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ORIGINAL ARTICLE

Separation/preconcentration of trace Pb(II) and Cd(II) with 2-mercaptobenzothiazole impregnated Amberlite XAD-1180 resin and their determination by flame atomic absorption spectrometry

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Abstract A new chelating resin, 2-mercaptobenzothiazole loaded Amberlite XAD-1180 was prepared and used for separation and preconcentration of Cd(II) and Pb(II) ions prior to their determinations by flame atomic absorption spectrometry. The optimum pH for simultaneous retention of the elements and the best elution means for their simultaneous elution were 9.5 and 2 mol L^{-1} HNO_3, respectively. The detection limits for Cd(II) and Pb(II) were 0.35 and 5.0 µg L^{-1}, respectively. The accuracy of the method was confirmed both by analyzing the certified reference material (RM 8704 Buffalo river sediment) and performing recovery studies.

1. Introduction

Trace metals play an important role in human metabolism and either excess or deficiency of them in the living organism can lead to biological disorders. Cadmium and lead are two elements that are most hazardous to human health. Cadmium, a metal with toxic effects, accumulates particularly in the liver and kidney. It may cause renal injuries and may interfere with the renal regulation of calcium and phosphate balance (Sung and Huang, 2003; Mondal et al., 2002). The entrance of lead at levels > 0.5–0.8 µg mL^{-1} into the blood causes various abnormalities. Lead accumulates in the skeleton, especially in the bone marrow. It is a neurotoxin and causes behavioral abnormalities, retarding intelligence and mental development. Lead interferes in the metabolism of calcium and vitamin D and affects hemoglobin formation and causes anemia. It damages the kidneys and leads to renal tumors (Memon et al., 2005). Therefore, it is very important to develop sensitive methods for quantitative determination of trace amounts of lead and cadmium.

Flame atomic absorption spectrometry (FAAS) has been widely used for the determination of trace metal ions, because of the relatively simple and inexpensive equipment required. However, the direct determination of trace concentrations of these elements by FAAS is generally difficult because of low

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concentrations which are below the detection limit of FAAS. The pre-treatment steps in analytical procedure, such as preconcentration of an analyte and/or its separation from the matrix components are frequently necessary. This process when applied enhances the sensitivity of the method. Solid phase extraction (SPE) is one of the pre-treatment methods for the concentration of trace analytes from a sample. Particularly, solid phase extraction, based on a solid support impregnated with a chelating agent, has gained special attention due to the advantages in the use of these substances in metal ion enrichment for the determination of trace levels of metallic species in environmental samples, biological samples and other complex matrices. The advantages of SPE over ion exchange and liquid–liquid extraction are selectivity, eco-friendliness, reusability and preconcentration from a larger sample volume (Ramesh et al., 2007; Baytak and Türker, 2006; Ghaedi et al., 2007; Liu et al., 2005).

A number of solid phase extraction studies using impregnated resins have been described for trace metal determinations. Liu et al. studied the preconcentration of Cd, Co, Cu and Zn in natural water samples using Amberlite XAD-4 loaded with 2,6-dihydroxyphenyl-diazoaminoazobenzene (Liu et al., 2007). Veni et al. have used Dowex 50W-X8 loaded with 2-amino-benzenethiol for the preconcentration of total chromium (Veni et al., 2006). Amberlite XAD-7 impregnated with morpholine dithiocarbamate has been used for the separation and preconcentration of Pb, Cu, Co, Fe, Ni, Cd and Zn by Rao et al. (Rao et al., 2006). Barrera et al. realized the determination of Cu, Pb and Cd using Amberlite XAD-2 loaded with 1-(2-pyridylazo)-2-naphthol (Bermejo-B et al., 2003). Tokalıoğlu and Kartal used Amberlite XAD-1180 impregnated with 4-(2-pyridylazo)-resorcinol for the determination of Cr(III), Fe(III), Co(II) and Pb(II) in water, salt and street dust samples (Tokalıoğlu and Kartal, 2006).

A few solid phase extraction studies have been performed for the determination of silver and mercury using 2-mercaptobenzothiazole (MBT) recently. Absalan and Mehrdjardi determined silver ion from aqueous sample solutions using MBT immobilized on surfactant-coated alumina (Absalan and Mehrdjardi, 2003). Ma et al. realized the separation and determination of trace Hg(II) in environmental samples with aminopropylbenzoylazo-MBT bonded to silica gel (Ma et al., 2000). Chwastowska et al. used MBT loaded Bio-Beads SM-7 for the separation and preconcentration of inorganic and alkylmercury from natural waters (Chwastowska et al., 1999). Safavi et al. performed synthesis of MBT bonded silica gel and used for the determination of silver by atomic absorption spectrometry (Safavi et al., 2004). To our literature knowledge, no studies have been performed on the solid phase extraction of trace metal ions by using 2-mercaptobenzothiazole loaded Amberlite XAD-resins. The structure of the MBT is shown in Fig. 1.

In the present study, MBT loaded Amberlite XAD-1180 resin was used as the column packing material for the preconcentration of Pb(II) and Cd(II) from environmental samples and their determination by FAAS. Various influencing factors on the separation and preconcentration of trace metal ions, such as type, volume and concentration of eluent, effect of pH, sample volume and effect of interfering ions have been investigated.

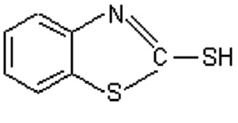

Figure 1 2-mercaptobenzothiazole.

2. Experimental

2.1. Apparatus

A PerkinElmer model AAnalyst 800 flame atomic absorption spectrometer equipped with an air-acetylene burner was used for the analysis under the conditions suggested by the manufacturer. The operating conditions for Pb(II) and Cd(II) were as follows: wavelength, 283.3 and 228.8 nm; bandwidth, 0.7 and 0.7 nm, lamp current, 12 and 12 mA; acetylene and air flow rates, 2.0 and 17 L min^{-1}, respectively. All pH measurements were made with a Consort C533 model digital pH meter equipped with a combined pH electrode. A Fisons SGP-202–010J model mixer was used to prepare the impregnated resin and a Clifton model shaker was used for batch experiments.

2.2. Reagents

All chemicals were of analytical reagent grade. Distilled–deionized water was used in all experiments. Pb(II) and Cd(II) stock solutions (1000 mg L^{-1}) were prepared from the nitrate salts of metals in acidic medium. The working solutions of metals were obtained by diluting these stock solutions prior to use. The calibration curve was prepared using the standard solutions in 1 mol L^{-1} HNO_3 by dilution from the stock solutions. 2-Mercaptobenzothiazole (MBT) solution of 0.5% (w/v) was prepared by dissolving 0.50 g of MBT (Rohm & Hass, Aldrich) in 100 mL of ethyl alcohol. The acetic acid/acetate buffer of pH 4–6 and ammonia/ammonium chloride buffer of pH 8–10 were used. Non-ionic Amberlite XAD-1180 resin (Acros Organics, NJ, USA) is a polystyrene divinylbenzene copolymer (surface area 500 m^2 g^{-1}, average porosity 400 Å and average diameter 530 μm). It was washed with 1 mol L^{-1} hydrochloric acid and ethanol, respectively, and then rinsed with water until obtaining a neutral solution prior to use. It was dried at 105 °C in an oven before use. A glass column (10 cm long, 1 cm i.d.), with a reservoir of 200 mL on the top and a porous disk made from sintered glass just placed above the stopcock at the bottom, was used.

2.3. Preparation of MBT impregnated Amberlite XAD-1180 resin

15 mL of 0.5% (w/v) MBT solution and 0.5 g of AXAD-1180 resin were mixed in a mixer for 25 min. Then the prepared mixture was placed into the glass column (10 cm long, 1 cm i.d.) and the fluidic portion of the mixture was allowed to pass through the column at a flow rate of 1 mL min^{-1}. The flow rate was controlled by adjusting the stopcock, because this could be easily obtained gravitationally. The impregnated resin was rinsed with distilled water and conditioned with 10–15 mL of buffer solution (pH 9.5) prior to passage of the sample solution.

2.4. General preconcentration procedure

The column method was tested with model solutions prior to its application to the natural samples. The pH of model solutions (50 mL) including 20 μg of Pb(II) and 2.5 μg of Cd(II) was adjusted to 9.5 using ammonia/ammonium chloride buffer solution. The column was preconditioned by passing the buffer solution with pH 9.5 through the column and then the model solutions were passed through the column at a flow rate of 1 mL min^{-1}. The metal complexes retained on the resin were eluted with 20 mL of 2 mol L^{-1} HNO_3 solution. The eluate was evaporated near to dryness on a hot plate. The residue was diluted to 5 mL with 1 mol L^{-1} HNO_3 solution. The concentration of the metal ions in the final solution was determined by FAAS.

2.5. Analysis and preparation of samples

The sea water sample was taken from Aegean Sea, İzmir, Turkey and immediately filtered through a Millipore cellulose membrane filter (0.45 μm pore size), acidified to pH 2 with HNO_3, and stored in precleaned polyethylene bottles. Tap water samples taken from our research laboratory were used without pretreatment. The untreated waste water samples were taken from the Organized Industry District of Kayseri. They were acidified to pH 2 with HNO_3 and filtered through a blue ribbon filter paper. To oxidize organic matter, 50 mL of concentrated HNO_3 (65%, w/w) was added to 500 mL of water sample and heated for 2 h. After cooling, 50 mL of concentrated H_2O_2 (35%, w/w) was added to this sample solution and evaporated to about 10–15 mL of volume. The solution was filtered through a Millipore cellulose membrane filter (0.45 μm pore size) with 5–6 mL of hot 1 mol L^{-1} HNO_3 and then diluted to 500 mL with distilled–deionized water. Aliquots of 25 mL of the sample solutions were analyzed by using the recommended procedure.

A 100-mg of the reference material (RM 8704 Buffalo river sediment, dried at 110 °C for 2 h) and sediment samples taken from the three main streets of Kayseri (Turkey) were dissolved in a beaker by adding 10 mL of aqua regia. The mixture was heated on a hot plate until to almost dryness. Then, 10 mL of aqua regia was added again to the residue and the mixture was evaporated to dryness. After dissolving the residue with about 10 mL of 1 mol L^{-1} HNO_3, the solution was filtered through a filter paper with blue ribbon by using some hot 1 mol L^{-1} HNO_3 for the separation of insoluble materials. 9 mL of 1 mol L^{-1} NaF was added to the filtrate in order to prevent the precipitation of Fe(III) and Al(III), in hydroxide forms, found in the sample in excess amounts. So, Fe(III) and Al(III) ions have been masked by F^- in the solution as FeF_6^{3-} and AlF_6^{3-} anionic complexes. The pH of this solution was adjusted to pH 9.5 by adding NH_3/NH_4Cl buffer. The total volume was made up to 50 mL with distilled–deionized water. The column procedure described above was applied to separate and preconcentrate the metal ions from the sample solution.

3. Results and discussion

3.1. Effect of pH

One of the most significant parameters, actually the first, is to investigate the effect of pH of sample solution during the optimization studies of a method. The effect of pH on the preconcentration of metal ions onto MBT coated Amberlite XAD-1180 was investigated by passing the model solution (50 mL) containing 20 μg of Pb(II) and 2.5 μg of Cd(II) adjusted at pH 9.5 through the column. The retained metal ions were eluted with 20 mL of 2 mol L^{-1} HNO_3. The eluate was evaporated near to dryness on a hot plate and it was diluted to 5 mL with 1 mol L^{-1} HNO_3 solution. The concentration of the metal ions in the final solution was determined by FAAS. The effect of pH on the preconcentration of metal ions is shown in Fig. 2. Quantitative recovery values (⩾95%) were found in the pH ranges 9–10 for Pb(II) and 8–10 for Cd(II). Hence, the pH 9.5 was selected for further studies.

3.2. Elution

In order to obtain the quantitative recovery of retained metal ions on MBT coated Amberlite XAD-1180, the different type (HCl and HNO_3), concentrations (1–3 mol L^{-1}) and volumes (5, 10 and 20 mL) of eluents were examined. During these studies, 50 mL aliquots of the sample solutions containing 20 μg of Pb(II) and 2.5 μg of Cd(II) were used at pH 9.5. Quantitative recovery values were obtained by using 20 mL of 2 mol L^{-1} nitric acid solution. The recoveries for the other eluting solutions were in the range of 52–83%. The effect of volume of 2 mol L^{-1} nitric acid solution was also studied. In the present investigation, 20 mL of 2 mol L^{-1} nitric acid solution was the best and thus selected as eluent for the elution of Pb(II) and Cd(II).

3.3. Effect of sample volume

The effect of sample volume on the retention of metal ions was studied. For this purpose, 50–150 mL of the model solutions adjusted to pH 9.5 and containing 20 μg of Pb(II) and 2.5 μg of Cd(II) was preconcentrated by passing through the column. To elute the metal ions retained on the column, 20 mL of 2 mol L^{-1} HNO_3 was used. As shown in Fig. 3, the recoveries of Pb(II) and Cd(II) were quantitative for the sample volumes up to 100 mL. When the final measurement volume is 5 mL, the preconcentration factor is 20. The decreased recovery with increasing sample volumes may be due to the low concentration of metal ions in the solution and/or the elution of the analytes by the sample solution itself.

3.4. Effect of coexisting ions

The effects of coexisting ions such as sodium, potassium, calcium, magnesium, chloride and sulfate usually found in natu-

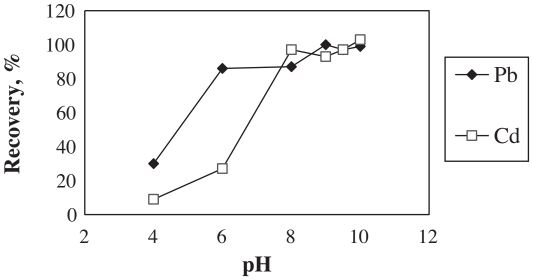

Figure 2 Effect of pH on the recovery of Pb(II) and Cd(II) on a column filled with the impregnated resin (sample volume: 50 mL, eluent: 20 mL of 2 mol L^{-1} HNO_3).

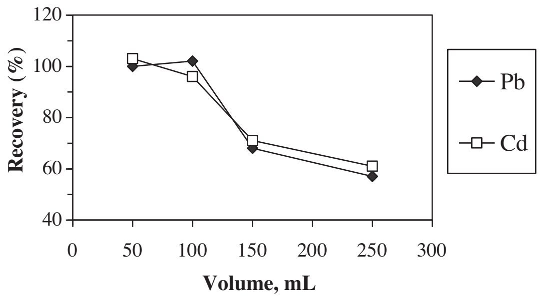

Figure 3 Effect of sample volume on the recovery of Pb(II) and Cd(II).

Table 1 Effect of some matrix ions on the recovery of Pb(II) and Cd(II) (pH: 9.5, eluent: 20 mL of 2 mol L^{-1} HNO_3, sample volume: 50 mL).

Ion (salt)	Concentration, µg mL^{-1}	Pb(II)	Cd(II)
Na^+(NaCl)	5000	98 ± 3[a]	92 ± 2
	10000	90 ± 3	96 ± 3
K^+ (KCl)	5000	97 ± 4	99 ± 6
Ca^{2+} ($Ca(NO_3)_2$)	5000	97 ± 5	99 ± 2
	10000	106 ± 5	93 ± 4
Mg^{2+} ($MgCl_2$)	500	96 ± 3	96 ± 6
	1000	87 ± 5	99 ± 2
Cl^- (NaCl)	5000	99 ± 6	96 ± 2
SO_4^{2-}(Na_2SO_4)	500	105 ± 5	101 ± 4

[a] $(\bar{x} \pm s)$, $n = 3$.

Table 2 Determination of Pb(II) and Cd(II) in a certified reference matter (RM 8704).

Element	Found (µg g^{-1})[a]	Certified value (µg g^{-1})	Recovery (%)
Pb(II)	149 ± 3	150 ± 17	99.3
Cd(II)	2.93 ± 0.31	2.94 ± 0.29	99.7

[a] $(\bar{x} \pm \frac{t.s}{\sqrt{N}})$, at 95% confidence level, $n = 5$.

ral samples were examined using model solutions containing 20 µg of Pb(II) and 2.5 µg of Cd(II) and excess matrix ions in 50 mL of model solutions. The experimental results are given in Table 1. The results show that the presence of high concentrations of major cations and anions has no obvious effect on the studied metal ion recoveries.

3.5. Precision and detection limit of the method

The precision of the method was determined by performing successive ten retention and elution cycles followed by FAAS. It was found that the recoveries (R% ± s) of Pb(II) and Cd(II) were 97.8 ± 2.4, and 99.0 ± 2.6, respectively. In order to determine the detection limit (DL, $n = 20$) of the proposed method, a 50-mL of blank solution was passed through the column under the optimal experimental conditions and the retained metal ions were eluted. The DLs obtained as concentration corresponding to three times the standard deviation of the blank solution were 5.0 µg L^{-1} for Pb(II) and 0.35 µg L^{-1} for Cd(II). In the calculation of the DLs of the method, the preconcentration factor (PF) of 20 was taken into consideration. The limit of quantification (LOQ, 10 s) values were found to be 16.5 µg L^{-1} for Pb(II) and 1.2 µg L^{-1} for Cd(II). The calibration graphs for Pb(II) and Cd(II) were found to be $A = 0.0017 + 0.008$ C in the interval of 1–12 µg mL^{-1} ($r = 0.9992$) and $A = 0.0032 + 0.152$ C in the interval of 0.1–2.0 µg mL^{-1} ($r = 0.9995$), respectively. The calibration data were obtained without application of the preconcentration procedure for FAAS.

3.6. Accuracy of the proposed method and application to real samples

The accuracy of the proposed method was evaluated by determination of the metal ions in the standard reference material, RM 8704-Buffalo river sediment (Table 2) and recovery studies in the water samples (Table 3). The results in Table 2 show that there is no significant difference between the results obtained by the proposed method and certified values. The accuracy of the method was also checked by measuring the recoveries for Pb(II) and Cd(II) in the spiked water samples. As can be seen from Table 3, the recovery values changing from 90% to 105% demonstrate that the described method can be applied to the analysis of the water samples without interference. The Pb(II) and Cd(II) results $(\bar{x} \pm s)$ obtained from the analysis of the three main street sediment samples ($n = 3$) were found to be 274 ± 4 and 5.55 ± 0.54, 258 ± 5 and 4.30 ± 0.93, 241 ± 6 and 5.34 ± 0.95 µg g^{-1}, respectively.

Table 3 Determination of Pb(II) and Cd(II) in various water samples (pH: 9.5, sample volume: 100 mL for tap water and sea water, 25 mL for waste water).

Element	Tap water			Sea water		Untreated waste water		
	Added[a], (µg mL^{-1})	Found[b] (µg mL^{-1})	R,%	Found[b] (µg mL^{-1})	R,%	Added[a] (µg mL^{-1})	Found[b] (µg mL^{-1})	R,%
Pb(II)	–	ND[c]		ND	–	–	0.50 ± 0.04	
	2.0	2.03 ± 0.08	102	2.13 ± 0.12	106	2.0	2.50 ± 0.04	100
	4.0	4.05 ± 0.04	101	4.14 ± 0.19	104	4.0	4.53 ± 0.15	101
Cd(II)	–	ND		ND	–	–	0.04 ± 0.01	
	0.2	0.18 ± 0.01	90	0.22 ± 0.01	96	0.2	0.25 ± 0.01	105
	0.5	0.51 ± 0.06	102	0.49 ± 0.03	98	0.4	0.45 ± 0.01	103

[a] For the added metal concentrations, final volume was taken into consideration.
[b] $(\bar{x} \pm s)$, $n = 3$.
[c] ND: Not detected.

Table 4 Comparison with the other preconcentration procedures used the impregnated adsorbent for the determination of Pb(II) and Cd(II) ions.

Support-impregnated ligand	DL (μg L^{-1})		RSD (%)		PF		Ref.
	Pb	Cd	Pb	Cd	Pb	Cd	
XAD-1180-MBT	5.0	0.35	2.4	2.6	20	20	This work
Nanometer sized alumina-chromotrophic acid	0.53	0.14	–	–	50	50	Ramesh et al. (2007)
XAD-4-2,6-Dihydroxyphenyl-diazoaminoazobenzene		0.1		2.4		42	Liu et al. (2007)
XAD-7-Morpholine dithiocarbamate	2.10	4.19	2.82	3.72	50	50	Rao et al. (2006)
XAD-2-1-(2-Pyridylazo)-2-naphthol	23.2	0.8	4.1	2.9	50	50	Bermejo-B et al. (2003)
XAD-4-2-Acetylmercaptophenyldiazoaminoazobenzene		0.028		3.1		80	Liu et al. (2005)
Nanometer TiO_2 -diethyldithiocarbamate	1.7	0.52	5.6	4.8	33	33	Zheng et al. (2006)
XAD-7-Xylenol orange		9.0		2.0		50	Tewari and Singh (2000)
XAD-4- Ammonium pyrrolidine dithiocarbamate	0.6	0.1	2.88	2.95	160	180	Ramesh et al. (2002)
XAD-4- Piperidine dithiocarbamate	1.7	0.7	3.19	3.21	150	150	Ramesh et al. (2002)

4. Conclusion

The 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 modified with MBT has good potential for the enrichment and separation of Cd(II) and Pb(II) ions from the water and street sediment samples and their determinations by FAAS. The tolerance limits of interfering ions on the recovery of analyte ions are quite high. A comparison of the proposed method with the other preconcentration procedures using various modified adsorbents is given in Table 4. The method has low RSD(%) values when compared with the others given in Table 4. Amberlite XAD-1180 resin loaded MBT seems to be stable up to at least 20 runs. The results acquired from the analysis of a standard reference material (RM 8704) confirmed the reliability of the method. The proposed technique can be applied to environmental samples for the determination of trace Pb(II) and Cd(II).

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