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Polyhydroxybutyrate-b-polyethyleneglycol block copolymer for the solid phase extraction of lead and copper in water, baby foods, tea and coffee samples

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ABSTRACT

A new adsorbent, polyhydroxybutyrate-b-polyethyleneglycol, was used for the separation and preconcentration of copper(II) and lead(II) ions prior to their flame atomic absorption spectrometric detections. The influences of parameters such as pH, amount of adsorbent, flow rates and sample volumes were investigated. The polymer does not interact with alkaline, alkaline-earth metals and transition metals. The enrichment factor was 50. The detection limits were 0.32 μg L^{-1} and 1.82 μg L^{-1} for copper and lead, respectively. The recovery values were found >95%. The relative standard deviations were found to be less than 6%. The validation of the procedure was performed by analysing certified reference materials; NIST SRM 1515 Apple leaves, IAEA-336 Lichen and GBW-07605 Tea. The method was successfully applied for the analysis of analytes in water and food samples.

1. Introduction

Because of the environmental issue and the toxicity of heavy metals on human health, the determinations of heavy metals have been investigated by many researchers (Chu, Ding, & Fan, 2010; Soylak, Saracoglu, Tuzen, & Mendil, 2005). Heavy metals cannot be metabolised by the body and are stable in environment because they are at least five times denser than water (Bagheri et al., 2012; Tuzen, Sesli, & Soylak, 2007b; Tuzen, Silici, Mendil, & Soylak, 2007a). The major pollution caused by heavy metals is waste water, waste residue, exhaust gases from different industries and traffic, etc. (Chu et al., 2010). The heavy metals in excess amounts are passed up to the food chain which adversely affect the human health. When a heavy metal is smeared into the environment through the air, drinking water, food, or synthetic chemicals and products, the body can take the toxicity via inhalation, ingestion, and skin absorption (Arain et al., 2008; Karve & Rajgor, 2007).

Excess level of copper is toxic although it is essential trace element. As industrial use of copper increases, environmental pollution due to copper also increases. Long term exposure of the toxic elements causes potentially toxic effects to human health, especially to infants and young children (Mahajan, Walia, & Sumanjit, 2005).

Lead is a non essential element for living bodies (Ascione, 2001). Lead is an enzyme inhibitor and a general toxic element in metabolism, and lead to mental retardation and semi-permanent brain damage in young children. Negative effects of lead on the bone formation are caused after for long term exposure. When the blood lead levels are lower than 5 μg dL^{-1}, a reduced performance can be observed with Pb exposure (Merrill, Morton, & Soileau, 2007). The accurate and sensitive measurement of trace amounts of heavy metals is the most significant task in analysis (Yildiz, Citak, Tuzen, & Soylak, 2011).

Atomic absorption spectrometry is a useful tool for the determination of heavy metals. The determination of trace metals by flame atomic absorption spectroscopy is quite difficult (Kazi et al., 2009; Nabid et al., 2012; Narin, Soylak, Kayakirilmaz, Elci, & Dogan, 2003; Saracoglu, Soylak, & Elci, 2002) because of low detection limit and matrix effects. To solve this problem, preconcentration techniques including liquid–liquid extraction, cloud point extraction, electrodeposition, co-precipitation, membrane filtration and solid phase extraction are used (Araneda et al., 2008; Behbahani et al., 2013a; Behbahani et al., 2013b; Behbahani et al., 2013c; Behbahani et al., 2013d). Solid phase extraction (SPE) is a good choice because of its simple application, easy methodology, high preconcentration

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factor and sensitivity (Hosseini, Dalali, & Karimi, 2010; Soylak, Saracoglu, & Elci, 2004; Yildiz et al., 2011). SPE consists of the recovery of hydrophobic metal species on a solid support of hydrophobic functionality (Ghaedi, Ahmadi, & Soylak, 2007). Various adsorbents such as solvent-impregnated resins, polyurethane foam, Amberlite resins, modified clinoptilolite zeolite etc. (Burham, Azeem, & Shahat, 2008; Ebrahimzadeh, Behbahani, Yamini, Adlnasab, & Asgharinezhad, 2013; Sorouraddin & Saadati, 2008) have been used for solid phase extraction of metal ions.

The purpose of this work is the preconcentration–separation of Pb(II) and Cu(II) onto polyhydroxybutyrate-b-polyethylene glycol (PHB-b-PEG) as a solid phase extractor. This polymer has not been used before for solid phase extraction of trace elements according to our literature survey.

2. Experimental

2.1. Instrumentation

A Perkin Elmer A Analyst 700 (Norwalk, CT, USA) atomic absorption spectrometer with deuterium background corrector was utilised for the study. Perkin Elmer single element hollow cathode lamps were used. All readings were taken using air/acetylene flame with a slot-burner with 10 cm long head (Yildiz et al., 2011). The operating conditions were set as per manufacturer's recommendations.

A pH metre, Sartorius pp-15 Model (Göttingen, Germany) glass-electrode was used for accurate measurements of the pH in the aqueous media. The pH metre was calibrated after each 10 measurements by using pH 4.01 (PY-Y01), pH 7.00 (PY-Y02) and pH 10.00 (PY-Y04) buffer standards provided by Sartorius. For microwave digestion, a Milestone Ethos D (Sorisole-Bg, Italy) closed vessel microwave system (maximum pressure 1450 psi, maximum temperature 300 °C) was used.

2.2. Reagents and solutions

All chemicals used were of analytical reagent grade throughout the experimentation. Deionised water (Milli-Q Millipore (Bedford, MA, USA) 18.2 MΩ cm^{-1}) was used for all initial and successive dilutions. All glassware and plastic were first soaked in dilute HNO_3 and then rinsed with distilled water before use. The required metal standard solutions for calibration were prepared from stock solution of 1000 mg L^{-1} purchased from Sigma (St. Louis, MO, USA) and Aldrich (St. Louis, MO, USA). Buffers from pH 2–9 were prepared from different reagents (Sodium dihydrogen phosphate, ammonium acetate, acetic acid, HCl, ammonium chloride and $NaBO_2$) obtained from Merck, Darmstadt, Germany. Three certified standard reference materials (NIST SRM 1515 Apple leaves, IAEA-336 Lichen and GBW-07605 Tea) were used.

Poly (3-hydroxy butyrate) (PHB), microbial polyester was supplied from BIOMER (Germany). Poly (ethylene glycol) bis (2-aminopropyl ether) with MW 2000 g/mol (PEG-2003) were a gift from Huntsman Corporation (Switzerland). Stannous 2-ethyl hexanoate and the other chemicals used were purchased from Aldrich.

2.3. Synthesis of PHB–PEG block copolymers

The procedure described in the cited references (Hazer, Baysal, Köseoğlu, Beşirli, & Taşkın, 2012; Taskın, Hazer, Besirli, & Cavus, 2012) was used for the synthesis of polymer used in this study. A chloroform solution (300 mL) of PHB Biomer (10 g) and PEG2003 (10 g) was refluxed in the presence of 0.1 g tin(II)-ethyl hexanoate. After evaporating the solvent, the white solid polymer was dried under vacuum at room temperature for 24 h. After washed with water several times to remove the unreacted PEG residue, it was dried in air and then under vacuum at room temperature for 24 h (Yildiz, Kemik, & Hazer, 2010). The synthesis of the polyhydroxybutyrate-b-polyethyleneglycol is shown in Fig. 1. The surface area and pore size of polyhydroxybutyrate-b-Polyethylene glycol (PHB-b-PEG) was 1.2867 m^2 g^{-1} and 85.8 nm according to BET method, respectively. The PEG content in PHB-b-PEG block copolymer was 9 mol%. The molecular weight of the block copolymer was 27961 Da.

2.4. Sampling

Bottled mineral water (BMW) samples were collected from a local market in the Tokat Province of Turkey. Tap water from our laboratory was allowed to run for 10 min and ~1000 mL of water were collected in a beaker. All water samples were filtered through a 0.45-mm pore size membrane filter (Millipore Corporation, Bedford, MA, USA). The water samples were stored at +4 °C till further analysis.

2.5. Column preparation

The column was filled with polyhydroxybutyrate-b-polyethylene glycol (PHB-b-PEG) as a block copolymer. About 500 mg of PHB-b-PEG were loaded into a 10 mm × 100 mm glass column containing porous discs. The polymer thickness was nearly 2 cm long. The column was each time conditioned with buffer solution before use. After every elution, the PHB-b-PEG in column was also washed with a 15 mL of water.

2.6. Procedure

A 50 mL of model solution was prepared containing lead(II) (0.3 mg L^{-1}) and copper(II) (0.1 mg L^{-1}) and the pH was maintain between 2 and 9 with different buffers. The column was first preconditioned by passing 10 mL of buffer solution through the polymer column and then the model solution at a flow rate of 5 mL min^{-1} was passed. After adsorption of the analytes, the column was rinsed with 10 mL of water. The adsorbed metal ions on the PHB-b-PEG were then eluted with 5 mL of 1 mol L^{-1} HCl. The eluent was analysed for the determination of Pb and Cu levels by using flame atomic absorption spectrometry.

2.7. Application on BMW and Tap water samples

The pH of the water samples was adjusted to 6.0 with acetate buffer solution; then the procedure given in Section 2.6 was applied. The water sample at a flow rate of 5 mL min^{-1} was passed. Blank samples were also analysed. The levels of analytes in the samples were determined by flame atomic absorption spectrometry.

2.8. Preparation and application on food and certified reference materials (CRM)

Each food sample was analysed and the certified reference materials CRM's were subjected to microwave digestion prior to using the proposed method. 100 mg of each CRM and 1.0 g of each food samples were digested in 9.0 mL of mixture of concentrated HNO_3 (65%) and concentrated H_2O_2 (30%) in ratio 2:1. The digestion conditions used were: 6 min for 250 W, 6 min for 400 W, 6 min for 550 W, 6 min for 250 W, ventilation: 8 min (Tuzen, Citak, Mendil, & Soylak, 2009). After digestion the final volume of each sample was made to 50 mL with deionized water. The blanks were also prepared the same way. Then the procedure as described in section 2.6 was applied.