



ELSEVIER

Contents lists available at ScienceDirect

Talanta

journal homepage: [www.elsevier.com/locate/talanta](http://www.elsevier.com/locate/talanta)

# 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



Şerife Tokaloğlu<sup>a,\*</sup>, Emre Yavuz<sup>a</sup>, Halil Şahan<sup>a,b</sup>, Süleyman Gökhan Çolak<sup>c</sup>, Kasım Ocakoğlu<sup>c,d</sup>, Mehmet Kaçer<sup>a</sup>, Şaban Patat<sup>a</sup>

<sup>a</sup> Erciyes University, Faculty of Science, Chemistry Department, TR-38039 Kayseri, Turkey

<sup>b</sup> Erciyes University, Nanotechnology Research and Application Center, TR-38039 Kayseri, Turkey

<sup>c</sup> Advanced Technology Research & Application Center, Mersin University, Ciftlikkoy Campus, TR-33343 Yenisehir, Mersin, Turkey

<sup>d</sup> Department of Energy Systems Engineering, Mersin University, Tarsus Faculty of Technology, TR-33480 Mersin, Turkey

## 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, <sup>1</sup>H NMR and <sup>13</sup>C 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<sup>-1</sup>, 60 mg g<sup>-1</sup> and 1.1% for copper and 300-fold, 1.76 µg L<sup>-1</sup>; 50.3 mg g<sup>-1</sup> 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.

© 2016 Elsevier B.V. All rights reserved.

## 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.

\* Corresponding author.

E-mail address: [serifet@erciyes.edu.tr](mailto:serifet@erciyes.edu.tr) (Ş. Tokaloğlu).

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  $^1\text{H}$ -nuclear magnetic resonance ( $^1\text{H}$  NMR) and  $^{13}\text{C}$ -nuclear magnetic resonance ( $^{13}\text{C}$  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 $\alpha$  radiation ( $\lambda=0.15406$  nm) in the range of  $2\theta=10$ – $90^\circ$ . 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  $4000$ – $400$   $\text{cm}^{-1}$  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  $300^\circ\text{C}$  for 48 h. The zeta potentials of CNSs and [NMIIM]Br-CNSs were measured with Malvern Instruments Zetasizer Nano system (England). The  $^1\text{H}$  NMR and  $^{13}\text{C}$  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  $2.0/17.0$   $\text{L min}^{-1}$ . 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  $1000$   $\text{mg L}^{-1}$  of Cu(II) and  $1000$   $\text{mg L}^{-1}$  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

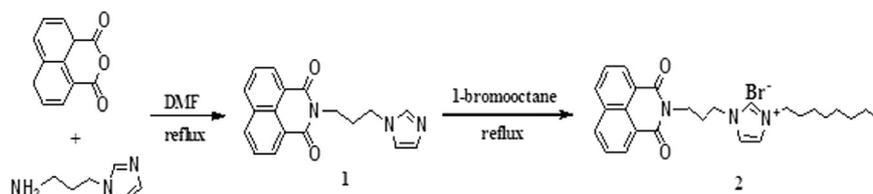


Fig. 1. Synthetic route for 1,8-naphthalene monoimide bearing imidazolium salt.

of N-(3-propylimidazole)-1,8-naphthalene monoimide (1.4 mmol) was dissolved in 10 mL  $\text{CHCl}_3$  under inert atmosphere. Then 3.3 g 1-bromooctane (1.7 mmol) was added dropwise to the solution, and the reaction mixture was heated under reflux for 24 h. The mixture was allowed to cool down to room temperature, and the solid was filtered. The solid was recrystallized from  $\text{CH}_2\text{Cl}_2$ /diethylether mixture. The synthetic route for 1,8-naphthalene monoimide bearing imidazolium salt (2) is shown in Fig. 1.

#### 2.4. Synthesis of CNSs

Five grams of D-glucose was dissolved in the mixed solution containing 10 mL ethanol and 30 mL UHP water and reacted in a stainless steel autoclave with 100 mL capacity for 14 h at 180 °C, and then allowed to cool to room temperature. The dark precipitate was collected and washed with absolute ethanol, UHP water and again with ethanol, then dried in vacuum at 80 °C for 6 h [37].

#### 2.5. Preparation of IL coated CNSs ([NMIIM]Br-CNSs)

[NMIIM]Br-CNSs were prepared as follows. A 80 mg of IL was dissolved in 100 mL acetone. A 3 mL of IL was added to a beaker containing 100 mg CNSs. The mixture was stirred with the use of a vortex for 3 min to facilitate the adsorption of IL on CNSs. After centrifuging at 4000 rpm for 1 min, the supernatant was discarded carefully. [NMIIM]Br-CNSs were used as an adsorbent for subsequent analyses.

#### 2.6. Solid phase extraction of copper and lead ions

SPE experiments were carried out by using the [NMIIM]Br-CNSs as adsorbent. Twenty milliliters of UHP water containing 0.3 mg  $\text{L}^{-1}$  Cu(II), 0.6 mg  $\text{L}^{-1}$  Pb(II) and 100 mg [NMIIM]Br-CNSs adsorbent were added to a 50 mL centrifuge tube. The pH of the solution was adjusted to 6 with acetate buffer. The [NMIIM]Br-CNSs adsorbent was separated from aqueous medium by centrifugation at 4000 rpm for 1 min. After centrifugation, the supernatant liquid was removed using a micropipette. A 3 mL of 1 mol  $\text{L}^{-1}$  HCl was added to the tube in order to elute analytes retained on the adsorbent. The centrifuge process was repeated in the same way and finally the copper and lead in the eluate were determined by FAAS. After elution, the adsorbent was washed with UHP water to allow the reusability of the solid. UHP water was used as the blank solution and subjected to SPE as described above.

#### 2.7. Pre-treatment and analysis of real samples

##### 2.7.1. Water samples

Two water samples, sea water and wastewater were collected from the Bosphorus (Istanbul, Turkey) and Organized Industrial Region of Kayseri (Turkey), respectively. First, water samples were filtered through a 0.45  $\mu\text{m}$  pore size membrane filter to remove suspended particles and they were acidified to a pH of 2 for storage. Then 150 mL of waste water, 250 mL of sea water and 15 mL

of LGC6016 Estuarine water certified reference material were used for analysis. The pH of samples was adjusted to 6 and the method described above was applied.

##### 2.7.2. Street dust sample

Street dust sample was collected from the Organized Industrial Region of Kayseri, Turkey. Then 0.10 g of dried street dust sample was placed into a beaker and 10 mL of aqua regia was added to it. The mixture was then evaporated to dryness on a hot plate. The digestion process was repeated by using ten milliliters of aqua regia. After the digestion process, the remaining residue was filtered through a blue band filter paper and the volume of the filtrate was completed to about 20 mL with UHP water. The pH of the obtained solution was adjusted to 6 with acetate buffer and the samples were subjected to the preconcentration procedure. For the accuracy of the method, 0.10 g Reference Material (RM) 8704 Buffalo River Sediment was analysed by using the same digestion method as street dust sample.

##### 2.7.3. Spice sample

A red pepper flakes sample was purchased from a local supermarket in Kayseri (Turkey). 1.00 g of dried sample was placed into a beaker. Then 10 mL concentrated nitric acid (65%, w/w) was added and it was evaporated on a hot plate. By cooling, a 3 mL of concentrated hydrogen peroxide (30%, w/w) was added to the beaker. After digestion treatment, the obtained clear solution was diluted to 20 mL. Finally, the described method was applied to determine copper and lead in the solution. BCR-482 Lichen certified reference material was analyzed. Two hundred milligrams of BCR-482 Lichen sample was put into a beaker. The sample was digested with a mixture of concentrated  $\text{HNO}_3$ :  $\text{HClO}_4$  (v/v 9:1) on a hot plate at about 130 °C for 3 h [21]. The obtained clear solution was diluted to 20 mL with UHP water and copper and lead were determined by FAAS after applying the preconcentration method.

### 3. Results and discussion

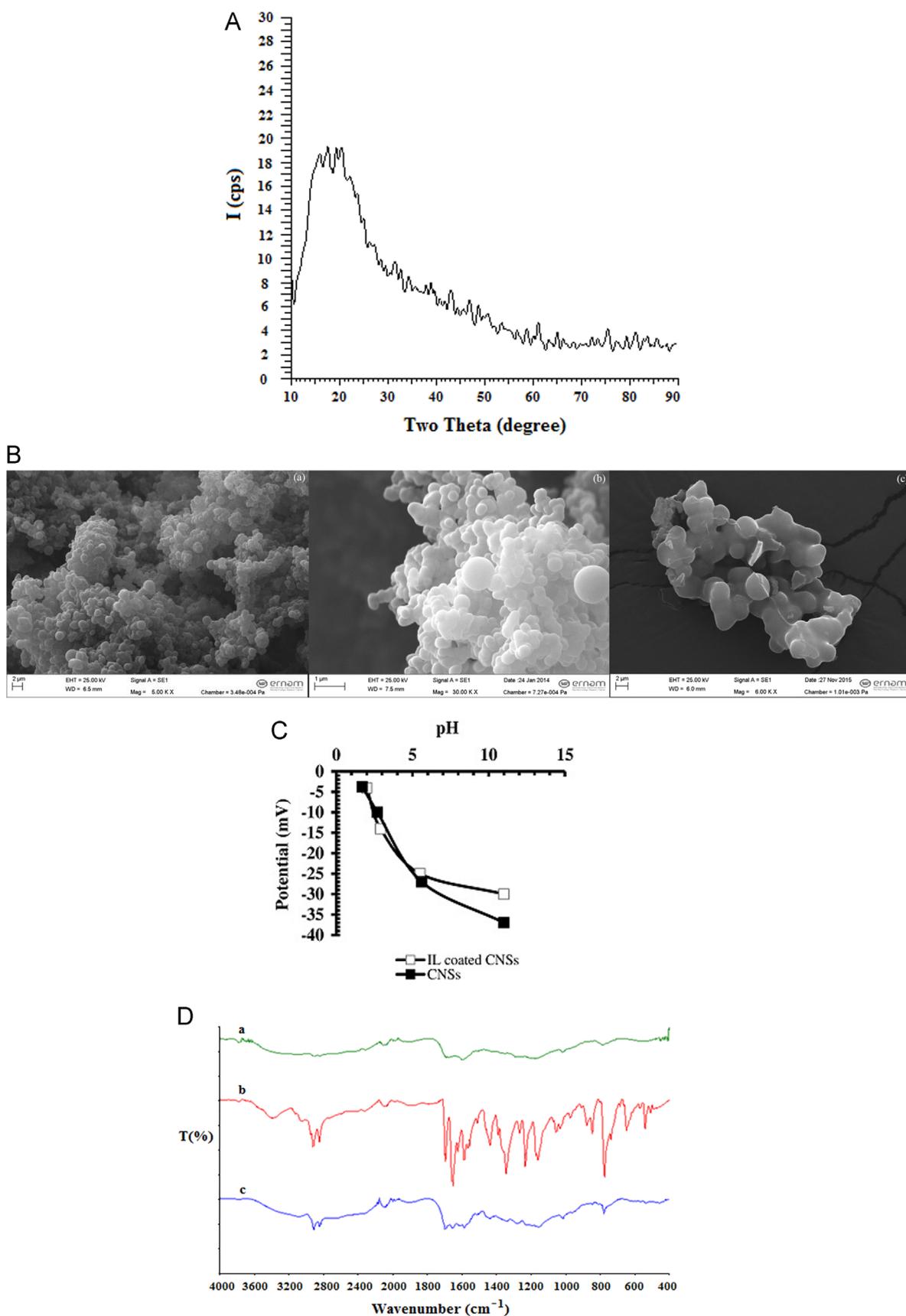
#### 3.1. Characterization of synthesized materials

##### 3.1.1. Carbon nanospheres (CNSs)

The crystal structure of the as-obtained carbon nanosphere was identified by the XRD technique. The broad diffraction peak demonstrates the amorphous nature of carbon (Fig. 2(A)). A broad characteristic peak of amorphous material is observed at around 22° (2 $\theta$ ). Fig. 2(B) (a and b) shows the SEM images of CNSs. It shows that carbon particles are composed of sphere based chains. The particle size of CNSs is approximately 100–500 nm. Fig. 2(B) (c) shows the SEM image of [NMIIM]Br-CNSs. From the image, it can be seen that CNSs are coated with IL.

The specific surface area of CNSs was calculated by using the BET. It was found to be 12.1  $\text{m}^2/\text{g}$ .

The zeta potential measurements of CNSs and [NMIIM]Br-CNSs versus pH are given in Fig. 2(C). The results indicate that surface charges on CNSs and [NMIIM]Br-CNSs are negative in the range of pH 2–11.



**Fig. 2.** Characterization: (A) X-ray diffraction pattern of CNSs, (B) SEM images of CNSs, (a) low and (b) high magnification (c) SEM image of [NMIIM]Br-CNSs, (C) Zeta potential curves versus pH for CNSs and [NMIIM]Br-CNSs and (D) FT-IR spectra of (a) CNSs, (b) IL and (c) [NMIIM]Br-CNSs.

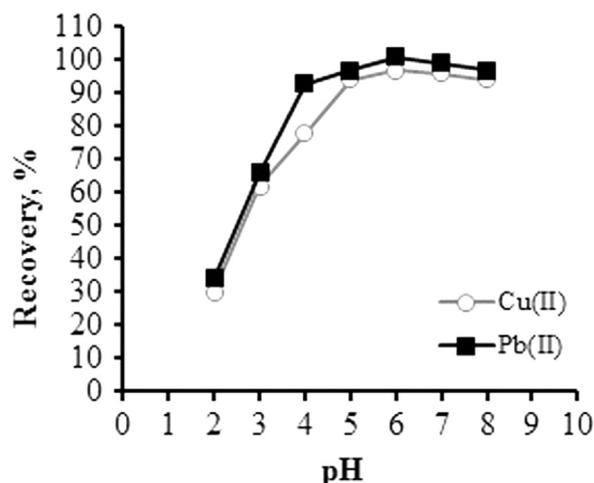


Fig. 3. Effect of pH on recovery of Cu(II) and Pb(II).

### 3.1.2. Ionic liquid

$^1\text{H}$  NMR ( $\delta_{\text{H}}$ , ppm, 400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR ( $\delta_{\text{C}}$ , ppm, 400 MHz,  $\text{CDCl}_3$ ) data for N-(3-propylimidazole)-1,8-naphthalene monoimide (1) and 1,8-naphthalene monoimide bearing imidazolium salt (2) are given in [Supplementary information](#).

### 3.1.3. IL coated CNSs ([NMIIM]Br-CNSs)

Fig. 2(D) shows the FT-IR spectra of CNSs, IL and [NMIIM]Br-CNSs. It is seen that the FT-IR spectrum of [NMIIM]Br-CNSs resembles the superimposed FT-IR spectrum of CNSs and IL, indicating that IL is coated on the surface of CNSs.

### 3.2. Effect of solution pH

pH is one of the main factors influencing the adsorption behaviour of metal ions because the surface charge of the adsorbent is pH-dependent and also the metal ions exist in different species depending on the pH [4,29]. The effect of pH on adsorption of Cu(II) and Pb(II) on [NMIIM]Br-CNSs was examined by varying the pH values from 2 to 8. The results are shown in Fig. 3. The [NMIIM]Br-CNSs adsorbent exhibited low adsorption between pH 2 and 4 for Cu(II) ( $R\% \leq 78$ ) and at pH 2 and 3 for Pb(II) ( $R\% \leq 66$ ). The low metal ion adsorption may be explained by adsorption of more hydrogen ions than metal ions due to the competition for adsorption sites between hydrogen ions and metal ions [22,38]. With the increase of pH, the recoveries for Cu(II) and Pb(II) were found to be in the range of 93–101%. Therefore all subsequent studies were carried out at pH 6. In experiments without using ionic liquid at pH 6, the recoveries for Cu(II) and Pb(II) were found to be 46% and 41%, respectively. As can be seen from the zeta potential results, the surface charge of the adsorbent at pH 6 is negative and it can easily adsorb Cu(II) and Pb(II) due to electrostatic interaction.

### 3.3. Effect of contact time for adsorption and elution

The contact times are key parameters for the fast adsorption and elution of the metal ions on adsorbent. For this, the pH of model solutions of 20 mL containing  $0.3 \text{ mg L}^{-1}$  Cu(II) and  $0.6 \text{ mg L}^{-1}$  Pb(II) and 100 mg [NMIIM]Br-CNSs adsorbent were adjusted to pH 6 and the adsorption and elution contact times of 0 s, 10 s, 30 s, 45 s, and 60 s were studied by using a vortex mixer. As can be seen from Fig. 4(a) and (b), the recoveries of Cu(II) and Pb(II) for both adsorption and elution were found to be quantitative ( $R\% = 95\text{--}102$ ) for all of the adsorption and elution contact times. The interaction of [NMIIM]Br-CNSs adsorbent with Cu(II) and Pb(II) occurs very fast. This means that an extra mechanic

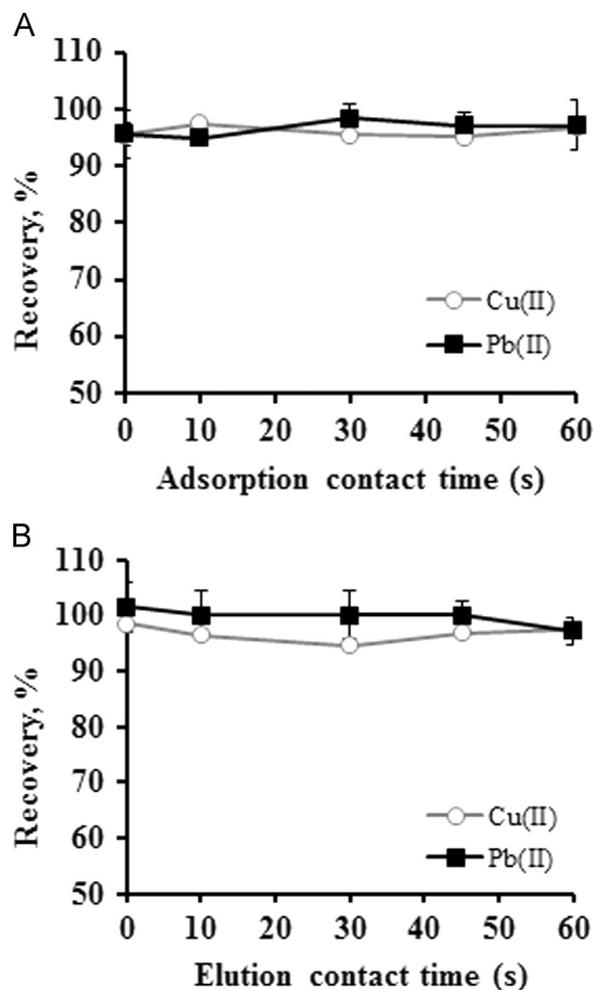


Fig. 4. Effect of adsorption (A) and elution (B) contact time on recovery of Cu(II) and Pb(II).

assist such as vortexing or ultrasonic shaking is not required. Therefore, a contact time was not used for the adsorption and elution times in further experiments. Since the CNSs has high surface area and surface activity it shows high adsorption speed and capacity [20–22,39]. As far as we know, there has been no report yet about adsorption and elution without shaking/vortexing for Cu(II) and Pb(II).

### 3.4. Effect of centrifugation time

The effect of the centrifugation times after adsorption and elution for the separation of solid and liquid phases was investigated for 1, 2, 3, 4, and 6 min at 4000 rpm. The results in Fig. S1(a) and (b) show that the recovery values for target ions were found to be between 94% and 102% for 1–6 min. Therefore 1 min was chosen as both adsorption and elution centrifugation times.

### 3.5. Effect of eluent type, concentration and volume

Eluent type, concentration and volume are important for the reusability of the adsorbent and to achieve a high preconcentration factor. Therefore HCl and  $\text{HNO}_3$  at various concentrations were used for the desorption of Cu(II) and Pb(II) from [NMIIM]Br-CNSs adsorbent. The concentration of 3 mL of HCl was changed in the range of  $0.5\text{--}2.0 \text{ mol L}^{-1}$  and also 3 mL of  $2 \text{ mol L}^{-1}$   $\text{HNO}_3$  was studied as eluent. The experimental results are given in Table S1. The recovery values for Pb(II) were quantitative ( $\geq 95\%$ ) for

0.5–2 mol L<sup>-1</sup> HCl concentrations while Cu(II) was recovered in the range of 90–98% for these concentrations. Three milliliters of 1 mol L<sup>-1</sup> HCl solution is sufficient for the quantitative recovery of target ions. Thus, 1 mol L<sup>-1</sup> HCl was used as eluent in subsequent experiments. When 2 mol L<sup>-1</sup> HNO<sub>3</sub> was used as eluent, the recovery values were found to be 88% for Cu(II) and 90% for Pb(II). The effect of the volume of 1 mol L<sup>-1</sup> HCl on the elution efficiency of the target analytes was investigated for 3, 4, 5, 6, 8 and 10 mL eluent volumes. The Cu(II) and Pb(II) could be eluted quantitatively from the [NMIIM]Br-CNSs adsorbent for all the volumes of 1 mol L<sup>-1</sup> HCl. When 2 mL of 1 mol L<sup>-1</sup> HCl was used, the supernatant liquid could not be separated from the adsorbent. Therefore 3 mL eluent volume was used in all subsequent experiments.

### 3.6. Effect of sample volume

Sample volume significantly affects the preconcentration factor of the method [24,38]. Therefore the volumes of model solutions containing 6 µg Cu(II), 12 µg Pb(II) and 100 mg [NMIIM]Br-CNSs adsorbent were changed from 20 mL to 1000 mL and the method described above was applied. As shown in Fig. S2, the recoveries for Cu(II) and Pb(II) were found between 90% and 100% in the volume ranges of 20–900 mL. When the sample volume was 1000 mL, the recoveries were 85% for Cu(II) and 86% for Pb(II). This means that the preconcentration factor of the method is 300 when an optimum sample volume of 900 mL and a eluent volume of 3 mL are used.

### 3.7. Reusability of the adsorbent

Reusability of the adsorbent is one of the important factors for evaluating the performance of the adsorbent. The developed SPE method was applied by using 100 mg of [NMIIM]Br-CNSs. Elution was made with 3 mL of 1 mol L<sup>-1</sup> HCl. Ten milliliters of UHP water was used for the regeneration of [NMIIM]Br-CNSs. The experimental results indicated that the adsorbent could be re-cycled eight times without any performance loss in adsorption and elution. The coating process with IL of the CNSs was repeated after being re-cycled eight times. The average recoveries and the relative standard deviation (RSD%) of Cu(II) and Pb(II) after being re-cycled eight times were found to be 95.4%, 97.6% and 0.54% and 0.94%, respectively.

### 3.8. Effect of interferences

The effect of interfering ions in real samples is one of the main problems due to the adsorption and elution together with analyte ions of the sample matrix components. The effect of possible interfering ions on the preconcentration and determination of target Cu(II) and Pb(II) ions was investigated in detail in view of the selectivity of the [NMIIM]Br-CNSs adsorbent. The developed SPE method was applied to 20 mL model solutions containing 0.3 mg L<sup>-1</sup> Cu(II), 0.6 mg L<sup>-1</sup> Pb and each interfering ion at different concentrations. The results (Table 1) revealed that the both Cu(II) and Pb(II) can adsorb on the [NMIIM]Br-CNSs with recovery  $\geq 91\%$  when interfering ion concentrations in the solution are 75,000 mg L<sup>-1</sup> of Na(I) as nitrate salt, 7500 mg L<sup>-1</sup> of K(I) as chloride salt, 75,000 mg L<sup>-1</sup> of Ca(II) as nitrate salt, 35,000 mg L<sup>-1</sup> Mg(II) as nitrate salt, 100 mg L<sup>-1</sup> of Al(III), Cd(II), Co(II), Cr(III), Fe(III), Mn(II), Ni(II), and Zn(II) as nitrate salts, 7500 mg L<sup>-1</sup> of Cl<sup>-</sup>, 500 mg L<sup>-1</sup> of SO<sub>4</sub><sup>2-</sup> and 100 mg L<sup>-1</sup> of HPO<sub>4</sub><sup>2-</sup>. The effect of target ions on each other was also studied. No negative effect was observed on Pb(II) of 100 mg L<sup>-1</sup> Cu(II) and on Cu(II) of 100 mg L<sup>-1</sup> Pb(II). From these results it can be said that the [NMIIM]Br-CNSs adsorbent is highly selective for matrix ions. The developed SPE method can be successfully used for the accurate

**Table 1.**  
Effect of interfering ions on the recovery of Cu(II) and Pb(II) by developed SPE method (n=3).

Interfering ion	Salt	Concentration, mg L <sup>-1</sup>	R (%) $\pm$ SD	
			Cu (II)	Pb (II)
Na(I)	NaNO <sub>3</sub>	7500	100 $\pm$ 1	97 $\pm$ 0
		10,000	97 $\pm$ 1	97 $\pm$ 1
		50,000	97 $\pm$ 1	91 $\pm$ 0
		75,000	101 $\pm$ 1	93 $\pm$ 3
K(I)	KCl	7500	99 $\pm$ 1	100 $\pm$ 0
		10,000	79 $\pm$ 1	87 $\pm$ 2
Ca(II)	Ca(NO <sub>3</sub> ) <sub>2</sub> · 4H <sub>2</sub> O	1000	98 $\pm$ 1	95 $\pm$ 5
		5000	102 $\pm$ 1	94 $\pm$ 2
		10,000	96 $\pm$ 0	99 $\pm$ 2
		50,000	98 $\pm$ 1	92 $\pm$ 4
		75,000	103 $\pm$ 1	106 $\pm$ 4
Mg(II)	Mg(NO <sub>3</sub> ) <sub>2</sub> · 6H <sub>2</sub> O	10,000	100 $\pm$ 1	99 $\pm$ 3
		35,000	94 $\pm$ 1	93 $\pm$ 2
Al(III)	Al(NO <sub>3</sub> ) <sub>3</sub> · 9H <sub>2</sub> O	100	98 $\pm$ 1	102 $\pm$ 4
		250	85 $\pm$ 1	86 $\pm$ 2
Cd(II)	Cd(NO <sub>3</sub> ) <sub>2</sub> · 4H <sub>2</sub> O	100	100 $\pm$ 1	95 $\pm$ 0
		250	93 $\pm$ 1	89 $\pm$ 0
Co(II)	Co(NO <sub>3</sub> ) <sub>2</sub> · 6H <sub>2</sub> O	100	107 $\pm$ 1	99 $\pm$ 2
Cr(III)	Cr(NO <sub>3</sub> ) <sub>3</sub> · 9H <sub>2</sub> O	100	97 $\pm$ 1	97 $\pm$ 2
Fe(III)	Fe(NO <sub>3</sub> ) <sub>3</sub> · 9H <sub>2</sub> O	100	97 $\pm$ 1	97 $\pm$ 2
Mn(II)	Mn(NO <sub>3</sub> ) <sub>2</sub> · 4H <sub>2</sub> O	100	95 $\pm$ 1	93 $\pm$ 2
Ni(II)	Ni(NO <sub>3</sub> ) <sub>2</sub> · 6H <sub>2</sub> O	100	104 $\pm$ 1	95 $\pm$ 1
		250	70 $\pm$ 1	63 $\pm$ 4
Zn(II)	Zn(NO <sub>3</sub> ) <sub>2</sub> · 6H <sub>2</sub> O	100	99 $\pm$ 1	92 $\pm$ 2
		7500	98 $\pm$ 1	95 $\pm$ 2
Cl <sup>-</sup>	NaCl	10,000	79 $\pm$ 1	83 $\pm$ 2
SO <sub>4</sub> <sup>2-</sup>	Na <sub>2</sub> SO <sub>4</sub>	250	96 $\pm$ 1	95 $\pm$ 5
		500	96 $\pm$ 1	91 $\pm$ 2
HPO <sub>4</sub> <sup>2-</sup>	Na <sub>2</sub> HPO <sub>4</sub> · 2H <sub>2</sub> O	100	91 $\pm$ 1	92 $\pm$ 4
		250	80 $\pm$ 1	84 $\pm$ 3

and selective determination of copper and lead from samples with complex matrices, such as sea water, wastewater, sediment and spices.

### 3.9. Adsorption capacity

The batch adsorption experiments were made at room temperature. A 20 mL of model solution including 100 mg of [NMIIM]Br-CNSs, 500 mg L<sup>-1</sup> Cu(II) or 500 mg L<sup>-1</sup> Pb(II) at pH 6 was shaken for 1 h to reach equilibrium. Then the mixture was filtered through a filter paper. After the filtrate was diluted 100 fold, the concentrations of target analytes were determined by FAAS. The adsorption capacity of adsorbent was found to be 55.3 mg g<sup>-1</sup> for Cu(II) and 50.3 mg g<sup>-1</sup> for Pb(II). The adsorption capacity ( $q_e$ , mg g<sup>-1</sup>) of [NMIIM]Br-CNSs for target ions was calculated using the following equation:

$$q_e = \frac{V(C_0 - C_e)}{W} \quad (1)$$

where,  $C_0$  (mg L<sup>-1</sup>) and  $C_e$  (mg L<sup>-1</sup>) are the initial and equilibrium concentrations of the target ions in model solution, respectively.  $V(L)$  is the volume of the model solution, and  $W(g)$  is the mass of the adsorbent.

The adsorption isotherm of the adsorbent for Cu(II) was studied under optimal experimental conditions without any shaking or vortexing to reach equilibrium. The developed SPE method was applied for the model solutions containing 25–500 mg L<sup>-1</sup> of Cu(II). The eluent was diluted 200-fold. The adsorption equilibrium isotherm obtained for Cu(II) is given in Fig. S3. To evaluate the

**Table 2**  
Analysis results of certified reference materials.

Element	BCR-482 Lichen			RM 8704 Buffalo river sediment			LGC6016 Estuarine water		
	Certified <sup>a</sup> (µg g <sup>-1</sup> )	Found <sup>b</sup> (µg g <sup>-1</sup> )	Recovery (%)	Certified <sup>a</sup> (µg g <sup>-1</sup> )	Found <sup>b</sup> (µg g <sup>-1</sup> )	Recovery (%)	Certified <sup>a</sup> (µg L <sup>-1</sup> )	Found <sup>b</sup> (µg L <sup>-1</sup> )	Recovery (%)
Cu	7.03 ± 0.19	7.45 ± 0.45	106	<sup>c</sup>			190 ± 4	200 ± 9	105
Pb	40.9 ± 1.4	37.6 ± 1.9	92	150 ± 17	137 ± 7	91	196 ± 3	196 ± 13	100

<sup>a</sup> At 95% confidence level.

<sup>b</sup> Mean concentration ± SD (n=3).

<sup>c</sup> No certified value.

**Table 3**  
Determination of Cu and Pb in sea water (250 mL), wastewater (150 mL), street dust (0.10 g) and red pepper flakes (1.00 g) samples (final volume: 3 mL).

Element	Sea water			Wastewater			Street dust			Red pepper flakes		
	Added (µg L <sup>-1</sup> )	Found <sup>a</sup> (µg L <sup>-1</sup> )	Recovery (%)	Added (µg L <sup>-1</sup> )	Found (µg L <sup>-1</sup> )	Recovery (%)	Added (µg g <sup>-1</sup> )	Found <sup>a</sup> (µg g <sup>-1</sup> )	Recovery (%)	Added (µg g <sup>-1</sup> )	Found <sup>a</sup> (µg g <sup>-1</sup> )	Recovery (%)
Cu	–	4.4 ± 0.1		–	1.5 ± 0.3		–	169 ± 5		–	0.70 ± 0.03	
	6	10.3 ± 0.1	98	2	3.4 ± 0.2	95	75	245 ± 2	101	1.5	2.10 ± 0.03	93
	12	16.3 ± 0.4	99	10	10.8 ± 0.3	93	150	320 ± 6	101	3.0	3.67 ± 0.03	99
Pb	–	5.6 ± 0.8		–	8.1 ± 1.1		–	36.7 ± 1.6		–	0.28 ± 0.0	
	12	17.4 ± 0.8	98	10	18.0 ± 1.1	99	60	93.8 ± 1.6	95	1.5	1.8 ± 0.2	101
	24	29.3 ± 0.7	99	20	26.6 ± 2.1	93	120	157 ± 2	100	3.0	3.1 ± 0.2	94

<sup>a</sup> Mean concentration ± SD, n=3.

adsorption capacity of the adsorbent, the experimental adsorption data were investigated by the Langmuir adsorption model equation [25].

$$\frac{C_e}{q_e} = \left( \frac{1}{K_L q_m} \right) + \left( \frac{C_e}{q_m} \right) \quad (2)$$

The Langmuir isotherm was used to determine the  $q_m$  and  $K_L$  values from the linear coefficients obtained by plotting  $C_e/q_e$  as a function of  $C_e$  ( $y=0.0167x+1.7415$ ,  $R^2=0.991$ ). The adsorption capacity and Langmuir constant for Cu(II) were found to be  $60 \text{ mg g}^{-1}$  and  $0.010 \text{ L mg}^{-1}$ , respectively. The adsorption capacities found by using batch (with 1 h shaking) and adsorption isotherm experiments (without shaking) for Cu(II) are consistent with each other. The adsorption isotherm study for Pb(II) could not be realized because lead precipitation occurred at concentrations higher than  $800 \text{ mg L}^{-1}$  at pH 6.

### 3.10. Analytical parameters

The detection limit of the method was calculated after applying the developed method to ten blank solutions of 300 mL. The detection limit (DL,  $3S_b/b$ ) and quantification limit ( $10S_b/b$ ), where  $S_b$  is the standard deviation of the blank solution and  $b$  is the slope of the calibration curve, were found to be  $0.30 \text{ µg L}^{-1}$  and  $1.0 \text{ µg L}^{-1}$  for Cu(II) and  $1.8 \text{ µg L}^{-1}$  and  $5.9 \text{ µg L}^{-1}$  for Pb(II) with a pre-concentration factor of 100. The DL values for Cu(II) and Pb(II) can be decreased when a 300-fold pre-concentration factor is used. The precision of the method as RSD% was investigated by repeating nine times intra-day and inter-day the SPE for Cu(II) and Pb(II) under the optimized experimental conditions. The precision as intra-day and inter-day was found to be 1.1% and 1.3% for Cu(II) and 2.2% and 3.0% for Pb(II), respectively.

A calibration graph was obtained from the FAAS measurements of Cu(II) and Pb(II) after applying the developed SPE method by using [NMIIM]Br-CNSs adsorbent. The calibration graph was linear in the range of  $0.04\text{--}0.75 \text{ mg L}^{-1}$  for Cu(II) and  $0.075\text{--}1.5 \text{ mg L}^{-1}$  for Pb(II). The equations of the calibration graphs for Cu(II) and Pb(II) concentration in the final solutions showed good linearity.

They are as follows:  $A=0.0319C+0.0073$  ( $R^2=0.9943$ ) for Cu(II) and  $A=0.0086C+0.0006$  ( $R^2=0.9983$ ) for Pb(II). The calibration graphs for Cu(II) and Pb(II) without pre-concentration were linear in the range of  $0.25\text{--}5 \text{ mg L}^{-1}$  and  $0.5\text{--}10 \text{ mg L}^{-1}$ , respectively.

### 3.11. Analysis of real samples

For the accuracy of the SPE method, the developed method was applied to the three certified reference materials (LGC6016 Estuarine Water, Reference Material 8704 Buffalo River Sediment and BCR-482 Lichen) for the determination of Cu(II) and Pb(II). The experimental values were in good agreement with the certified values (Table 2). In addition the sea water, wastewater, street dust and spice samples were analyzed after being spiked with different amounts of the target Cu(II) and Pb(II). The results in Table 3 show that good recoveries (93–101%) were obtained by applying the developed SPE procedure. Therefore the method can be effectively applied for the determination of copper and lead independent from the matrix effects in high salinity sea water, wastewater, street dust and spice samples.

### 3.12. Comparison of the present SPE method with others

The SPE extraction performances of the prepared [NMIIM]Br-CNSs adsorbent for Cu(II) and Pb(II) were compared with recently reported nano adsorbents in the literature. As can be seen in Table 4, [NMIIM]Br-CNSs adsorbent has higher adsorption capacity, higher pre-concentration factor, comparable DL and better precision. The most important advantage of the adsorbent is that it reaches equilibrium very quickly without vortexing. This reduced the time required for analysis. The sample application of the developed method can be performed for complex matrices such as high salinity sea water, wastewater, street dust and spice. Low pH (6), simplicity, the use of non-organic and low eluent concentration ( $1 \text{ mol L}^{-1}$  HCl) are among the other significant advantages of the developed method.

**Table 4**  
Comparison of some solid phase extraction methods on nano-sized adsorbents.

Adsorbent/detection technique	Element	pH	AC <sup>a</sup> (mg g <sup>-1</sup> )	PF <sup>b</sup>	DL <sup>c</sup> (µg L <sup>-1</sup> )	RSD (%)	Adsorption and elution contact time (min)	Sample	Ref.
Thiosemicarbazide grafted multiwalled carbon nanotubes/ICP-OES	Cu, Pb	6	10.94, 3.69	60	0.22, 0.18	2.5, 1.6	10	Tap water, river water	[26]
A new chrysin-based silica core-shell magnetic nanoparticles/FAAS	Cu	6	24.34	100	0.3	1.9	30, 5	Tap, lake and river water	[38]
<sup>60</sup> Co- MCNTs-DETA/ICP-OES	Pb	4	6.6	75	0.24	<3.0	30	Wastewater	[40]
Bismuth(II)-immobilized magnetic nanoparticles/ICP-OES	Cu, Pb	7	5.3, 9.4	95, 87	0.058, 0.085	4.6, 3.7	10, 5	River water, lake water	[41]
N-2-Pyridylsuccinamic acid functionalized halloysite nanotubes/ICP-OES	Pb	5	23.58	67	0.32	3.4		River, lake water, rice flour and tea	[42]
Nano-TiO <sub>2</sub> modified with 2-mercaptobenzothiazole/FAAS	Cu, Pb	5.5	3.95, 3.17	83.3	0.15, 1.38	4.63, 4.83		River, tap water, ore sample	[43]
4-(2-pyridylazo) resorcinol functionalized magnetic nanosorbent/FAAS	Cu, Pb	6	92, 78	250	0.07, 0.7	5.4, 4.6	5, 10	Tap water, sea water and fruit samples	[44]
Dithizone modified magnetic nanoparticles/ICP-OES	Cu, Pb	7	20.5, 60.9	100	0.011, 0.062	2.4, 3.1	> 5, > 15	CRMs (water and hair)	[45]
Nanometer-sized alumina coated with chromotropic acid/ICP-AES	Cu, Pb	8	14.5, 15.4	100, 50	0.22, 0.53		30	River water and vegetable leaves	[46]
[NMIIM]Br-CSs/FAAS	Cu, Pb	6	60, 50.3	300	0.30, 1.76	1.1, 2.2	No need	Sea water, waste water, street dust, and spice	This work

<sup>a</sup> AC: Adsorption capacity.

<sup>b</sup> PF: Preconcentration factor.

<sup>c</sup> DL: Detection limit.

<sup>d</sup> GO-MCNTs-DETA: Multi-walled CNTs dispersed in graphene oxide colloids and modified with diethylenetriamine.

## 4. Conclusion

A new adsorbent, [NMIIM]Br-CNSs, was used in this study for the first time for the separation and preconcentration of trace copper and lead ions from various samples. A small amount of ionic liquid (3 mL from the solution of 80 mg ionic liquid in 100 mL acetone) as a chelating reagent is used for the coating of CNSs. The prepared adsorbent, [NMIIM]Br-CNSs can be used eight times and the coating procedure for 100 mg CNSs can be repeated about 33 times. This means that the CNSs can be used 264 times for SPE of copper and lead after coating with [NMIIM]Br. The preparation of the adsorbent is easy, simple and fast. The centrifuge time is only 1 min. Three mL of eluent is enough for elution. The experimental studies showed that the developed method is more selective than other SPE methods. The recovery values in complex sample matrices (sea water, wastewater, street dust and spice) and in CRMs indicate that the accuracy of the method is excellent. The most prominent property of the method is that it is faster than the other SPE methods because there is no need for vortexing/shaking during the adsorption and elution of copper and lead ions.

## Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.talanta.2016.06.022>.

## References

- [1] P. Sun, D.W. Armstrong, Ionic liquids in analytical chemistry, *Anal. Chim. Acta* 661 (2010) 1–16.
- [2] L. Vidal, M.-L. Riekkola, A. Canals, Ionic liquid-modified materials for solid-phase extraction and separation: a review, *Anal. Chim. Acta* 715 (2012) 19–41.
- [3] T.D. Ho, A.J. Canestraro, J.L. Anderson, Ionic liquids in solid-phase microextraction: a review, *Anal. Chim. Acta* 695 (2011) 18–43.
- [4] Q. Cheng, F. Qu, N.B. Li, H.Q. Lu, Mixed hemimicelles solid-phase extraction of chlorophenols in environmental water samples with 1-hexadecyl-3-methylimidazolium bromide-coated Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles with high-performance liquid chromatographic analysis, *Anal. Chim. Acta* 715 (2012) 113–119.
- [5] A. Berthod, M.J.R. Angel, S.C. Broch, Ionic liquids in separation techniques, *J. Chromatogr. A* 1184 (2008) 6–18.
- [6] Y. Zhang, R. Wang, P. Su, Y. Yang, Ionic liquid-based solvent bar microextraction for determination of organophosphorus pesticides in water samples, *Anal. Methods* 5 (2013) 5074–5078.
- [7] M. Yang, X. Xi, X. Wu, R. Lu, W. Zhou, S. Zhang, H. Gao, Vortex-assisted magnetic β-cyclodextrin/attapulgite-linked ionic liquid dispersive liquid-liquid microextraction coupled with high-performance liquid chromatography for the fast determination of four fungicides in water samples, *J. Chromatogr. A* 1381 (2015) 37–47.
- [8] F.G. Cano, R. Lucena, S. Cárdenas, M. Valcárcel, Dispersive micro-solid phase extraction with ionic liquid-modified silica for the determination of organophosphate pesticides in water by ultra performance liquid chromatography, *Microchem. J.* 106 (2013) 311–317.
- [9] T. Payagala, Y. Zhang, E. Wanigasekara, Ke Huang, Z.S. Breitbach, P.S. Sharma, L. M. Sidisky, D.W. Armstrong, Trigonal tricationic ionic liquids: a generation of gas chromatographic stationary phases, *Anal. Chem.* 81 (2009) 160–173.
- [10] W. Qin, S.F.Y. Li, An ionic liquid coating for determination of sildenafil and UK-103,320 in human serum by capillary zone electrophoresis-ion trap mass spectrometry, *Electrophoresis* 23 (2002) 4110–4116.
- [11] B.H. Fumes, M.R. Silva, F.N. Andrade, C.E.D. Nazario, F.M. Lancas, Recent advances and future trends in new materials for sample preparation, *Trends Anal. Chem.* 71 (2015) 9–25.
- [12] N. Fontanals, F. Borrull, R.M. Marce, Ionic liquids in solid-phase extraction, *Trends Anal. Chem.* 41 (2012) 15–26.
- [13] I.L. García, Y.V. Martínez, M.H. Córdoba, Determination of lead and cadmium using an ionic liquid and dispersive liquid-liquid microextraction followed by electrothermal atomic absorption spectrometry, *Talanta* 110 (2013) 46–52.
- [14] R.-S. Zhao, X. Wang, J. Sun, C. Hu, X.-K. Wang, Determination of triclosan and triclocarban in environmental water samples with ionic liquid/ionic liquid dispersive liquid-liquid microextraction prior to HPLC-ESI-MS/MS, *Microchim. Acta* 174 (2011) 145–151.
- [15] Y. Liu, E. Zhao, W. Zhu, H. Gao, Z. Zhou, Determination of four heterocyclic insecticides by ionic liquid dispersive liquid-liquid microextraction in water

- samples, *J. Chromatogr. A* 1216 (2009) 885–891.
- [16] E.M. Martinis, P. Berton, R.G. Wuilloud, Ionic liquid-based microextraction techniques for trace-element analysis, *Trends Anal. Chem.* 60 (2014) 54–70.
- [17] E. Stanisz, J. Werner, A.Z. Grzeskowiak, Liquid-phase microextraction techniques based on ionic liquids for preconcentration and determination of metals, *Trends Anal. Chem.* 61 (2014) 54–66.
- [18] G.V. Myasoedova, N.P. Molochnikova, O.B. Mokhodoeva, B.F. Myasoedov, Application of ionic liquids for solid-phase extraction of trace elements, *Anal. Sci.* 24 (2008) 1351–1353.
- [19] H. He, D. Yuan, Z. Gao, D. Xiao, H. He, H. Dai, J. Peng, N. Li, Mixed hemimicelles solid-phase extraction based on ionic liquid-coated Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub> nanoparticles for the determination of flavonoids in bio-matrix samples coupled with high performance liquid chromatography, *J. Chromatogr. A* 1324 (2014) 78–85.
- [20] E. Yavuz, Ş. Tokaloğlu, H. Şahan, Ş. Patat, Nano sponge Mn<sub>2</sub>O<sub>3</sub> as a new adsorbent for the preconcentration of Pd(II) and Rh(III) ions in sea water, wastewater, rock, street sediment and catalytic converter samples prior to FAAS determinations, *Talanta* 128 (2014) 31–37.
- [21] E. Yavuz, Ş. Tokaloğlu, H. Şahan, Ş. Patat, Ultralayered Co<sub>3</sub>O<sub>4</sub> as a new adsorbent for preconcentration of Pb(II) from water, food, sediment and tobacco samples, *Talanta* 115 (2013) 724–729.
- [22] E. Yavuz, Ş. Tokaloğlu, H. Şahan, Ş. Patat, Nanosized spongelike Mn<sub>3</sub>O<sub>4</sub> as an adsorbent for preconcentration by vortex assisted solid phase extraction of copper and lead in various food and herb samples, *Food Chem.* 194 (2016) 463–469.
- [23] X. Chen, L. Hu, J. Liu, S. Chen, J. Wang, Nanoscale carbon-based materials in protein isolation and preconcentration, *Trends Anal. Chem.* 48 (2013) 30–39.
- [24] S. Tokaloğlu, E. Yavuz, A. Aslantas, H. Şahan, F. Taskin, S. Patat, Spectrophotometric determination of basic fuchsin from various water samples after vortex assisted solid phase extraction using reduced graphene oxide as an adsorbent, *Spectrochim. Acta A* 149 (2015) 378–384.
- [25] G. Yıldırım, S. Tokaloğlu, H. Şahan, S. Patat, Preconcentration of Ag and Pd ions using graphite oxide and 2,6-diaminopyridine from water, anode slime and catalytic converter samples, *RSC Adv.* 4 (2014) 18108–18116.
- [26] J. Zhang, Preparation, characterization and application of thiosemicarbazide grafted multiwalled carbon nanotubes for solid-phase extraction of Cd(II), Cu(II) and Pb(II) in environmental samples, *J. Environ. Sci.* 25 (2013) 2331–2337.
- [27] S.-X. Gong, X. Wang, Y. Chen, C.-G. Cheng, M.-L. Wang, R.-S. Zhao, Carboxylated solid carbon spheres as a novel solid-phase microextraction coating for sensitive determination of phenols in environmental water samples, *J. Chromatogr. A* 1401 (2015) 17–23.
- [28] P. Liang, L. Peng, Ionic liquid-modified silica as sorbent for preconcentration of cadmium prior to its determination by flame atomic absorption spectrometry in water samples, *Talanta* 81 (2010) 673–677.
- [29] H.M.A. Bishri, T.M.A. Fattah, M.E. Mahmoud, Immobilization of [Bmim+Tf<sub>2</sub>N<sup>-</sup>] hydrophobic ionic liquid on nano-silica-amine sorbent for implementation in solid phase extraction and removal of lead, *J. Ind. Eng. Chem.* 18 (2012) 1252–1257.
- [30] L. Vidal, J. Parshintsev, K. Hartonen, A. Canals, M.-L. Riekkola, Ionic liquid-functionalized silica for selective solid-phase extraction of organic acids, amines and aldehydes, *J. Chromatogr. A* 1226 (2012) 2–10.
- [31] F.G. Cano, R. Lucena, S. Cárdenas, M. Valcárcel, Dispersive micro-solid phase extraction with ionic liquid-modified silica for the determination of organophosphate pesticides in water by ultra performance liquid chromatography, *Microchem. J.* 106 (2013) 311–317.
- [32] X. Zheng, L. Hea, Y. Duan, X. Jianga, G. Xianga, W. Zhaoa, S. Zhang, Poly(ionic liquid) immobilized magnetic nanoparticles as new adsorbent for extraction and enrichment of organophosphorus pesticides from tea drinks, *J. Chromatogr. A* 1358 (2014) 39–45.
- [33] J. Chen, X. Zhu, Ionic liquid coated magnetic core/shell Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanoparticles for the separation/analysis of linuron in food samples, *Spectrochim. Acta A* 137 (2015) 456–462.
- [34] M. Amjadi, A. Samadi, Modified ionic liquid-coated nanometer TiO<sub>2</sub> as a new solid phase extraction sorbent for preconcentration of trace nickel, *Colloid Surf. A* 434 (2013) 171–177.
- [35] M. Luo, D. Liu, L. Zhao, J. Han, Y. Liang, P. Wang, Z. Zhou, A novel magnetic ionic liquid modified carbon nanotube for the simultaneous determination of aryloxyphenoxy-propionate herbicides and their metabolites in water, *Anal. Chim. Acta* 852 (2014) 88–96.
- [36] S. Ozdemir, C. Varlikli, I. Oner, K. Ocakoglu, S. Icli, The synthesis of 1, 8-naphthalimide groups containing imidazolium salts/ionic liquids using I<sup>-</sup>, PF<sub>6</sub><sup>-</sup>, TFSI<sup>-</sup> anions and their photophysical, electrochemical and thermal properties, *Dyes Pigment.* 86 (2010) 206–216.
- [37] P. Qi, Y. Siyuan, G. Chunyu, L. Yingju, L. Xiaotang, F. Yueping, Z. Jianmin, L. Zesheng, Z. Liya, Mesopore-functional carbon sphere nanochains and their integration with alloy nanoparticles for enhanced electrochemical performances, *Electrochim. Acta* 114 (2013) 334–340.
- [38] L.I.A. Ali, W.A.W. Ibrahim, A. Sulaiman, M.A. Kamboh, M.M. Sanagi, New chrysin-functionalized silica-core shell magnetic nanoparticles for the magnetic solid phase extraction of copper ions from water samples, *Talanta* 148 (2016) 191–199.
- [39] L. Xu, X. Qi, X. Li, Y. Bain, H. Liu, Recent advances in applications of nanomaterials for sample preparation, *Talanta* 146 (2016) 714–726.
- [40] X. Zhu, Y. Cui, X. Chang, H. Wang, Selective solid-phase extraction and analysis of trace-level Cr(III), Fe(III), Pb(II), and Mn(II) ions in wastewater using diethylenetriamine-functionalized carbon nanotubes dispersed in graphene oxide colloids, *Talanta* 146 (2016) 358–363.
- [41] J.S. Suleiman, B. Hu, H. Peng, C. Huang, Separation/preconcentration of trace amounts of Cr, Cu and Pb in environmental samples by magnetic solid-phase extraction with Bismuthiol-II-immobilized magnetic nanoparticles and their determination by ICP-OES, *Talanta* 77 (2009) 1579–1583.
- [42] Q. He, D. Yang, Xi Deng, Q. Wu, R. Li, Y. Zhai, L. Zhang, Preparation, characterization and application of N-2-Pyridylsuccinamic acid-functionalized halloysite nanotubes for solid-phase extraction of Pb(II), *Water Res.* 47 (2013) 3976–3983.
- [43] N. Pourreza, S. Rastegarzadeh, A. Larki, Simultaneous preconcentration of Cd(II), Cu(II) and Pb(II) on Nano-TiO<sub>2</sub> modified with 2-mercaptobenzothiazole prior to flame atomic absorption spectrometric determination, *J. Ind. Eng. Chem.* 20 (2014) 2680–2686.
- [44] A.A. Asgharinezhad, H. Ebrahimzadeh, M. Rezvani, N. Shekari, M. Loni, A novel 4-(2-pyridylazo) resorcinol functionalised magnetic nanosorbent for selective extraction of Cu(II) and Pb(II) ions from food and water samples, *Food Addit. Contam.* 31 (2014) 1196–1204.
- [45] G. Cheng, M. He, H. Peng, B. Hu, Dithizone modified magnetic nanoparticles for fast and selective solid phase extraction of trace elements in environmental and biological samples prior to their determination by ICP-OES, *Talanta* 88 (2012) 507–515.
- [46] A. Ramesh, B.A. Devi, H. Hasegawa, T. Maki, K. Ueda, Nanometer-sized alumina coated with chromotropic acid as solid phase metal extractant from environmental samples and determination by inductively coupled plasma atomic emission spectrometry, *Microchem. J.* 86 (2007) 124–130.