Capacity	
	($\mu\text{g g}^{-1}$)	(mmol g ⁻¹)
Cu(II)	5380	857×10^{-2}
Cd(II)	4436	403×10^{-2}

then 50 mL of Cu(II) and Cd(II) solutions containing 250, 500, 1000, 1500, 2000 μg of each metal specie were passed through the column under optimum experimental conditions (pH, flow rate). The metal ions concentrations in the supernatant liquid were determined by FAAS. The loading capacity for each metal ions on the resin was evaluated from the breakthrough curve plot by a method given by Bağ et al. [30]. The capacities were found as to be 0.0857 and 0.0403 mmol g⁻¹ for Cu(II) and Cd(II), respectively. The results are given in Table 3.

3.10. Analytical characteristics

Table 4 summarizes the analytical characteristics of the optimized method, including regression equation, linear range, limit of detection, limit of quantification, preconcentration factors, improvement factors for Cu and Cd. The limit of detection, defined as three times of standard deviation of the blank, and limit of quantification defined as ten times of standard deviation of the blank (standard deviations were obtained from 20 experiments). The improvement factor, defined as the slope ratio of the calibration graph of method to that of the calibration graph without preconcentration.

Precision of the method was determined by applying the method by five times to same concentration of analyte on optimum condition. The mean recovery for five determinations were 100 ± 215 and 100 ± 140 at the 95% confidence level for 1 $\mu\text{g mL}^{-1}$ Cu(II) and Cd(II), respectively. The recoveries of Cu(II) and an Cd(II) are quantitative and the precision of the method is very good.

3.11. Accuracy of the method

In order to evaluate the accuracy of the developed preconcentration method, certified reference material (leaves of poplar, NCS-DC 73350) was analyzed and standard addition method was applied. The certified reference material sample was mineralized by using the dissolution procedure described in Section 2 and was subjected to preconcentration and determination by adopting the recommended procedure. As shown in Table 5 the results found were in good agreement with the certified values of reference material.

Table 4
Analytical characteristics of the method.

Parameter	Cu(II)	Cd(II)
Linear range (ng mL ⁻¹) ^a	100–1500	100–1500
Calibration equation ^a	$y = 0.0002x + 0.008$	$y = 0.0006x + 0.0227$
Correlation coefficient ^a	1.0000	0.9988
LOD (ng mL ⁻¹) ^a	25.0	9.0
LOQ (ng mL ⁻¹) ^a	80.0	30.0
Linear range (ng mL ⁻¹)	10–1000	10–1000
Calibration equation	$y = 0.0087x + 0.0376$	$y = 0.0163x + 0.4712$
Correlation coefficient	0.9976	0.9842
LOD (ng mL ⁻¹)	0.33	1.19
LOQ (ng mL ⁻¹)	1.1	4.0
Precision (%)	2.15	1.40
Preconcentration factors	100	100
Improvement factor	40	30

^a Values given for FAAS.

Table 5
Determination of Cu(II) and Cd(II) in a certified reference sample ($N=5$).

Analyte	Certified value ^a ($\mu\text{g g}^{-1}$)	Founded by present method ^b ($\mu\text{g g}^{-1}$)
Cu(II)	9.30	9.35 \pm 0.40
Cd(II)	0.32	0.31 \pm 0.02

^a Certified reference material (leaves of poplar -NCS-DC 73350).^b Average of N determinations with 95% confidence level, $R \pm ts/\sqrt{N}$.**Table 6**
Application of standard addition method to sample from Tigris river in Diyarbakir city.

Metal ion	Spiked $\mu\text{g L}^{-1}$	Found $\mu\text{g L}^{-1} R \pm ts/\sqrt{N}$	% RE ^a	% RSD ^b
Cu(II)	0	56.44 \pm 2.47	–	3.81
	50	112.4 \pm 0.90	+4.51	0.70
Cd(II)	0	68.40 \pm 1.71	–	2.18
	100	160.76 \pm 1.26	–4.54	0.70

^a Relative error percentage.^b Relative standard deviation $N=5$.**Table 7**
Concentration of analyte ions in natural water samples as $\mu\text{g L}^{-1}$ ($N=5$, sample volume 500 mL, final volume: 5 mL).

Water samples	Cu(II) $R \pm ts/\sqrt{N}$	Cd(II) $R \pm ts/\sqrt{N}$
River water from Tigris in Diyarbakir	56.44 \pm 2.47	68.40 \pm 1.71
River water from Tigris in Elazığ	39.72 \pm 2.70	11.60 \pm 1.11

The estimation of Cu(II) and Cd(II) ions was made with and without (referred as direct determination) standard addition by passing 500 mL of Tigris river water sample (spiked with 50 $\mu\text{g L}^{-1}$ Cu(II) and 100 $\mu\text{g L}^{-1}$ Cd(II) ions in the case of standard addition method) through the column packed with 0.25 g adsorbent after adjusting the pH to an optimum value and determining the metal ions as described in the recommended column procedure. The results are given in Table 6. The concentrations reported in Table 6 as estimated by standard addition method are the values obtained by subtracting the amount of metal added for spiking from the total metal recovered. The closeness of results of direct and standard addition method indicates the reliability of present results of metal analyses in water samples.

3.12. Application to real samples

To check the applicability of the proposed method for preconcentration and determination of Cu(II) and Cd(II) ions, the resin was subjected to the real samples such as two parts of Tigris river water in Diyarbakir and Elazığ cities in Turkey, automobile exhaust particles obtained from the places where crowded traffic exist, romaine lettuce and parsley grown up in Diyarbakir. The results for natural water samples were given in Table 7.

The proposed method has been combined with the microwave assisted digested samples including a automobile exhaust particles, romaine lettuce and parsley. For this purpose, these samples were digested by closed microwave system and then preconcentration/separation procedure given in Section 2 was applied.

Table 8
The application of presented method in microwave-digested samples for copper and cadmium contents ($\mu\text{g g}^{-1}$, $N=5$).

	Cu(II) $R \pm ts/\sqrt{N}$	Cd(II) $R \pm ts/\sqrt{N}$
Automobile exhaust particles	nd ^a	6.72 \pm 0.33
Romaine lettuce	nd ^a	3.73 \pm 0.40
Parsley	3.77 \pm 0.17	nd ^a

^a Not detected.

Concentrations of the investigated ions in our samples were $\mu\text{g g}^{-1}$ level. The results are given in Table 8.

4. Conclusion

The newly synthesized resin that Amberlite XAD-16-1,6-bis(2-carboxy aldehyde phenoxy)butane shows good potential for trace enrichment of copper and cadmium and their efficient separation is possible in the presence of various interfering ions. The proposed method is simple, sensitive and accurate. The capacities were found as to be 0.0857 and 0.0403 mmol g^{-1} for Cu(II) and Cd(II), respectively. The reusability of Amberlite XAD-16-1,6-bis(2-carboxy aldehyde phenoxy)butane was high as greater than 10 cycles without any loss in its sorption behaviour. The system was also successful in preconcentrating metal ions from large sample volumes. The proposed method has been applied for the determination of Cu(II) and Cd(II) ions to the real samples such as two different parts of Tigris river water in Diyarbakir and Elazığ cities, automobile exhaust particles obtained from the places where crowded traffic exist, romaine lettuce and parsley grown up in Diyarbakir. In addition it was highlighted that concentration of Cd in lettuce samples was high because of the fact that it was irrigated with River of Dicle (Table 8). The method was validated by standard addition and analysing leaves of poplar (NCS-DC 73350) certified reference material. The results found were in good agreement with the certified values of reference material (Table 5). The closeness of results of direct and standard addition method indicates the reliability of present results of metal analyses in water samples.

References

- [1] M. Soylak, N.D. Erdogan, Copper(II)-rubeanic acid coprecipitation system for separation–preconcentration of trace metal ions in environmental samples for their flame atomic absorption spectrometric determinations, *J. Hazard. Mater.* B 137 (2006) 1035–1041.
- [2] E. Sesli, M. Tuzen, Macro- and micro-element contents in fruiting bodies of edible wild growing mushrooms in Artvin province of Turkey, *Asian J. Chem.* 18 (2006) 1423–1429.
- [3] S. Onder, S. Dursun, Air borne heavy metal pollution of Cedrus libani (A. Rich.) in the city centre of Konya (Turkey), *Atmos. Environ.* 40 (2006) 1122–1133.
- [4] B. Verep, O. Serdar, D. Turan, C. Sahin, Iyidere (Trabzon)'nin fizikokimyasal acidan su kalitesinin belirlenmesi, *Ekoloji* 14 (2005) 26–35.
- [5] T. Kovács, Activity concentration of ^{222}Rn , ^{226}Ra and ^{210}Po in Hungarian drinking waters and their contribution to the ingested dose, PhD Thesis, University of Semmelweis, Budapest, 2004.
- [6] P. Bermejo-Barrera, M.A. Nancy, D.L. Cristina, B.B. Adela, Use of Amberlite XAD-2 loaded with 1-(2-pyridylazo)2 naphthol as a preconcentration system for river water prior to determination of Cu^{2+} , Cd^{2+} and Pb^{2+} by flame atomic absorption spectroscopy, *Microchim. Acta* 142 (2003) 101–108.
- [7] A.R. Türker, A. Tunçeli, Preconcentration of copper, nickel and zinc with Amberlite XAD-16 resin, *Fresenius J. Anal. Chem.* 345 (1993) 755–758.
- [8] P.K. Tewari, A.K. Singh, Preconcentration of lead with Amberlite XAD-2 and amberlite XAD-7 based chelating resins for its determination by flame atomic absorption spectrometry, *Talanta* 56 (2002) 735–744.
- [9] P. Metilda, K. Sanghamitra, J. Mary Gladis, G.R.K. Naidu, T.P. Rao, Amberlite XAD-4 functionalized with succinic acid for the solid phase extractive preconcentration and separation of uranium (VI), *Talanta* 65 (2005) 192–200.
- [10] T. Prasada Rao, C.R. Preetha, Naphthols as reagents for solid phase preconcentrative separation of inorganics, *Sep. Purif. Rev.* 32 (2003) 1–17.
- [11] V. Camel, Solid phase extraction of trace elements, *Spectrochim. Acta Part B* 58 (2003) 117–1233.
- [12] R. Ziyadanogullari, I. Dolak, I. Tegin, R. Guzel, Synthesis and preconcentration of Amberlite XAD-4 resin modified by dithioethylenediamine, *Asian J. Chem.* 21 (2009) 165–175.
- [13] C.R. Preetha, J.M. Gladis, T. Prasada Rao, Solid phase extractive preconcentration of thorium onto 5,7-dichloroquinoline-8-ol modified benzophenone, *Talanta* 58 (2002) 701–709.
- [14] M. Dogru, R. Gul-Guven, S. Erdogan, The use of *Bacillus subtilis* immobilized on Amberlite XAD-4 as a new biosorbent in trace metal determination, *J. Hazard. Mater.* 149 (2007) 166–173.
- [15] T.P. Rao, P. Metilda, J.M. Gladis, Preconcentration techniques for uranium (VI) and thorium (IV) prior to analytical determination—an overview, *Talanta* 68 (2006) 1047–1064.
- [16] V.A. Lemos, P.X. Baliza, Amberlite XAD-2 functionalized with 2-aminothiophenol as a new sorbent for on-line preconcentration of cadmium and copper, *Talanta* 67 (2005) 564–570.

- [17] E.J. dos Santos, A.B. Herrmann, A.S. Ribeiro, A.J. Curtius, Determination of Cd in biological samples by flame AAS following on the preconcentration by complexation with O,O-diethylthiophosphate and solid phase extraction with Amberlite XAD-4, *Talanta* 65 (2005) 593–597.
- [18] S. Baytak, A.R. Turker, The use of *Agrobacterium tumefaciens* immobilized on Amberlite XAD-4 as a new biosorbent for the column preconcentration of iron(II), cobalt(II), manganese(II) and chromium(II), *Talanta* 65 (4) (2005) 938–945.
- [19] S. Erdogan, M. Merdivan, C. Hamamci, O. Akba, A. Baysal, Polymer supported humic acid for separation and preconcentration of thorium(VI), *Anal. Lett.* 37 (12) (2004) 2565–2575.
- [20] A. Tunceli, A.R. Turker, Flame atomic absorption spectrometric determination of silver after preconcentration on Amberlite XAD-16 resin from thiocyanate solution, *Talanta* 51 (2000) 889–894.
- [21] G. Venkatesh, A.K. Singh, 2-[[1-(3,4-Dihydroxyphenyl) methylidene] amino]benzoic acid immobilized Amberlite XAD-16 as metal extractant, *Talanta* 67 (2005) 187–194.
- [22] P.K. Tewari, A.K. Singh, Amberlite XAD-2 functionalized with chromotropic acid: synthesis of a new polymer matrix and its applications in metal ion enrichment for their determination by flame atomic absorption spectrometry, *Analyst* 124 (1999) 1847–1851.
- [23] M. Kumar, D.P.S. Rathore, A.K. Singh, Amberlite XAD-2 functionalized with o-aminophenol: synthesis and applications as extractant for copper(II), cobalt(II), cadmium(II), nickel(II), zinc(II) and lead(II), *Talanta* 51 (2000) 1187–1196.
- [24] S. İlhan, H. Temel, A. Kilic, Synthesis and spectral studies of macrocyclic Cu(II) complexes by reaction of various diamines, copper(II) perchlorate and 1,4-bis(2-carboxyaldehyde phenoxy)butane, *J. Coord. Chem.* 61 (2008) 277–284.
- [25] S. Baytak, A.R. Turker, Determination of lead and nickel in environmental samples by flame atomic absorption spectrometry after column solid-phase extraction on Amberlite XAD-2 with EDTA, *J. Hazard. Mater.* 129 (2006) 130–136.
- [26] T. Oymak, S. Tokalıoğlu, V. Yılmaz, S. Kartal, D. Aydın, Determination of lead and cadmium in food samples by the coprecipitation method, *Food Chem.* 113 (2009) 1314–1317.
- [27] G. Venkatesh, A.K. Singh, 4-[[2-(2-Hydroxyphenyl)imino]methyl]-1,2-benzenediol (HIMB) anchored Amberlite XAD-16: preparation and applications as metal extractants, *Talanta* 71 (2007) 282–287.
- [28] O.D. Uluozlu, A. Sari, M. Tuzen, M. Soylak, Biosorption of Pb(II) and Cr(II) from aqueous solution by lichen (*Parmelia tiliaceae*) biomass, *Bioresour. Technol.* 99 (2008) 2972–2980.
- [29] S. İlhan, H. Temel, A. Kilic, E. Tas, Synthesis and spectral characterization of macrocyclic Ni(II) complexes derived from various diamines, Ni(II) perchlorate and 1,4-bis(2-carboxyaldehydephenoxy)butane, *Trans. Metal Chem.* 32 (2007) 1012–1017.
- [30] H. Bağ, M. Lale, A.R. Turker, Determination of iron and nickel by flame atomic absorption spectrophotometry after preconcentration on *Saccharomyces cerevisiae* immobilized sepiolite, *Talanta* 47 (1998) 689–696.