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Column preconcentration of lead in aqueous solution with macroporous epoxy resin-based polymer monolithic matrix

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Abstract

The objective of this article was to investigate the feasibility of epoxy resin-based monoliths prepared by stepwise polymerization and column preconcentration of metal ions using large-scale monolithic matrix. A novel macroporous polymer monolith matrix was prepared from epoxy resin (EP) and ethylenediamine (EDA) and pore-forming reagent (polyethylene glycol, PEG-1000) by in situ step-addition polymerization. The morphology of the resulting polymer monolith was characterized by scanning electron microscopy (SEM). A solid-phase extraction (SPE) cartridge prepared from a simple glass-tube was used for the preconcentration and determination of Pb(II) combined with flame atomic absorption spectroscopy (FAAS). The characteristics of the monoliths for the extraction of Pb(II) in aqueous solution were investigated. The experimental results showed that trace Pb(II) ions could be quantitatively preconcentrated in the pH range of 4.0–9.0 with recoveries of >95%. The maximum static adsorption capacity of the monolith adsorbent was 106.8 $mg\,g^{-1}$. The column was eluted by 1.0 $mol\,L^{-1}$ HNO_3 and recovery of Pb(II) was more than 97%. Moreover, the polymer monolith adsorbent shows superior reusability and stability. The precision and the accuracy of the proposed procedure were satisfactory by analyzing a standard reference material and three natural water samples. It was shown that the EP–EDA monolith was suitable for the preconcentration of environmental Pb(II) as an ion-selective SPE adsorbent.

Keywords: Monolithic column; Step-addition polymerization; Epoxy resin; Preconcentration; Lead; Flame atomic absorption spectroscopy

1. Introduction

Heavy metal ions are increasingly being released into the environment, leading to serious pollution, particularly as a result of industrialization. Lead is the most common environmental pollutant with no biological function, and poses a threat to human health [1–3]. Therefore, the preconcentration and determination of lead from aqueous samples have received increasing importance in environmental evaluation and protection in recent years [4,5]. Though numerous adsorbents have been reported for the preconcentration of lead, such as activated carbon [6], chitosan, zeolites [7], clay, and even industrial wastes [8], additional alternative materials for this purpose are still needed.

An efficient adsorbing material should consist of a stable and insoluble porous matrix [9]. Epoxy resin is ideal because of its inexpensive, stable under acidic and alkali conditions, non-swelling, high thermal resistance [10,11]. Ammonia derivatives including one or two hydrogen atoms are good curing agents for epoxy resin. Hence, epoxy resin (EP) and ethylenediamine (EDA) were selected as basic materials. Meanwhile, the macroporous adsorbent possesses higher adsorption capacity and velocity of mass transfer than micro-porous or non-porous solid-phase adsorbent does. Therefore, in the preparation process of EP–EDA polymer, the polyethylene glycol (PEG-1000) was added as porogen for controlling pore size. After polymerization completing, PEG-1000 was completely removed from polymer by water-cleaning process and the macropore structure formed.

The shapes of porous adsorbents are mainly particulate or fiberized. In recent years, porous monolithic stationary-phase media for high-performance separation of inorganic and organic ions has attracted increasing interests [12]. The monolithic stationary-phase have been widely applied in conventional liquid-chromatography (LC) due to their following advantages, such as: easy and cheaper preparation, high capacity

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and performance, simple and reproducible column filling, extremely high porosity, transport based on convection and better hydrodynamic properties compared to conventional packed columns, easy production in various shapes and dimensions in contrast to membranes, and so on [13,14]. The preparation of monoliths mainly utilized inorganic oxides or polymer matrixes [15,16]. The polymer-based monoliths are usually prepared via the single-step in situ copolymerization of monomers (e.g. methacrylates, acrylamide, styrene and their derivations), cross-linkers, initiators, inert solvents and porogens, so-called vinyl radical polymerization [17]. Two aspects would lead to heterogeneous macroporous structures: high polymerization heat released cannot be dissipated fast enough, especially large-scale monoliths, which results in significant temperature increase inside the polymerization mixture [18]; high polymerization velocity makes the phase separation process between growing polymer chains and porogenic solvent very fast, which produces the coarsening of monolithic structure inherently [19]. Stepwise polymerization produces relatively lower polymerization heat and slower reaction velocity, which would be beneficial to homogeneous porous structure. A new EP–EDA monolith was simply and successfully prepared by step-addition polymerization.

At present, more reported applications of monoliths on other fields are increased continuously and gradually, such as capillary electrophoresis (CE) [20], frontal affinity chromatography (FAC) [21], immobilized metal-chelate chromatography (IMAC), micro-fluid chip devices [22], and preparative chromatography. While the monoliths have been already applied in many chromatographic interaction modes, there are only few reports about application of the monoliths for conventional column chromatography. The target analytes were mainly focused on relative large organic molecules and bio-molecules (e.g. DNA, protein and viruses) [23,24], and inorganic ions were relatively neglected [12]. So, we selected Pb(II) ion as target analyte of preconcentration and determination on prepared monolithic column.

In our knowledge, macroporous EP–EDA monolith has not been employed previously for the preconcentration and determination of Pb(II) from aqueous solution. The synthesis, structure and evaluation of the monolith for the preconcentration of Pb(II) were investigated.

2. Experimental

2.1. Instruments and apparatus

A Perkin-Elmer AA-6800 FLAME atomic absorption spectrometer equipped with Perkin-Elmer single element hollow cathode lamp and an air–acetylene burner was used for the determination of Pb(II). The wavelength selected for the determination of Pb was 283.3 nm. A model pHS-3CT digital pH meter (Shanghai Dazhong Analysis Instrument Factory, China) was used to measure pH values. The flow rate of liquid through columns was controlled by a model BT00-100M peristaltic pump (Baoding Laonger Precision Pump Limited Company). The shape and surface morphology of the monoliths were examined on a scanning electron microscope (S-570, Hitach, Japan). Super constant temperature bath vibrator (Nantong Experimental Instruments Factory, Jiangsu Province, China) was used for controlling temperature.

2.2. Reagents and standards

Stock solutions ($1.0\,\mathrm{mg\,mL^{-1}}$) of the elements were prepared by dissolving appropriate amounts of nitrate salts in 1.0% HNO_3 and further diluted daily prior to use. The pH was adjusted with diluted HNO_3 and $NH_3{\cdot}H_2O$. Epoxy resin, ethylenediamine, PEG-1000 and other reagents were purchased from Shanghai Chemistry Regent Limited Company, PR China (http://www.reagent.com.cn). They were not purified further. The standard reference material (GBW 08619, water) was purchased from National Research Center for GeoAnalysis, PR China (http://nrcga.cags.ac.cn).

Unless otherwise stated, all water is $18\,\mathrm{M\Omega\,cm}$ distilled deionized water (DDI) purified with a Milli-Q system (Millipore, USA) and all reagents used were of analytical grade and all solutions were prepared with DDI water. Standard lab-ware and glassware used were repeatedly cleaned with HNO_3 and rinsed with DDI water.

2.3. Preparation of monolithic column

3.0 g epoxy resin and 1.5 g ethylenediamine were dissolved in 20.0 g melted PEG-1000 under strong agitating for about 20 min. The initial pre-polymerization heat has dissipated. The homogenous transparent mixture presented more viscous sol solution, and then was poured into an i.d. 1.0 cm × 10.0 cm glass-tube which the bottom could be controlled by a stopcock. With polymerizing, the transparent liquid gradually turned into white and opaque as result of phase separation in the process of curing. Sometimes, the solution became totally opaque (phase separation) and the opaque phase lost its ability to flow (gelation) before being transferred into glass-tube. It means that reaction velocity is too quick because of higher temperature or slower stirring. In the case, the experiment would be redone under improved conditions. After completing polymerization in oven at 50 °C for 24 h, the white monolith with glass-tube was cut into 1.0 cm × 1.0 cm pieces. The 1.0 cm i.d. × 1.0 cm length columns were treated with large amount of hot DDI water till to remove all of PEG-1000 and dried in a vacuum oven at room temperature for 48 h. The structures of monomers and polymer are shown in Fig. 1. From the results of density determination and scanning electron microscopy (SEM) observation, there are no differences in different pieces. Hence, the selection of piece as experimental material is random.

A disadvantage of the method was noted: removal of PEG-1000 from the monolith was relatively difficult because of its higher molecular weight and longer polymer chains than low-molecular weight organic solvents. It would be expensive to remove the porogen completely from a large-scale in-tube monolith by cleaning with water.