Preparation of a new polymeric ionic liquid-based sorbent for stir cake sorptive extraction of trace antimony in environmental water samples

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ABSTRACT

In this work, a new polymeric ionic liquid (PIL)-based sorbent was prepared by *in-situ* polymerization of 3-(1-ethyl imidazolium-3-yl) propyl-methacrylamido bromide and ethylene dimethacrylate and was used as medium for stir cake sorptive extraction (SCSE) of trace antimony in environmental water samples. The sorbent EPBED was characterized with infrared spectroscopy, elemental analysis, scanning electron microscopy and mercury intrusion porosimetry. A method for determination of trace antimony in water samples was developed based on the combination of SCSE/EPBED and hydride generation atomic fluorescence spectrometry (HG-AFS). Under the optimal extraction conditions, the linear dynamic range of developed method was found to be 0.20–100.0 µg/L with good coefficients of correlation ($R^2=0.9904$) and LOD value as low as 0.084 µg/L. The method showed good reproducibility of results in terms of intra- and inter-day precisions with corresponding relative standard deviations (RSDs) of less than 9%. Recoveries obtained for the determination of antimony in spiked samples ranged from 80.4% to 107% with RSDs below 10% in all cases.

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1. Introduction

Heavy metals such as antimony are persistent environmental contaminants, and having a high enrichment factor and slow removal rate [1]. Heavy metals are considered as toxic elements for humans and can cause fatal diseases such as cancer. Therefore, development of sensitive determination methods for heavy metal ions at trace level is highly desired. So far, several modern instrumental techniques including electrothermal (ET) graphite furnace atomic absorption spectrometry (GF-AAS) [2], inductively coupled plasma-optical emission spectrometry (ICP-OES) [3], inductively coupled plasma-mass spectrometry (ICP/MS) [4], electroanalytical techniques [5], and X-ray fluorescence spectrometry [6] have been used to detect heavy metals. However, because of the complex matrix in real samples and lower level of the targeted metals, suitable sample preparation is necessary in order to concentrate target analytes and reduce the matrix interferences.

According to the different extraction phases used, sample-preparation procedure for the extraction of metals can be divided into solvent-based and sorbent-based extraction methods [7]. Compared with solvent-based extraction, sorbent-based extraction has received wide acceptance because it can circumvent the disadvantages of consuming large amounts of organic solvents. At the same time, sorbent-based extraction is cost-effective because the sorbents can be reused. In sorbent-based extraction method, the core is the extraction medium (sorbent). Different sorbents possess different extraction performance for metals. High extraction capacity and selectivity, good life-span and regenerability, and low-cost have been the desirable objectives of selection of appropriate sorbents. So far, only a few of sorbents has been reported and some of them are commercially available. Impregnated multiwalled carbon nanotubes [8], surface-modified silica [9,10] and styrene-divinylbenzene polymers [11], chelating celluloses [12] and ion-imprinted polymers [13] have been developed and widely used to extract all kinds of metals from environmental, biological and food samples. Although some new materials are emerging, developing sorbents with promising structural and chemical reactive properties for the effective extraction of metals is highly desired.

Ionic liquids (ILs) have attracted significant attention over the last decade because of their unique properties, such as negligible vapor pressure, excellent thermal and chemical stability, designable structures, high ionic conductivity [14]. Polymeric ionic liquids (PILs) belong to a subclass of polyelectrolytes, which bear an ionic liquid species in each monomer repeating unit. PILs combine the unique properties of ILs and the macromolecular architecture

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together with intrinsic polymer characteristics such as mechanical stability, improved processability, durability and spatial controllability [15]. Based on these advantages, PILs have stirred great interests in sample pretreatment. So far, several kinds of sorbents based on PILs have been synthesized, but most of them were used to extract organic compounds [16–19]. Recently, PIL gels were prepared and used to enrich heavy metals [20,21]. The developed PIL gels showed selective adsorption capacity to targeted metals. However, because of insufficient rigidity of the three-dimensional networks, the PIL gel would shrink in air and swell in aqueous solution resulting in poor life-span. Moreover, a long time is required for them to reach adsorption equilibrium. Zhai et al. [20] prepared a PIL gel based on ionic liquid monomer 1-allyl-3-vinylimidazolium chloride which could adsorb Cr (VI) effectively but the adsorption equilibrium time was as long as 12 h. Previous workers [20,21] have noted that PILs could be effective as metal extraction agents provided these observed drawbacks were circumvented.

Antimony is an element of environmental concern due to its toxicity and biological effects. Antimony and its compounds are considered to be priority pollutants by the U.S. Environmental Protection Agency (EPA) [22], declaring a maximum allowable contaminant level of 6.0 μg/L Sb for drinking water. A maximum admissible concentration of 5.0 μg/L Sb in drinking water was defined by European Union (EU) [23] and Chinese government [24]. Therefore, there is a need to develop a simple and sensitive method to monitor trace antimony in water samples.

In this work, a new PIL-based sorbent, EPBED, has been prepared by *in-situ* polymerization process using a monolithic ionic liquid monomer, EPB and a cross-linker, ED. The new sorbent has been used for extraction of antimony by SCSE method which was earlier developed by our research group [25]. A new procedure for the determination of antimony has been developed in a combined process of SCSE/EPBED followed by liquid desorption (LD) of Sb and its subsequent determination using hydride generation atomic fluorescence spectrometry (HG-AFS). The method was tested for the determination of Sb in environmental water samples.

2. Experimental

2.1. Chemicals

High purity reagents were used in all experiments. All plastic and glass ware were cleaned with hot concentrated nitric acid and stored soaked in 10% (wt/wt) nitric acid, they were rinsed several times with water immediately before use. Ultrapure water (18 MΩ cm) obtained from a Milli-Q water system (Milli-pore, Bedford, MA, USA) was used throughout.

EPB (97%) was purchased from Cheng Jie Chemical Co. LTD (Shanghai, China) and ED (97%) was supplied by Alfa Aesar Ltd. (Tianjin, China). Azobisisobutyronitrile (AIBN) (97%, re-crystallized before use), 1-propanol (97%), 1,4-butanediol (98%), potassium borohydride (KBH$_4$) ($\geq$95.0%) and ascorbic acid ($\geq$99.7%) were purchased from Shanghai Chemical Co. (China). Methanol was purchased from Tedia Company (Fairfield, USA). Hydrochloric acid and nitric acid (Jincheng Chemical Co., Jiangsu, China) was Metal-oxide semiconductor (MOS) grade (with lower blank antimony levels than analytical grade ones).

Standard stock solution of Sb (III) (1000 mg/L) was purchased from the National Center for Reference Material (Beijing, China). Working solutions were prepared by appropriate dilution of the stock solution with doubly distilled water daily. Thiourea (5%, w/v)-ascorbic acid solution (3%, w/v) was dissolved in high-purity de-ionized water. KBH$_4$ (2%, m/v) was dissolved in 0.5% KOH (m/v). Ar (99.99%) was used as a carrier gas.

2.2. Instruments

An AFS8220 non-dispersive atomic fluorescence spectrometer (Beijing Titan Instruments Co, Ltd, Beijing, China) equipped with antimony hollow cathode lamp was used for the determination of antimony. The instrumental conditions for the analysis are listed in Supporting materials and the detailed HG-AFS principle and process for the analysis of antimony can be found in Qian's work [26]. Polymerization reaction temperature was maintained constant in ET constant temperature oven (YueJin, Shanghai, China).

The morphologies of sorbent were examined by a Model XL30 scanning electron microscopy (SEM) instrument (Philips, Eindhoven, The Netherlands). The pore size distribution of the sorbent was measured on mercury intrusion porosimeter (MIP) Model PoreMaster-60 (Quantachrome Instruments, Florida, USA). Elemental analysis (EA) was carried out on PerkinElmer (Shelton, CT, USA) Model PE 2400. FT-IR was performed on an Avatar-360 FT-IR instrument (Thermo Nicolet, Madison, WI, USA).

2.3. Preparation of SCSE/EPBED

The whole preparation procedure of SCSE/EPBED is quite simple. Three steps were involved. In the first step, the PIL-based monolithic cake was synthesized. In the polymerization reaction, AIBN (2% (w/w) of the total polymerization solution) and the mixture of 1-propanol and 1,4-butanediol were used as polymerization initiator and porogen solvent, respectively. Typically, 140 mg EPB, 110 mg ED, 190 mg 1-propanol, 50 mg 1,4-butanediol and 10 mg AIBN were mixed ultrasonically into a homogenous solution. After that, the reactant solution was purged with nitrogen for 5.0 min to remove the air in the polymerization solution. The reactant mixture was poured into a syringe cartridge (1.2 cm i. d.), one side of which was blocked by the plug of syringe. Subsequently, the cartridge was sealed with septa and put in oven and kept at 70 °C for 12 h. After polymerization, the monolithic cake was pushed out slowly by a handspike of syringe. The cake was Soxhlet-extracted with methanol (50 mL) for 24 h to remove the residue monomers, porogen, uncross-linked polymers and initiator. Finally, the adsorbent was dried in air for 0.5 h to obtain the final monolithic cake (EPBED) (1.2 cm in diameter and 0.3 cm in thickness). The polymerization sketch is depicted in Fig. 1. In the second step, extraction holder of SCSE was constructed according to our previous study [25]. After the construction of extraction holder, the PIL-based cake was inserted into the holder gently to get the final SCSE/EPBED. Before the SCSE/EPBED was used to extract target analytes, it was conditioned in two consecutive steps of 20–30 min by immersion in HCl (15%, v/v) and de-ionized water, respectively.
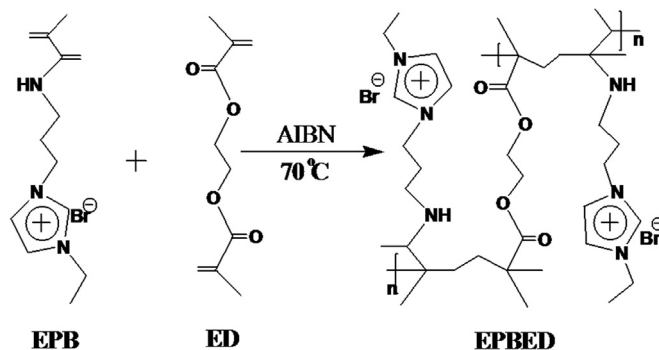

Fig. 1. The reaction sketch of poly (EPB-*co*-ED).