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Determination of Cd(II), Co(II), Cu(II), Ni(II), and Pb(II) Ions by FAAS after Separation/Preconcentration using Amberlite XAD-1180 Chelating Resin Chemically Modified with o-Aminophenol

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Abstract: The use of a newly synthesized chelating resin with an o-aminophenol–type functional groups and Amberlite XAD-1180–type supporting material for separation/preconcentration of trace metal ions from various water samples was described. Amberlite XAD-1180-o-aminophenol chelating resin (XAD-o-AP) was synthesized using Amberlite XAD-1180 resin as solid support and o-aminophenol as the chelating ligand. The determination of Cd(II), Co(II), Cu(II), Ni(II), and Pb(II) ions was made by flame atomic absorption spectrometry (FAAS). Studying with model solutions for the optimization of the method was based on the measurement of recovery values (between 92–106%) of the analyte elements. Some analytical parameters such as pH (6.0), volume of the sample ($\sim$250 mL), effect of matrix ions, flow rates of the sample (2.5 mL min^{-1}) and elution solutions (2.5 mL min^{-1}), concentration, type and volume of the eluent (4 mol L^{-1} HNO_3, 20 mL) were investigated. The detection limit (3s/b, $n = 20$) and the relative standard deviation ($n = 7$) of the method were found to be in the range 0.9–4.3 μg L^{-1} and 4.4–5.5%, respectively.

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The proposed method was successfully applied to the real samples such as wastewater, boiler feeding water and a certified reference material (Estuarine water, LGC 6016).

Keywords: Amberlite XAD-1180-o-aminophenol chelating resin, solid–phase extraction, heavy metal ions, separation/enrichment, water analysis, FAAS

INTRODUCTION

In the determination of trace metals in natural waters, wastewaters, and aqueous solutions including matrix components in large amounts by FAAS, electrothermal atomic absorption spectromery (ET–AAS) and other atomic spectrometric methods such as inductively coupled plasma–optical emission spectrometry (ICP–OES) etc., a separation/preconcentration procedure is generally required due to the low levels of analyte elements and strong matrix effects of the environmental samples. A survey of the literature revealed that various techniques, such as liquid–liquid extraction (1, 2), coprecipitation (3, 4), electrochemical deposition, (5) ion–exhange (6, 7) and solid–phase extraction (8–10) have been tried for the separation and preconcentration of metal ions from aqueous solutions of various samples. The focus of current research in this area is on the development of sorbents with high sorption capacity. Before the determination of trace metal ions present in aqueous media, the separation/preconcentration procedures being performed with chelating resins are the most popular solid–phase extraction techniques recently (11–15). In this technique, a chelating agent is bound chemically to a solid adsorbent such as a polymeric materials, i.e., Amberlite XAD series resins (11–14, 16–20), chloromethylated polystyrene divinylbenzene co-polymer (21), glycidyl methacrylate/divinylbenzene (22), sepiolite (23), cellulose (24), and/or silicagel etc. (25, 26). As polymeric supports, the commercially available resins of Amberlite series have been found very promising for designing chelating matrices (11–14, 16–20, 27–32). Chelating resins are more attractive for the metal ions occuring at two or three oxidation state rather than the ions with one oxidation state. The resins include good selectivity, preconcentration factor, binding energy, mechanical stability, and easy regeneration for multiple sorption-desorption cycles, and good reproducibility in the sorption characteristics. Generally, chelating ligands bound to copolymers by covalent bonds are much more resistant to external effects than those immobilized by simple impregnation (17). Due to these properties, the chelating resins have also applications in separation and/or preconcentration of metal ions from wastewater, aqueous solutions and concentrated salt solutions.

The present work aims to throw light on the use of chemically modified XAD-o-AP chelating resin as a new system for the preconcentration and separation of the five heavy metal ions. After the preconcentration, the studied metal ions in the boiler feeding and waste water samples were determined using FAAS.

EXPERIMENTAL

Instrumentation

A Perkin–Elmer model 3110 atomic absorption spectrometer (Norwalk, CT, USA) equipped with a hollow cathode lamp and an air-acetylene burner was used for the determination of the analyte elements. The instrument was optimized daily and operated under typical conditions as recommended by the manufacturer. pH measurements and adjustments were carried out using a Jenco 672 model pH-meter apparatus with a combined glass electrode. Functional groups of the chelating resin synthesized, were identified with a Jasco 460 model FT–IR spectrometer by measuring the FT–IR spectrum of the resin on a pressed pellet with KBr. All glassware was maintained in nitric acid $(1 + 1)$ for 24 h at least and washed with pure water before use.

Reagent and Standard Solutions

The chemicals used were of analytical reagent grade and distilled deionized water was used throughout the experiments. Stock solutions of the analyte elements ($1000\ \mu g\ mL^{-1}$) were prepared from their nitrate salts weighing the appropriate amounts of the salts and then solving them in water and completing to 1000 mL with $1\ mol\ L^{-1}$ HNO_3. Working solutions and calibration standards were prepared from these solutions by diluting appropriate amounts. To adjust the pH of solutions, the acetic acid/acetate and ammonia/ammonium chloride buffer systems were used for pH range 4–6 and 8–10, respectively.

Amberlite XAD-1180 resin (Acros Organics, NJ, USA) is a polystyrene divinylbenzene copolymer (surface area $500\ m^2/g$, average porosity 400 Å and average diameter $530\ \mu m$). Due to containing NaCl and Na_2CO_3 to prevent bacterial growth, it was washed with water, $0.5\ mol\ L^{-1}$ HCl and $0.5\ mol\ L^{-1}$ NaOH, respectively, and then with water until a neutral solution was obtained. It was dried at 105°C in an oven and prepared for synthesizing the chelating resin. o-Aminophenol reagent (Merck, Darmstadt, Germany) was used as purchased.

Synthesis of Amberlite XAD-1180-o-Aminophenol Chelating Resin

To prepare the XAD-o-AP chelating resin, the procedure given in the literature was performed (13, 17). 5 g of Amberlite XAD-1180 resin dried at 105°C was slowly put into a 100 mL of beaker containing a mixture of 10 mL of concentrated HNO_3 and 25 mL of concentrated H_2SO_4 within 30 minutes by stirring (in a hood). The reaction mixture was hold at 60°C on a water bath by stirring. After cooling, the mixture was poured into a beaker containing iced-water and filtered. The nitrated resin was repeatedly washed with water until free from acid. It was added to a reducing mixture of 40 g of $SnCl_2$, 45 mL of concentrated HCl and 50 mL of ethyl alcohol, and heated thereafter at 90°C for 12 h under a reflux system. After filtering off, the aminated resin was washed with some water, 50 mL of 2 mol L^{-1} NaOH, and 50 mL of 2 mol L^{-1} HCl, respectively, and then washed again with water to remove excess HCl. After the aminated resin was taken into an ice-water mixture, 100 mL of 1 mol L^{-1} HCl and then 75 mL of 1 mol L^{-1} $NaNO_2$ were slowly added to it at 0–5°C. The diazotized resin was quickly filtered, washed with ice-water and added to the solution of o-aminophenol (5 g of o-aminophenol dissolved in 100 mL of 10% NaOH, w/v) at 0–5°C for 24 h. The resulting resin beads with brown color were filtered, washed with water, dried in air, and then maintained in a desiccator until the use. The proposed structure of the chelating resin is given in Fig. 1.

The Characterization of the XAD-o-AP Chelating Resin

The FT–IR spectrum of the XAD-o-AP chelating resin has shown that the peak at 3434 cm^{-1} is attributed to the N-H stretching vibrations, which generally appears in the IR spectrum of o-aminophenol as two peaks at about 3200 and 3250 cm^{-1}, and also to the phenol O-H stretching vibrations (at 3550–3200 cm^{-1}, broad and strong). The peak at 2928 cm^{-1} is attributed to the C-H stretching vibrations of the $-CH_2-$ groups of the support material. The peak at 1618 cm^{-1} is attributed to the azo group, -N=N-, stretching vibrations of the chelating resin. Two small peaks at 1522 and 1449 cm^{-1} are attributed to the -C=C- bending vibrations of the benzene ring. A small peak at 1384 cm^{-1} appears in the spectrum but disappears in the FT–IR spectrum of o-aminophenol, may be attributed to the C-O-H deformation vibrations. The peak at 1263 cm^{-1} is attributed to the C-N stretching vibrations. This is because the C-N stretching vibrations in aromatic amines are in the range of 1280–1180 cm^{-1}. The peak at 1089 cm^{-1} appeared in

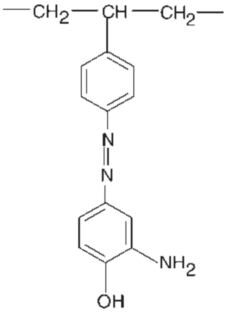

Figure 1. The proposed structure of the Amberlite XAD-o-AP chelating resin.

the IR spectrum of the chelating resin may be attributed to the C-O stretching vibrations because C-O stretching frequencies are between 1020 and 1275 cm^{-1}. The two small peaks appeared at 801 and 711 cm^{-1} may be attributed to the phenyl ring substitution bands (bending vibrations) which appear at 870–675 cm^{-1}.

Recommended Analysis Procedure for Separation/Preconcentration

0.3 g of XAD-o-AP chelating resin was filled into a glass column with a porous disk (10 mm i.d. × 100 mm height). The resin was washed with diluted acid (0.01 mol L^{-1} HCl or HNO_3), diluted base (0.01 mol L^{-1} NaOH) and then with water until the neutrality was obtained. The column was conditioned with acetic acid/acetate buffer solution (pH 6.0). About 250 mL of sample solution, after adjusting its pH to 6, was passed through the column at a flow rate of 2.5 mL min^{-1}. The metal ions retained on the column were eluted with 20 mL of 4 mol L^{-1} HNO_3 elution solution at a flow rate of 2.5 mL min^{-1}. After evaporating the eluate near to dryness, it was taken into 5 mL of 1 mol L^{-1} HNO_3. The metals in the final measurement solution were determined by flame AAS using the calibration graph method.

Sample Preparation

Water samples (wastewater and boiler feeding water) were filtered through cellulose acetate membrane filters (0.45 μm porosity, 47 mm diameter; Advantec MFS, Inc., CA, USA) using a filtration apparatus (Schleicher&Schuell, Dassel, Germany), then acidified with HNO_3 to pH ~ 2 and stored in a refrigerator at +4°C until the analysis.

Isotherm Study

The adsorption isotherm and the adsorption capacity of the resin for cadmium(II), cobalt(II), copper(II), nickel(II), and lead(II) were studied by using the column method. The amount of the adsorbent was 0.3 g and the pH of solutions was 6.0. The analyte concentrations were increased up to 100 mg L^{-1} for Ni, 120 mg L^{-1} for Co, 250 mg L^{-1} for Cd, 320 mg L^{-1} for Cu, and 500 mg L^{-1} for Pb. The adsorption capacity (n_m) of the chelating resin for the elements was obtained by using the Langmuir equation (26) based on the following equation:

$$\frac{C}{n} = \frac{1}{n_m \cdot K} + \left(\frac{1}{n_m}\right) \cdot C \tag{1}$$

The adsorption capacity (n_m) and the binding equilibrium constant (K) were calculated from the slope and the intercept of the least squares regression plot, respectively.

RESULTS AND DISCUSSION

Effect of pH

The first parameter investigated was the pH of the sample solution. Because it is well known that metal ions retention on the chelating resin is pH-dependent. For this purpose we used model solutions of 50 mL containing 10 μg of Co(II) and Ni(II), 5 μg of Cu(II), 2.5 μg of Cd(II), and 20 μg of Pb(II) ions. The pH values of model solutions were adjusted with CH_3COOH/CH_3COONH_4 buffer and NH_3/NH_4Cl buffer solutions in the range of 4 to 6 and 8 to 10, respectively. The retained metal ions on the column were eluted with 20 mL of 4 mol L^{-1} HNO_3 solution. The eluate was evaporated near to dryness on a heater and then the moist residue completed to 5 mL with 1 mol L^{-1} HNO_3. The experiments were performed in triplicates at each pH value. The effect of pH value of the sample solution on sorption of Cd(II), Co(II), Cu(II), Ni(II), and Pb(II) ions on the column filled with XAD-o-AP chelating resin is depicted in Fig. 2. As can be seen from Fig. 2, the optimal pH range for quantitative recoveries of all the metals investigated is between 5 and 7. Because of that the optimum pH value was chosen as 6 and then used for all the experiments.

Effect of Concentration, Type and Volume of the Eluent

The type, amount, and concentration of eluent are other important parameters for this kind of studies. In order to determine type and amount of elution

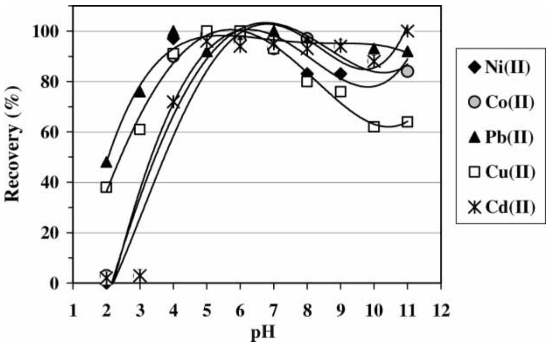

Figure 2. Effect of pH on the recovery of metal ions.

solution, 50 mL of model solutions having pH 6.0 and containing 10 μg of Co(II) and Ni(II), 5 μg of Cu(II), 2.5 μg of Cd(II), and 20 μg of Pb(II) ions were used. For the elution process, the following eluents having 20 mL of 2, 3, 4, and 5 mol L^{-1} HNO_3, and also 2, 3, and 4 mol L^{-1} HCl, were tested. The eluate solutions were evaporated near to dryness and the moist residues completed to 5 mL with 1 mol L^{-1} HNO_3 for matrix matching purpose (matching the sample solutions to the calibration standards). For determining the eluent volume, 10, 15, and 20 mL of the eluent were tested. The best results were obtained with the elution solution of 20 mL of 4 mol L^{-1} HNO_3. The results obtained are shown in Figs. 3 (a), (b), and (c).

Effect of Flow Rates of Eluent and Sample

In order to determine flow rate of the sample, the model solutions including analyte ions were passed through the column containing 0.3 g of XAD-o-AP chelating resin at flow rates of 1, 2, 2.5, and 5 mL min^{-1}. Desorption of the metal ions from the column was made with 20 mL of 4 mol L^{-1} HNO_3. The recoveries were quantitative (≥95%) up to flow rate of 2.5 mL min^{-1}.

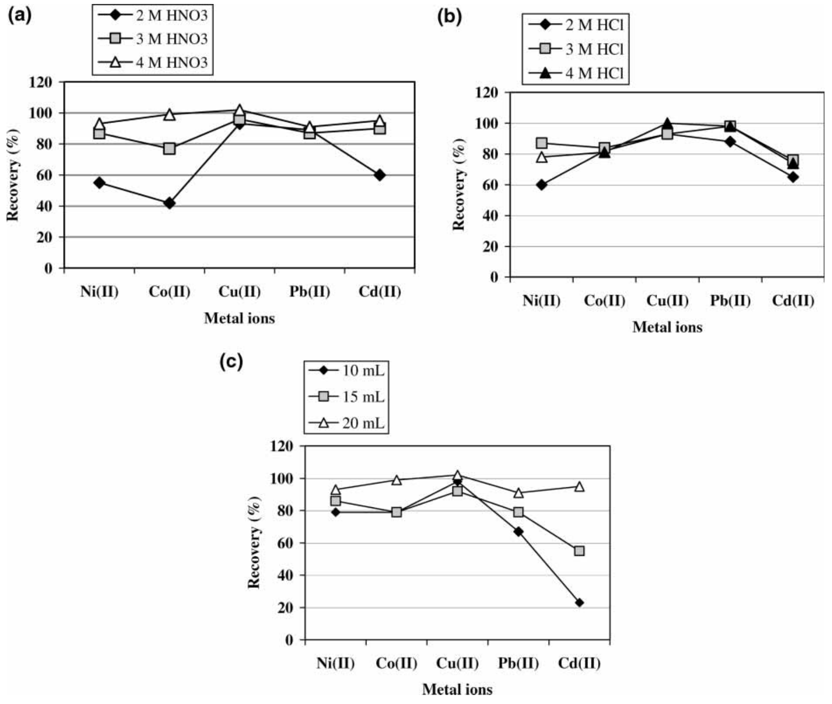

Figure 3. Effect of (a) concentration of HNO_3, (b) concentration of HCl, (c) volume of 4 mol L^{-1} HNO_3 as eluent ($n = 3$).

In order to determine optimum flow rate of the eluent, the model solutions containing 10 μg of Co(II) and Ni(II), 5 μg of Cu(II), 2.5 μg of Cd(II), and 20 μg of Pb(II) ions were passed through the column at a flow rate of 2.5 mL min^{-1}. The elution process was performed with 20 mL of 4 mol L^{-1} HNO_3 at different flow rates of the eluent, namely, at 2.5, 3.5, and 5 mL min^{-1}. The recoveries were quantitative (≥95%) only up to an eluent flow rate of 2.5 mL min^{-1} for all the metal ions, while for Pb(II) and Cu(II) ions recovered quantitatively up to flow rate of 3.5 mL min^{-1}. After this flow rate, the desorption of the other three metal ions from the column was not quantitative (their recovery values were about 91–92%). Consequently, a flow rate of 2.5 mL min^{-1} was chosen as suitable flow rate for both the sample and the elution solutions to pass through the column.

Effect of Sample Volume

Another parameter investigated for the best experimental conditions is the effect of sample volume on the recovery. Under the optimized circumstances, model solutions having volumes between 50 and 500 mL and containing the analyte ions, 10 μg of Co(II) and Ni(II), 5 μg of Cu(II), 2.5 μg of Cd(II), and 20 μg of Pb(II), were passed through the column at flow rates of 2.5 mL min^{-1}. Desorption of the metal ions was made with 20 mL of 4 mol L^{-1} HNO_3. As can be seen from Fig. 4, the recovery values decrease after 250 mL of sample volume. At 300 mL of the sample volume, the elements have satisfactory recovery values (≥90%), except for Co(II), while the recoveries for all the elements are ≤90% at 400 mL of sample volume.

Effect of Matrix Ions

The preconcentration procedures for trace metals can be strongly affected by other constituents of the samples. For this reason, the reliability of the proposed method was examined in the presence of possible interfering ions

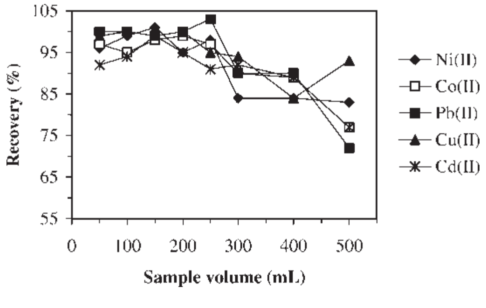

Figure 4. Effects of sample volume on the recoveries of the analyte ions.

Table 1. The tolerance limits for the matrix ions (based on the approach in which recovery was $\geq 95\%$, $n = 3$)

The diverse ions and their studied concentrations in μg mL^{-1}		Metal ions				
		Co(II)	Ni(II)	Cu(II)	Cd(II)	Pb(II)
Na^+ (NaCl)	25, 50, 100, 250, 500, and 1000	1000	500	1000	250	500
K^+ (KNO_3)	20, 50, 100, 250, and 500	250	500	500	250	500
Ca^{2+} ($CaCl_2$)	10, 20, 50, 100, 250, 500, and 1000	1000	1000	500	10	1000
Mg^{2+} Mg $(NO_3)_2$	1, 2.5, 5, 25, 100, and 250	100	25	250	25	100
Al^{3+} ($AlCl_3$)	1, 2.5, 5, 10, and 25	2.5	5	10	1	5
Fe^{3+} ($FeCl_3$)	0.5, 1, 5, and 15	0.5	5	5	5	5
Zn^{2+} ($ZnCl_2$)	2.5, 5, 10, and 25	5	10	25	2.5	10
Mn^{2+} ($MnCl_2$)	1, 2.5, and 5	<1	1	5	<1	2.5
SO_4^{2-} (Na_2SO_4)	100, 250, and 500	250	500	500	100	500
NO_3^- (KNO_3)	40, 100, 200, 500, and 1000	500	500	500	500	1000
Cl^- (NaCl)	25, 50, 100, 250, 500, and 1000	1000	500	1000	250	500

of the water samples. The interfering elements were added to the model solutions containing 10 μg of Co(II) and Ni(II), 5 μg of Cu(II), 2.5 μg of Cd(II), and 20 μg of Pb(II) ions as their nitrate or chloride salts. The tolerance limit is defined as the ion concentration causing a relative error smaller than ±5% related to the preconcentraion and determination of analytes. Table 1 shows the tolerance limits for interfering ions.

Adsorption Isotherms

Figure 5 shows the adsorption isotherms of Co(II), Ni(II), Cu(II), Cd(II), and Pb(II) ions at pH 6.0 and at room temperature. Inspection of Fig. 5 reveals that the uptake order or sequence of the metal ions are Pb(II) > Cu(II) > Cd(II) > Co(II) > Ni(II) almost at all concentrations. The uptake of the metal ions increases markedly until reaching maximum values at 320, 220, 100, 60, and 40 mg L^{-1} of the sample solutions for Pb(II), Cu(II), Cd(II), Co(II), and Ni(II) ions, respectively (22). While the adsorption capacity of the chelating resin (μmol g^{-1}) was 124 for Co(II), 123 for Ni(II), 503 for Cu(II), 136 for Cd(II), and 226 for Pb(II), the binding equilibrium constants (L mg^{-1}) were 0.285, 0.283, 0.063, 0.407, 0.030 for Co(II), Ni(II), Cu(II), Cd(II), and Pb(II), respectively.

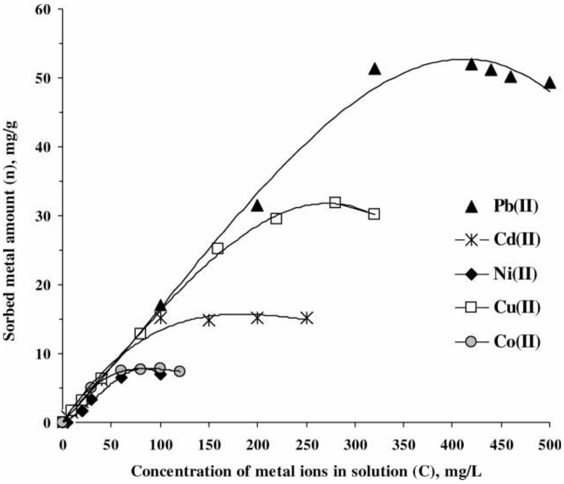

Figure 5. Adsorption isotherms of Amberlite XAD-1180-o-AP chelating resin for metal ions.

Analytical Performance of the Method

In order to determine the method detection limit value for each analyte, a-50 mL of blank solution was passed through the column filled with Amberlite XAD-1180-o-AP chelating resin ($n = 20$). The method detection limits (DL) of the elements based on the ratio of three standard deviations of the blank to the slope of the calibration curve (3s/b) were 1.2, 1.1, 0.9, 1.0, and 4.3 μg L^{-1} for Co(II), Ni(II), Cu(II), Cd(II), and Pb(II), respectively. They can be improved by increasing the sample volume.

The precision of the proposed method was examined under the optimum experimental conditions described above by using the model solutions. The relative standard deviation of the method was in the range of 4.4–5.5% ($n = 7$).

Table 2. The recovery of the elements added to the wastewater (sample volume: 250 mL, $n = 3$)

Metal	Added, μg mL^{-1}	Found, μg mL^{-1}	Recovery (%)
Co(II)	2.0	1.93	97
Ni(II)	2.0	2.10	105
Cu(II)	2.0	2.08	104
Cd(II)	0.4	0.38	95
Pb(II)	4.0	3.66	92

Table 3. Results obtained for the certified material of estuarine water (LGC 6016) ($n = 3$)

Metal	Certified values (μg kg^{-1})	Found values (μg kg^{-1})	Recuperation (%)
Co(II)	—	—	—
Ni(II)	186 ± 3	207.3 ± 8.5	111.5
Cu(II)	190 ± 4	189.1 ± 7.1	99.5
Cd(II)	101 ± 2	95.7 ± 4.7	94.7
Pb(II)	196 ± 3	202.5 ± 13.9	103.3

The accuracy of the described separation/preconcentration method was tested with the recovery studies made by adding known amounts of the elements to the wastewater sample of 250 mL. The obtained results were shown in Table 2. The recoveries calculated for the additions were quantitative.

The influence of the sample volume on the recoveries of the analyte ions is another crucial parameter for the calculation of preconcentration factors. As can be seen from Fig. 4, the breakthrough volumes were 200 mL for Cd(II), 250 mL for Co(II), Ni(II), and Pb(II), and 300 mL for Cu(II) ions. For 5 mL of the final measurement volume, the enrichment factors were found to be 40 for Cd, 50 for Co, Ni, and Pb, and 60 for Cu.

Analysis of a Certified Reference Material (Estuarine water: LGC 6016)

The accuracy of the proposed method was also evaluated by the analysis of a estuarine water reference material for the determination of Co(II), Ni(II), Cu(II), Cd(II), and Pb(II). The determination for the certified sample was

Table 4. Concentration of the elements in boiler feeding water (200 mL) and wastewater (250 mL) samples ($n = 3$)

	Concentration, μg mL^{-1} ($\bar{x} \pm t \times s/\sqrt{n}$)^{a}	
	Boiler feeding water	Wastewater
Co(II)	<DL	<DL
Ni(II)	<DL	0.037 ± 0.002
Cu(II)	0.0112 ± 0.0004	0.018 ± 0.001
Cd(II)	<DL	0.0013 ± 0.0010
Pb(II)	<DL	<DL

[a] At 95% confidence level.

Table 5. Comparison of sorption capacities (μmol g^{-1}) of some metal ions using the chelating resins prepared with different ligands and support materials

		Metal ion					
Support	Immobilized ligand	Co(II)	Ni(II)	Cu(II)	Cd(II)	Pb(II)	Ref.
Amberlite XAD-1180	o-Aminophenol	124	123	503	136	226	This work
Amberlite XAD-2	1-(2-Thiazolylazo)-2-naphthol			490			(13)
	o-Vanillinthio-semicarbazone			13.4		9.7	(16)
	o-Aminophenol	55.8	55.2	53	30.4	16	(27)
	Thiosalicylic acid	106.9	309.9	214	197.5		(28)
	Chromotropic acid	65.1	103.4	133.8	83.2		(29)
	2-Aminoacetylthio-phenol	325.8	299.9	379.2	190.4		(30)
	2-(Methylthio)aniline	175.7	239.9	139.2	210.6		(31)
	Pyrocatechol	23	53.1	92.5	40.9		(32)
	1-(2-Pyridylazo)-2-naphthol (PAN)			108	22.8	6.5	(33)
Amberlite XAD-4	Salen			272.2		129.8	(19)
	APDC		122.8	174.4	84.2	49.5	(34)
	pipDTC		127.1	169.3	81.7	47.6	(34)
Amberlite XAD-7	Xylenol Orange	44.1	44.3	25.2	17.8		(35)
Amberlite XAD-16	Bis-2,3,4-trihydroxy benzyl ethylene diamine				1010	780	(11)
	2-{[1-(3,4-Di-hydroxy-phenyl)methylidene] amino} benzoic acid	221	269	468	128	97	(18)
Silica gel	Resacetophenone	365	253.8	186.4	57.8	66.6	(36)
	1,8-Dihyroxy-anthraquinone				70.2	76.4	(37)
Cellulose	2,3-Dihydroxy-pyridine	145.7	207.8	342.5	69.7	82.7	(38)
Chloromethyl polystyrene	2-Aminothiophenyl S-acetic acid					30	(15)

Table 6. Comparison of preconcentration factors of some metal ions using the chelating resins prepared with different ligands and support materials (Recovery was assumed ≥95%, the final measurement volume was 5 mL for the method presented)

		Metal ion					
Support	Immobilized ligand	Co(II)	Ni(II)	Cu(II)	Cd(II)	Pb(II)	Ref.
Amberlite XAD-1180	o-Aminophenol	50	50	60	40	50	This work
	1-(2-Pyridylazo)-2-naphthol		100	100	150	100	(17)
Amberlite XAD-2	o-Aminophenol	100	65	50	50	40	(27)
	o-Vanillinthio-semicarbazone			90		100	(16)
	Thiosalicylic acid	180	200	200	200		(28)
	Chromotropic acid	150	200	100	100		(29)
	2-Aminoacetylthio-phenol	150	400	100	400		(30)
	2-(Methylthio) aniline	150	400	100	300		(31)
	Pyrocatechol	200	200	100	200		(32)
	1-(2-Pyridylazo)-2-naphthol (PAN)			50	50	50	(33)
	2-(2′-Benzothiazolylazo)-p-cresol					19–60	(20)
Amberlite XAD-4	Salen			272.2		129.8	(19)
	APDC		130	230	180	160	(34)
	pip-DTC		120	200	150	150	(34)
Amberlite XAD-7	Xylenol Orange	100	100	50	50		(35)
Amberlite XAD-16	Bis-2,3,4-trihydroxy benzyl ethylene diamine				500	450	(11)
	2-{[1-(3,4-Di-hydroxyphenyl) methylidene]amino} benzoic acid	167	100	300	250	250	(18)
Silica gel	Resacetophenone	300	200	250	200	250	(36)
	1,8-Dihyroxy-anthraquinone				200	200	(37)
Cellulose	2,3-Dihydroxy-pyridine	100	125	250	200	200	(38)

carried out using the optimized parameters of the method. Analytical results are given in Table 3 for LGC 6016 reference sample. According to Table 3 the analyte recovery for the certified material changed from 94.7 to 111.5%, with satisfactorily results. For all the elements investigated, except for Co(II) since it was not certified, the results are in very good agreement with the certified values. The results obtained from the analysis of the standard reference material confirm the accuracy of the presented method.

Application of the Method

To check the applicability of the proposed method for preconcentrating and determining Co(II), Ni(II), Cu(II), Cd(II), and Pb(II) ions, the synthesized resin Amberlite XAD-o-AP was subjected to analysis of boiler feeding water and wastewater samples. The results listed in Table 4 indicate the suitability of the present resin for preconcentration of the analyte ions from the water samples.

Comparison with Other Chelating Matrices

The sorption capacities of the presented resin are compared with those of other promised chelating resins in Table 5. It shows better or comparable sorption capacities than most of the other chelating sorbents, particularly with those having Amberlite XAD series support materials with some exceptions. Especially, the adsorption capacities of the presented chelating resin for Cu (503 μmol g^{-1}) and Pb (226 μmol g^{-1}) are higher than those of the others given in Table 5. The only disadvantage of the proposed method may be seen as its low preconcentration factors when compared with the other chelating extractors given in Table 6. However, our results were comparable with those of o-aminophenol and 1-(2-pyridylazo)-2-naphthol functionalized Amberlite XAD-2 systems (27, 33), and also to some extent xylenol orange anchored Amberlite XAD-7 chelating matrix (35).

CONCLUSIONS

The proposed solid phase extraction method described in this paper provides a simple, sensitive, precise, reliable and accurate technique. The investigations indicate that the Amberlite XAD-1180-o-aminophenol chelating resin has good potential for the enrichment and separation of Co(II), Ni(II), Cu(II), Cd(II), and Pb(II) ions from the water samples and their determinations by FAAS. The matrix effects appeared with the use of the proposed method were reasonably tolerable. The Amberlite XAD-1180-o-aminophenol chelating resin was quite stable with a recycling period greater than 100 cycles, without any major loss in its quantitative metal recovery property, despite the elution solution used is 4 mol L^{-1} of HNO_3. This indicates that the synthesized chelating resin is much more stable than the others, for example, the cycles of sorption-desorption of a few similar resins are 50 for 2-{[1-(3,4-dihydroxyphenyl) methylidene]amino}benzoic acid immobilized Amberlite XAD-16 (18), >15 for o-aminophenol anchored Amberlite XAD-2 (27), >12 for thiosalicylic acid immobilized Amberlite XAD-2 (28), 15 for 2-aminoacetylthiophenol functionalized Amberlite XAD-2 (30), and 15 for 2-(methylthio)aniline functionalized Amberlite XAD-2 (31). Also the method has low detection limit values, changing between 0.9 and 4.0 $\mu g\ L^{-1}$, for the studied metal ions. High adsorption capacities were obtained when compared with the others given in Table 5, especially for Cu and Pb, 503 and 226 $\mu mol\ g^{-1}$, respectively. Furthermore, the preconcentration factor of the method was 50. The results acquired from the analysis of a standard reference material (estuarine water, LGC 6016) confirmed the reliability of the method. The proposed technique can be applied to environmental samples for the determination of traces of the studied metals without the risk of contamination.

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