Ecotoxicology and Environmental Safety 112 (2015) 74–79

Contents lists available at ScienceDirect

Ecotoxicology and Environmental Safety

journal homepage: www.elsevier.com/locate/ecoenv

Solid phase extraction of metal ions in environmental samples on 1-(2-pyridylazo)-2-naphthol impregnated activated carbon cloth

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ARTICLE INFO

Article history:
Received 27 July 2014
Received in revised form
22 October 2014
Accepted 24 October 2014
Available online 7 November 2014

Keywords:
1-(2-Pyridylazo)-2-naphthol
Activated carbon cloth
Lead
Cadmium
Nickel
Flame atomic absorption spectrometry

ABSTRACT

1-(2-Pyridylazo)-2-naphthol impregnated activated carbon cloth (PAN-imp-ACC) was prepared as a solid phase sorbent and, for the first time, was used for the simultaneous separation and preconcentration of trace amounts of lead, cadmium and nickel in water, soil and sewage sludge samples prior to determination by flame atomic absorption spectrometry (FAAS). The parameters governing the efficiency of the method were optimized, including the pH, the eluent type and volume, the sample and eluent flow rates, diverse ions effects and the sample volume. A preconcentration factor of 100 was achieved for all the metal ions, with detection limits of 0.1–2.8 $\mu g\ L^{-1}$ and relative standard deviations below 6.3%. The adsorption capacity of the PAN-imp-ACC for Pb(II), Cd(II) and Ni(II) ions was found to be 45.0mg g^{-1}, 45.0 mg g^{-1} and 43.2 mg g^{-1}, respectively. The method was validated by the analysis of the certified reference materials TMDA-64.2 fortified Lake Ontario water and BCR-146R Sewage Sludge Amended Soil (Industrial Origin). The procedure was applied to determine the analytes content in real samples.

1. Introduction

Heavy metals such as lead, cadmium and nickel are common pollutants of water, food, soil and biological samples and have generated intense research interest due to their toxicity to humans, animals, and other living creatures (Somer et al., 2006; Ibrahim et al., 2009; Narin and Soylak., 1999; Doker et al., 2014; Aday and Yuceer, 2014; Ugulu, 2015). Hence, the development of fast, reliable and effective analytical methods for the determination of trace amounts of lead, cadmium and nickel in real samples is an important area of research (Tuzen and Soylak, 2007; Soylak et al., 2007; Tuzen et al., 2009; Tajik and Taher, 2011; Acar et al., 2014; Szymczycha-Madeja et al., 2014).

Several analytical methods, including flame atomic absorption spectrometry (FAAS), electrothermal atomic absorption spectrometry (ETAAS), inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma-mass spectrometry (ICP-MS) and electroanalytical instruments are widely used for the determination of trace amounts of heavy metal ions in various matrices (Tuzen et al., 2004; Ghaedi et al., 2009; Hajiaghababaei et al., 2012; Yilmaz et al., 2013; Eskandari, 2012; Kalfa et al., 2012; Turkmen et al., 2014). However, the direct determination of trace amounts of these ions in real samples using these techniques is challenging due to matrix effects and the need for extremely low detection limits. Hence, sample pre-treatment, such as preconcentration of the analyzed elements and matrix separation, is often necessary (Rojas et al., 2003; Ghaedi et al., 2010; Sadeghi et al., 2012).

A number of separation and preconcentration procedures, such as solid phase extraction (SPE) (Incili and Aycik, 2014; Naraghi et al., 2014), coprecipitation (Saracoglu et al., 2012), cloud point extraction (CPE) (Tavallali et al., 2010) and liquid–liquid extraction (LLE) (Ikeda and Abe, 1998), have been developed and used for the enrichment and separation of heavy metals at trace levels in various environmental samples. Among these, solid phase extraction is a widely accepted, ideal, and powerful technique because of its simplicity, high enrichment factor, low cost, low or no consumption of organic solvents, ease of automation and ability to be coupled with various modern detection techniques (Poole et al., 2000; Soylak, 2003; Alothman et al., 2012).

Activated carbon materials are versatile adsorbents that can be used for extraction due to their excellent physical and chemical properties. Compared with other activated carbon products, activated carbon cloth (ACC) has the advantages of mechanical robustness and easy utilization. ACC provides a higher surface area and mechanical strength and the possibility for regeneration (Ayranci et al., 2005; Hoda et al., 2006). These unique properties of ACC make it an attractive sorbent (Rangel-Mendez and Streat, 2002; Fallah and Azizian, 2012; Ayranci and Hoda, 2004a, 2004b; Ayranci and Duman, 2007).

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http://dx.doi.org/10.1016/j.ecoenv.2014.10.032
0147-6513/

In the present study, activated carbon cloth impregnated with PAN (PAN-imp-ACC) was used for the solid phase extraction of trace amounts of lead, cadmium and nickel from environmental samples prior to their detection by FAAS.

2. Material and methods

2.1. Instrument

A Perkin-Elmer Model 3110 (Norwalk, CT, USA) flame atomic absorption spectrometer equipped with a hollow cathode lamp and an air/acetylene flame as an atomizer was used for the measurements. A Sartorius PT-10pH meter (Germany) with a glass-electrode was used during the adjustment of the pH. Water was purified by reverse osmosis (18.2 MΩ cm, Millipore) and used in the preparation of solutions.

The FT-IR spectra were recorded on a Perkin-Elmer Spectrum 400 FT-IR spectrometer (Waltham, MA, USA). Scanning electron microscope (SEM) images were obtained on a LEO 440 SEM (Leo Electron Microscopy, Cambridge, UK). Spectrophotometric measurements were carried out by using Hitachi Model 150-20 UV–vis double beam spectrophotometer carrying a 10 mm optical path cell.

2.2. Reagents and chemicals

All chemicals were of analytical grade and used without further purification. Diluted HNO_3, HCl and CH_3COOH were used as eluents and purchased from Merck (Darmstadt, Germany). A 0.5% 1-(2-pyridylazo)-2-naphthol (PAN) solution was prepared by dissolving 0.25 g of PAN (E. Merck, Darmstadt) in 50 mL of ethanol. A buffer solution of H_3PO_4/NaH_2PO_4 was used for pH 3.0, and a buffer solution of CH_3COONa/CH_3COOH was used for pH 4.0. For pH values of 5.0, 6.0 and 7.0, NaH_2PO_4/Na_2HPO_4 was used as the buffer solution. Finally, an NH_3/NH_4Cl buffer solution was used for pH 8.0.

The activated carbon cloth (Code: Norm/AW1105, Norm company, Turkey) displayed a BET surface area and thickness of 1000 $m^2\,g^{-1}$ and 0.4 ± 0.1 mm, respectively. The average diameter of the fibrils was 10–12 µm.

2.3. Preparation of impregnated activated carbon cloth and the extraction system

Preparation of the PAN-impregnated activated carbon cloth followed a procedure given in the literature (Alothman et al., 2012). A mass of 0.500 g of two pieces of ACC were added to 50 mL of a 0.5% PAN solution and incubated with continuous shaking for 6 h. Afterwards, the PAN-impregnated activated carbon cloth was collected from the solution, washed with ethanol and water and dried overnight at 80 °C. To prepare the solid phase extraction system used in our method, the PAN-impregnated activated carbon cloths were fixed in a filtration system comprising 47 mm disc filters and a 100 mL reservoir. Prior to use, the PAN-imp-ACC was preconditioned with a buffer solution at pH 7.0. After each experiment, the column was washed with water.

2.4. General procedure

A 50-mL aqueous sample solution containing 15 µg of Pb(II) and Ni(II) and 5 µg of Cd(II) was prepared and adjusted to pH 7.0 using 5 mL phosphate buffer. The PAN-imp-ACC was preconditioned with the pH 7.0 buffer solution. The solution was passed through the PAN-imp-ACC filtration system under vacuum at a 4 mL min^{-1} flow rate. The target analytes adsorbed on the PAN-imp-ACC were eluted with 10 mL 3 mol L^{-1} HNO_3 at a 4 mL min^{-1} flow rate. The extracts were collected in a volumetric flask and analyzed for the analyte metals by FAAS.

2.5. Applications

Soil samples were collected from various farming locations around a metallurgical factory primarily producing zinc, cadmium and lead in Kayseri, Turkey and coded as Soil-1, Soil-2 and Soil-3. The collected soil samples were dried at a temperature of 80 °C for 24 h and were homogenized using an agate mortar and pestle.

A 0.1-g mass of BCR-146R-Sewage sludge amended Soil (Industrial Origin) certified reference materials and 1.0 g of soil sample were transferred to a beaker. Next, 16 mL of aqua regia was added, and the solution was heated on a hot plate to near dryness at approximately 100 °C. After cooling, the residue was again treated with the same volume of aqua regia ($HCl:HNO_3$, 12/4) on a hot plate until dryness. The digested samples were then dissolved in 20 mL of distilled water. The SPE procedure was subsequently applied to the samples. Various amounts of Pb(II), Cd(II) and Ni(II) ions were spiked in the soil sample coded Soil-1 to verify the accuracy of the procedure.

A water sample was collected from the Yamula Dam in Kayseri, Turkey. Wastewater samples were collected from mine factories located in Kayseri and Yozgat, Turkey. A river water sample was collected from the Sari River in Çanakkale, Turkey. Before use, the collected water samples were filtered through a 0.45-µm Millipore cellulose membrane. The developed SPE procedure was then applied to the samples. To validate the developed SPE procedure, various amounts of Pb(II), Cd(II) and Ni(II) ions were spiked into the waste and dam water samples (100 mL). Water certified reference material coded as TMDA 64.2 fortified Lake Ontario water (25 mL) was also analyzed to verify the accuracy of the proposed method.

3. Results and discussion

3.1. Characterization of PAN-IMP-ACC

The amount of 1-(2-pyridylazo) 2-naphtol (PAN) deposited on activated carbon cloth was estimated by spectrophotometric measurements from the residual amount of a 1-(2-pyridylazo) 2-naphtol (PAN) in the solution. It was found that 92.3% of PAN was retained on activated carbon cloth.

The activated carbon cloth impregnated 1-(2-pyridylazo)-2-naphthol was characterized by using Fourier transform infrared spectrometer (Supplemental Fig. S1). In the IR spectrum of (PAN-imp-ACC), peaks at 3439.65 cm^{-1}, 3008.62 cm^{-1}, 2892.24 cm^{-1}, 1800.06 cm^{-1}, 1720.52 cm^{-1}, 1548.54 cm^{-1}, 1469.00 cm^{-1}, 1433.81 cm^{-1}, 1187 cm^{-1} and 1135.78 cm^{-1}, correspond to the stretching frequencies of OH (phenolic), CH, =CH, N=N (azospacer), C=O (tautomer), C=N, C=C (pyridylazo group), C=C (naphthol group), C–O and C–C, respectively. While, The peaks at 834.42 cm^{-1} and 737.99 cm^{-1} shows bending frequencies of C–H. The peak at 3788.79 is belonging to the stretching frequencies of N–H because of tautomer of the molecule.

Fig. 1 illustrates the SEM images of pristine activated carbon cloth and PAN-IMP-ACC. The morphology of the pristine ACC and PAN-IMP-ACC shows some differences. The coverage of the surface of the ACC due to the impregnation of the PAN over the ACC surface is evidence for impregnation.