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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.

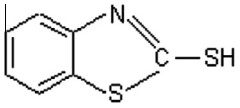

Figure 1 2-mercaptobenzothiazole.

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 solu-

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