



Ionic liquid coated carbon nanospheres as a new adsorbent for fast solid phase extraction of trace copper and lead from sea water, wastewater, street dust and spice samples

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ARTICLE INFO

Article history:

Received 31 March 2016

Received in revised form

4 June 2016

Accepted 10 June 2016

Available online 16 June 2016

Keywords:

Ionic liquid

Carbon nanospheres

Solid phase extraction

Fast kinetic

ABSTRACT

In this study a new adsorbent, ionic liquid (1,8-naphthalene monoimide bearing imidazolium salt) coated carbon nanospheres, was synthesized for the first time and it was used for the solid phase extraction of copper and lead from various samples prior to determination by flame atomic absorption spectrometry. The ionic liquid, carbon nanospheres and ionic liquid coated carbon nanospheres were characterized by using Fourier transform infrared spectroscopy, X-ray diffraction, scanning electron microscopy, ¹H NMR and ¹³C NMR, Brunauer, Emmett and Teller surface area and zeta potential measurements. Various parameters for method optimization such as pH, adsorption and elution contact times, eluent volume, type and concentration, centrifuge time, sample volume, adsorption capacity and possible interfering ion effects were tested. The optimum pH was 6. The preconcentration factor, detection limits, adsorption capacity and precision (as RSD%) of the method were found to be 300-fold, 0.30 µg L⁻¹, 60 mg g⁻¹ and 1.1% for copper and 300-fold, 1.76 µg L⁻¹; 50.3 mg g⁻¹ and 2.2%, for lead, respectively. The effect of contact time results showed that copper and lead were adsorbed and desorbed from the adsorbent without vortexing. The equilibrium between analyte and adsorbent is reached very quickly. The method was rather selective for matrix ions in high concentrations. The accuracy of the developed method was confirmed by analyzing certified reference materials (LGC6016 Estuarine Water, Reference Material 8704 Buffalo River Sediment, and BCR-482 Lichen) and by spiking sea water, wastewater, street dust and spice samples.

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1. Introduction

Ionic liquids (ILs) are salts formed by organic cations (e.g. imidazolium, pyrrolidinium, pyridinium, tetraalkyl ammonium or tetraalkyl phosphonium) and inorganic or organic anions (e.g. tetrafluoroborate, hexafluorophosphate, bromide, trifluoromethylsulfonate). Generally, ILs melt at or below 100 °C and low vapor pressure at room temperature. One important feature of ILs is that varying the cation or anion may significantly affect their physical and chemical properties. The relatively large size of one or both ions in ILs and low symmetry account for the lower melting points of these materials [1–3]. ILs have many unique physicochemical properties, such as low vapor pressure, good thermal stability, high conductivity, wide range of viscosities

and miscibility with water and organic solvents [2–4]. The extremely low volatility of most ILs renders them both non-flammable and useful in green chemistry so they could be candidates to replace organic toxic solvents [5,6]. The unique properties of ILs have given rise to a great number of applications in analytical chemistry. The main applications are associated with extraction and separation techniques, such as dispersive liquid liquid microextraction (DLLME), solid phase microextraction, gas chromatography, liquid chromatography and capillary electrophoresis [7–10].

Sample pre-treatment is one of the most important parts of the whole analysis. In spite of the evolution of analytical instrumentation, complex sample analysis is still a problem without a sample pretreatment. The direct determination of trace metals in most environmental (such as sea water, wastewater, and sediment) and food samples is very difficult by atomic absorption spectrometry because of low concentrations of these metals and/or interfering effects of matrix components in these samples.

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Therefore this stage aims both analyte preconcentration and minimization of sample complexity after eliminating most matrix interferences before introduction into the analytical instrument [11,12]. ILs have been used in DLLME as extraction solvents for the preconcentration and separation of a number of organic pollutants and metal ions [13–17].

Solid phase extraction (SPE) is the most widely used separation/preconcentration technique mainly due to the variety of different materials employed as sorbents [2,18]. The development of new materials as adsorbent in sample preparation has been widely exploited to obtain more selective materials with higher adsorption capacity [2,11]. The solid phase extractants are distinguished by fast kinetic properties, as well as by the simplicity of their preparation [18]. The studies related to nanosized SPE sorbents indicate that they have very high extraction capacities with rapid extraction dynamics performance [19–22]. Among them, nanoscale carbon-based materials, such as fullerenes, nanodiamond, carbon nanofiber, carbon nanotubes, and graphene/graphene oxide have attracted great interest as powerful SPE materials because of their attractive physical and chemical properties including large surface area, favorable chemical and thermal stability, and ease of surface functionalization or modification [23–26]. As an important member of the carbon family, carbon nanospheres (CNSs) have attracted considerable attention due to their unique structure and potential applications, such as reinforcing agents, supports for catalysts, lubricants, and electrode materials [27].

In recent years, IL modified materials such as silica [28–31], polymeric support [32], magnetic nanoparticles [33,34] or carbon nanotubes [35] have been successfully employed for the extraction of heavy metals and/or organic molecules as a solid phase in SPE. As a consequence of this, ILs lose their liquid nature but they maintain their exceptional physical and chemical properties. In addition, the presence of ILs in the final eluate is avoided [31]. The use as adsorbent of IL modified materials significantly affects the enrichment factor, extraction efficiency and selectivity of the described preconcentration method because the prepared material combines the advantages of IL and solid support [11].

In this work, nano-sized CSs, a new kind of IL, 1,8-naphthalene monoimide bearing imidazolium salt ([NMIIM]Br) and IL coated carbon nanospheres [NMIIM]Br-CNSs were synthesized. The [NMIIM]Br was used for the first time as a chelating reagent for the preconcentration of Cu(II) and Pb(II) ions. The characterization of synthesized nano-sized CSs was made by using X-ray diffraction (XRD), scanning electron microscopy (SEM), and Brunauer, Emmett and Teller (BET) surface area. The synthesized IL was characterized by ^1H -nuclear magnetic resonance (^1H NMR) and ^{13}C -nuclear magnetic resonance (^{13}C NMR). Then [NMIIM]Br-CNSs were prepared and characterized by Fourier transform infrared spectroscopy (FT-IR). It was employed as an adsorbent for the preconcentration/separation of Cu(II) and Pb(II) ions from sea water, wastewater, street dust and spice samples. The effect of certain variables on the recovery of each analyte, including sample solution pH, adsorption and elution contact times, the volume, type and concentration of eluent, centrifuge time, sample volume, adsorption capacity and possible interfering ion effects, was investigated. To the best of our knowledge, this work is the first report about the use of [NMIIM]Br-CNSs for the preconcentration of Cu(II) and Pb(II) ions. Moreover, as far as we know, there has been no report yet about adsorption and elution without shaking/vortexing for Cu(II) and Pb(II).

2. Experimental

2.1. Instrument

The X-ray diffraction (XRD) pattern of the CNSs was obtained using a Bruker AXS D8 Advance X-ray diffractometer (Karlsruhe, Germany) with monochromatized Cu-K α radiation ($\lambda=0.15406$ nm) in the range of $2\theta=10$ – 90° . In order to analyze the functional groups of CNSs, IL and IL-modified CNSs, Fourier transform infrared spectra (FT-IR) were recorded on a Perkin Elmer 400 FT-IR Spectrometer (Waltham, MA, USA) in the range of 4000 – 400 cm^{-1} with KBr pellets. The morphology of the synthesized CNSs and [NMIIM]Br-CNSs was investigated by using a Zeiss EVO LS 10 Lab6 model scanning electron microscopy (SEM, Germany) operated at 20 kV. The specific surface area of CNSs was calculated by the Brunauer–Emmett–Teller (BET). The BET surface area of CNSs was determined from low-temperature nitrogen adsorption isotherms at 77 K using a Micromeritics Gemini VII analyzer (Norcross, USA) in which CNSs were previously degassed at 300°C for 48 h. The zeta potentials of CNSs and [NMIIM]Br-CNSs were measured with Malvern Instruments Zetasizer Nano system (England). The ^1H NMR and ^{13}C NMR spectra of synthesized IL were recorded with a Bruker Avance III 400 MHz instrument (Karlsruhe, Germany).

A Perkin Elmer AAnalyst 800 model flame atomic absorption spectrometer (FAAS) equipped with a deuterium-lamp background corrector (Waltham, MA, USA) was used to determine copper and lead. The instrumental parameters were as follows: wavelength, 324.8 and 283.3 nm; lamp current, 30 and 10 mA; and band width, 0.7 and 0.7 nm; for copper and lead, respectively. The acetylene-air flow rates were adjusted to $2.0/17.0$ L min^{-1} . The pH values of aqueous solutions were measured with a Sartorius PT-10 pH meter (Göttingen, Germany). A vortex stirrer (Wiggen Hauser, Malaysia) and a centrifuge (Annita ALC PK120, Buckinghamshire, England) were used in the extraction procedures.

2.2. Reagents and solutions

All reagents used in the experiments were of analytical reagent grade. The 1,8-naphthalic anhydride, 1-(3-Aminopropyl) imidazole and 1-bromooctane were purchased from Aldrich and used as received. Ultra high purity water (UHP, 18.2 $\text{M}\Omega$ cm) obtained from a Milli-Q system (Millipore Corp., Bedford, MA) was used for the preparation of solutions in experiments. The stock standard solutions of 1000 mg L^{-1} of Cu(II) and 1000 mg L^{-1} Pb(II) were prepared from their nitrate salts (Merck, Darmstadt, Germany) in UHP water and used throughout the study. Working standard solutions of Cu(II) and Pb(II) were freshly prepared by appropriate diluting of stock standard solutions. The phosphate buffer solution ($\text{H}_3\text{PO}_4/\text{NaH}_2\text{PO}_4$) for pH 2 and 3, acetate buffer solution ($\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$) for pH 4–6, ammonium acetate solution ($\text{CH}_3\text{COONH}_4$) for pH 7 and ammonia buffer solution ($\text{NH}_3/\text{NH}_4\text{Cl}$) for pH 8 and 9 were used to adjust the pH values of the solutions. All the glassware were cleaned by soaking in 10% nitric acid solution for at least 24 h before use and later rinsed thoroughly with UHP water.

2.3. Synthesis of IL

N-(3-propylimidazole)-1,8-naphthalene monoimide (1) starting material was synthesized according to the previously reported method [36]. Naphthalene monoimide (1) was synthesized through a simple method which is used for the preparation of a wide range of imide derivatives between a naphthalene anhydride and corresponding amino derivative. This reaction is easily carried out at high temperatures by water elimination. A 430 mg aliquot

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