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RESEARCH ARTICLE

Optimization of ethylenediamine-grafted multiwalled carbon nanotubes for solid-phase extraction of lead cations

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Abstract

Introduction Ethylenediamine-grafted multiwalled carbon nanotubes (MWCNTs-EDA-I and MWCNTs-EDA-II) are optimized and employed to investigate the preconcentration of lead ions (Pb(II)) in trace level.

Results The results show that Pb(II) can be adsorbed quantitatively on the optimized MWCNTs in the range of pH 4–7 and MWCNTs-EDA-I has a higher maximum Pb (II) adsorption capacity (157.19 mg/g) than MWCNTs-EDA-II (89.16 mg/g). The adsorbed Pb(II) can be eluted completely using 5 mL of 1 mol/L HNO_3.

Discussion A new approach using a microcolumn packed with the obtained MWCNTs-EDA-I has been developed for the preconcentration of trace amount of Pb(II). Parameters influencing the preconcentration of Pb(II), such as pH of the sample, sample volume, elution solution, and interfering ions, have been examined and optimized in detail. Under optimum experimental conditions, the limit of detection is 0.30 ng/mL with the enrichment factor of 60. The relative standard deviation (R.S.D) was 2.6% at the 20 ng/mL Pb (II) level.

Conclusion The method has been applied for the preconcentration of trace amount of Pb(II) in environmental water samples with satisfying results.

Keywords Carbon nanotubes · SPE · Preconcentration · Heavy metals · Lead cation

Abbreviations

SPE	Solid-phase extraction
CNTs	Carbon nanotubes
MWCNTs	Multiwall carbon nanotubes
EDA	Ethylenediamine
CA	Carboxylic acid
DCC	*N*,*N*'-Dicyclohexylcarbodiimide
DCU	1,3-Dicyclohexylurea
DDW	Double-distilled water

1 Introduction

The determination of trace level toxic heavy metals plays an increasingly important role in food, environment, agriculture, industry, etc., owing to the warrant for good qualities. However, the direct detection is very hard due to low concentrations and matrix interferences. To cope with the issues, many methods have been proposed for separation and preconcentration prior to the determination of trace heavy metals. They include ion exchange (Yang et al. 1993), coprecipitation (Soylak et al. 2005), liquid–liquid extraction (Safavi et al. 2004), and so on (Djozan et al. 2005; Gazda et al. 2004; Mercier and Pinnavaia 1998). Among others, solid-phase extraction (SPE) has been proved as one of the most prominent methods due to its

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simplicity, rapidity, and ability to readily achieve a higher concentration factor (Saracoglu and Elci 2002). Recently, developing novel absorbents for SPE has been paid much attention (Ciftci et al. 2010; Djozan et al. 2010; Marahel et al. 2009). Silica gel (Madrakian et al. 2008; Xie et al. 2008) ion-exchange resins (Leal et al. 2004), activated carbon (Ensafi and Shiraz 2008), carbon nanotubes (El-Sheikh et al. 2011; Li et al. 2002; Tuzen et al. 2008), and chelating resins (Garg et al. 1999) have been widely investigated. Meanwhile, chemical or physical modifications also have been usually applied to load the surface of these absorbents with donor atoms such as oxygen, nitrogen, sulfur, or phosphorus. It results in numerous new species of SPE absorbents (Djozan et al. 2009; Sinner et al. 1998; Tokuyama and Iwama 2007).

Carbon nanotubes (CNTs), a fascinating new member in the carbon family, have attracted much more intensive research efforts (Iijima 1991; Niyogi et al. 2002). The large specific surface area, the hexagonal arrays of carbon atoms, and the unique tubular structure suggest CNTs be a promising support for SPE absorbents. Thus, both untreated and oxidized CNTs are exclusively employed as absorbents in SPE technique (Cai et al. 2003; El-Sheikh 2008; Tuzen and Soylak 2007). CNTs modified with organic molecule have been revealed to be more selective than untreated and oxidized CNTs in the SPE of metal ions (Liu et al. 2008). However, to some extent, the studies of organic molecule-modified CNTs for SPE, especially SPE of metallic species, are still limited so far and attracting the researchers' interests (Scidaa et al. 2011).

In order to achieve highly qualified CNT-supported metal absorbents for SPE, it is necessary to immobilize functional organic units onto carbon nanotubes as far as possible. To obtain highly dispersed and high loading metal nanoparticles on CNTs with dispersed carboxylic units (–COOH), Xing and his co-workers have developed a sonochemical technology for oxidation of CNTs (Xing 2004). It arouses our interests whether the highly dispersed –COOH units can be used to load more dispersed organic units onto CNTs via a further amidation reaction. Thus, the simplest and most popular chelating agent, ethylenediamine, was proposed to investigate the optimization intention.

For comparison purposes, two approaches for oxidizing multiwall carbon nanotubes (MWCNTs) were performed. Both oxides were treated by thionyl chloride and further reacted with ethanediamine (EDA) (Sun et al. 2001) to give absorbents (MWCNTs-EDA-I and MWCNTs-EDA-II) (Fig. A.1 in the Electronic supplementary material), as opposed to using *N*,*N*'-dicyclohexylcarbodiimide (DCC) as dehydrating agent in the amidation reaction (Zang et al. 2009). In that amidation reaction, equimolar DCC will produce a definite side-product 1,3-dicyclohexylurea (DCU, see Fig. A.2 in the Electronic supplementary material), which has a poor aqueous solubility in normal solvents, hard to be removed in the final solid product (Wahlstrom et al. 2007). From chemical structure of DCU, it should be a good chelating reagent for metal ions evidently. If the specific purification was not carried out, it would affect the anti-interference capacities of the absorbents. However, there is no similar case for the amidation reaction from acyl chloride (Chen et al. 1998). The separation and preconcentration capacities of Pb(II) cations were evaluated for the absorbents. The experimental results demonstrate that MWCNTs-EDA-I and MWCNTs-EDA-II possess higher absorption and anti-interference capacities on Pb(II) preconcentration after optimization (Zang et al. 2009). To further investigate the obtained absorbents, the MWCNTs-EDA-I with higher capacity (comparing with MWCNTs-EDA-I) was also evaluated as absorbents for Pb(II). Using a microcolumn packed with obtained MWCNTs-EDA-I, it was successfully applied in the preconcentration of trace amount of Pb(II) from a variety of environmental water samples.

2 Experimental

2.1 Materials and instrumentation

Stock standard solution (1,000 mg/L) of lead was obtained from the National Institute of Standards (Beijing, China). Working standard solutions were obtained by appropriate dilution of the stock standard solutions. All reagents used were of the highest available purity and at least of analytical reagent grade. Double-distilled water (DDW) was used throughout. The MWCNTs (5–15 μm in length, 20 nm in diameter) used in this study were purchased from Shenzhen Nanotech Port Co. Ltd., purity >95%. Thionyl chloride ($SOCl_2$), ethylenediamine, vitriolic and nitric acid (AR, First Chemical Reagent Factory, Shanghai, China) were used without further purification.

The Raman spectra were recorded on a confocal Raman microscope (Rainshaw, UK). The thermal gravimetric analysis (TGA) of the absorbents was carried out with a Q600 SDT thermal analysis system (TA, USA) under nitrogen atmosphere at a heating rate of 5°C/min. X-ray photoelectron spectroscopy (XPS) was employed on an Axis Ultra DLD spectrometer to investigate the functional group on the surface of the MWCNTs-EDA. An analyst 400 atomic absorption spectrophotometer (AAS) (PerkinElmer Instruments, USA) was used for concentration determination of metal ions. A pHS-25 pH-meter (Shanghai Precision & Scientific Instrument Co. Ltd, China) was used for pH adjustment. A CHA-2 multifunctional shaker (Jiangsu Jintan Eltong Electric Co. Ltd., China) was used for the equilibration for the metal ion sorption measurement. A PSPE01 portable solid-phase extractor (Greenempire Environmental Protection S&T Co.

Ltd., Shanghai, China) was used as solid-phase extraction system.

2.2 Syntheses of MWCNTs-EDA

Carboxylic acid (CA)-functionalized MWCNTs-I (MWCNTs-CA-I) According to the reported method (Xing et al. 2005), the surface treatment process is as follows. MWNTs (0.20 g) were weighed and placed in a 500 mL Pyrex glass flask; 188 mL of HNO_3 (69%), 160 mL of H_2SO_4 (96.2%), and 12 mL of deionized H_2O were added to the flask. The solution was first stirred using a vortex mixer for about 1 min, and then was put in a laboratory ultrasonic bath (160 W, 50 Hz) for 5 min to allow dispersion. This mixing and dispersion process was repeated twice to break carbon nanotube aggregates. The flask was then put in the ultrasonic bath, and the bath temperature was raised to 60°C. The treatment process lasted for 8 h. After the surface treatment, the carbon nanotubes were separated from the acids by centrifugation and washed with DDW until the pH of the filtrate was 7.0; and dried under vacuum for 24 h at 60°C to give approximately 0.15 g of MWCNTs-CA-I.

MWCNTs-CA-II (Satishkumar et al. 1996) Pristine MWCNTs (1.00 g) and 30 mL of 60% HNO_3 aqueous was sonicated for 5 min in a 100-mL flask to allow dispersion of the carbon nanotubes and stirred and refluxed for 20 h. After cooling to room temperature, the carbon nanotubes were separated from the mixture by centrifugation and washed with DDW until the pH of the filtrate was 7.0. The filtered solid was dried under vacuum for 24 h at 60°C to give about 0.80 g of MWCNTs-CA-II.

MWCNTs-EDA-I and MWCNTs-EDA-II Dried MWCNTs-CA-I or MWCNTs-EDA-II (1.0 g) was reacted with excess neat $SOCl_2$ (25 mL) at 70°C for 24 h. The excess of $SOCl_2$ was evaporated under vacuum at 30°C. The residue was then reacted with 50 mL of ethylenediamine at 100°C for 48 h. After cooling to room temperature, the residues were washed with ethanol to remove excess ethylenediamine. Finally, the black solid was dried at room temperature overnight under vacuum to give MWCNTs-EDA-I or MWCNTs-EDA-II.

2.3 Procedures

Batch experiments A series of standards or sample solutions containing Pb(II) was transferred into a 25-mL triangular flask, and the volume was adjusted to 10 mL with pH of solution adjusted to the desired values with 0.1 mol/L hydrochloric acid and 0.1 mol/L ammonia water. Then, 10 mg of MWCNTs-EDA was added; the mixture was shaken vigorously for 20 min for fully adsorption of the metal ions onto the absorbents. The concentrations of the metal ions in the solution were directly determined by AAS.

Column preparation and SPE procedure Twenty milligrams of MWCNTs was introduced into a polytetrafluoroethylene microcolumn (20×3.0 mm i.d) plugged with a small portion of glass wool at both ends. Before use, 1.0 mol/L HCl solution and DDW were passed through the column in order to clean and condition it. The column was conditioned to the desired pH with buffer solution. Each solution was passed through the column at a flow rate of 4.0 mL/min by solid-phase extraction system. Afterwards, the metal ions retained in column were eluted with 1.0 mol/L HNO_3 and the analytes in the elution were determined by AAS.

General procedure of sample treatment Two different water samples were collected from Huangpu River (Shanghai, China) and Nanxi River (Wenzhou, China). The polyethylene bottles for filling the water samples were cleaned with detergent, DDW, dilute nitric acid, and DDW in sequence before the use. The samples were immediately filtered by a cellulose filter membrane of 0.45 μm and were maintained around pH 2.0 for storage. Before concentration determination, the samples were adjusted to pH 5.0 according to the optimized experiment conditions.

3 Results and discussion

3.1 Preparation and characterization of MWCNTs-EDA

As described in the experimental section, two oxidization routes of MWCNTs were carried out to provide MWCNTs-CA-I and II. To compare the quantity and dispersity of carboxylic units on the surfaces of treated MWCNTs, the Raman spectra and settling experiments were performed. As shown in Fig. 1a, Raman stack plots of the MWCNTs show D and G bands at 1,352 and 1,596 cm^{-1} corresponding to the sp^3- and sp^2-hybridized carbons, signifying the disordered and the ordered state on the MWCNTs surface, respectively (Hull et al. 2006). The Raman D-to-G integrated peak area ratios are 0.78, 1.04, and 1.12 for pristine MWCNTs, MWCNTs-CA-II and MWCNTs-CA-I (Fig. 1a), respectively. It indicates that MWCNTs-CA-I contains the highest ratio of sp^3-hybridized carbons, which means that sonochemical oxidization helps MWCNTs-CA-I to load more carboxylic groups. It will favor further loading much more amino units by the

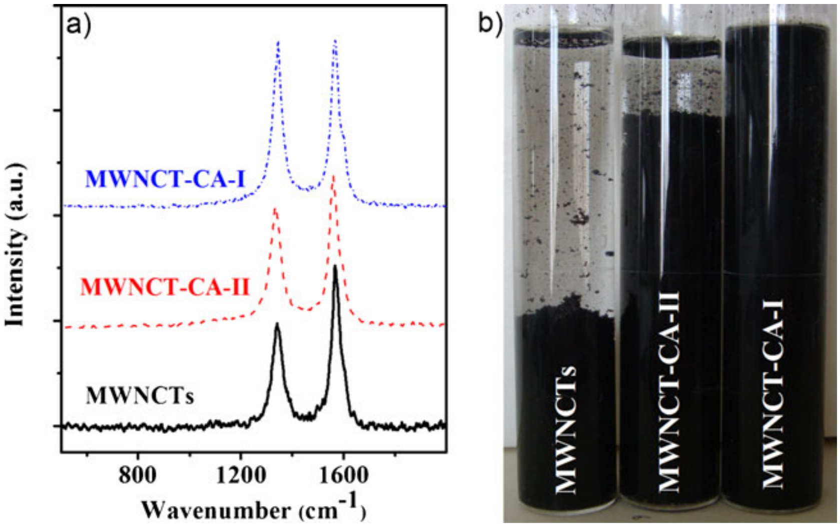

Fig. 1 **a** Raman shifts showing the emergence of the D and G bands of oxidized MWCNTs; **b** Photographs of MWCNTs drifting downward in test tubes for 5 mg MWNCTs, MWNCTs-CA-I and II in 10 mL H_2O for 8 h after ultrasonication

amidation reaction. Photographs of MWCNTs settlings in the test tubes were taken for the samples from different treatments (Fig. 1b). Initially, the MWCNTs were uniformly dispersed in water by ultrasonication. The pristine MWCNTs formed large aggregates immediately after ultrasonication and began to settle. In contrast, the oxidized MWCNTs (MWCNTs-CA) had much better dispersity and need more time to settle, remaining dispersed in water over 8 h. Notably, the MWNCTs-CA-I without any settling shows better dispersity than MWNCTs-CA-II, demonstrating MWNCTs-CA-I has a higher degree of oxidation.

To confirm that the amidation reaction was performed successfully, XPS measurements were carried out. High-resolution XPS spectra for MWCTs-EDA-I are presented in Fig. 2 and Fig. A.3 in the Electronic supplementary material. The detailed analysis of N_{1s} core level recorded for the MWCNTs-EDA-I (Fig. 2a) shows one unique component at 399.65 eV corresponding to the binding energy characteristic of the amino group in its neutral form ($-NH_2$) (Mukherjee et al. 2008). In the detailed C_{1s} spectra (Fig. 2b), peak at 284.35 eV is attributed to the typical graphitic carbon. The other three shoulder peaks of the main peak with higher binding energies, 285.05, 286.35, and 288.95 eV, are assigned to C–N, C–O, and –COO species, respectively (Ago et al. 1999). The results confirmed the amidation reaction was successful.

Further evidence that EDA definitely grafted on the surface of MWCNTs via amidation reaction is provided by the TGA. Figure 3 displays the TGA weight loss curves of pristine MWCNTs, MWCNTs-EDA-I and MWCNTs-EDA-II. The sample of pristine MWCNTs is stable without evident weight loss below 500°C. On the contrary, there are weight loss stages between 150 and 520°C for MWCNTs-EDA-I (23%) and MWCNTs-EDA-II (8%), corresponding to EDA-containing groups on the surface of MWCNTs. The results verify that more dispersed carboxylic units in MWCNTs-CA advantages a higher EDA loading on the MWCNTs-EDA-I, which implies a higher performance in absorption of heavy metal ions.

3.2 Evaluation of MWCNTs-EDA for SPE of Pb(II)

EDA-based absorbents are well-known to exhibit efficient Pb(II) adsorption (Zang et al. 2009). In this work, Pb(II) was chosen to estimate the adsorption performances of the heavy metals for the optimized WMCNTs-EDA.

It has been reported that the pH value is a very important factor for the extraction process of metals on amino units. It is related to protonation and deprotonation processes on amino groups, and the metal species present in solution (Liu et al. 2008). According to the batch procedure (static method), the effect of pH on the adsorption of Pb(II) was tested by equilibrating 10 mg of MWCNTs-EDA-I with 10 mL of Pb(II) (10 mg/L). There is a strong pH dependence of the Pb(II) capacity value, and the capacities

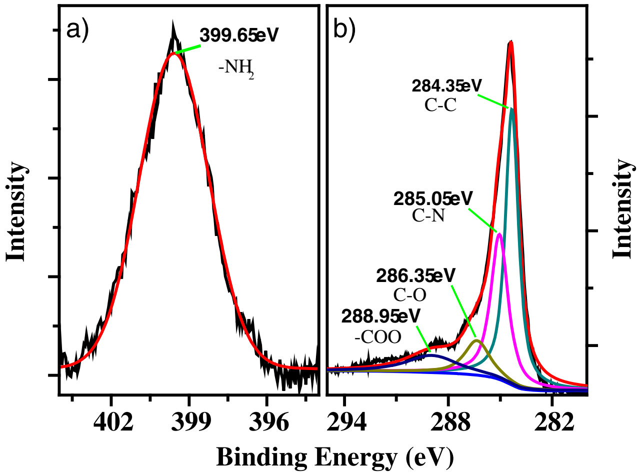

Fig. 2 XPS spectra for MWCNTs-EDA-I: **a** N_{1s}, **b** C_{1s}

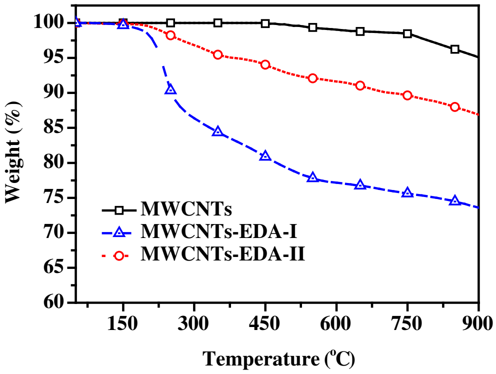

Fig. 3 TGA weight loss curves of pristine MWCNTs, MWCNTs-EDA-I and -II

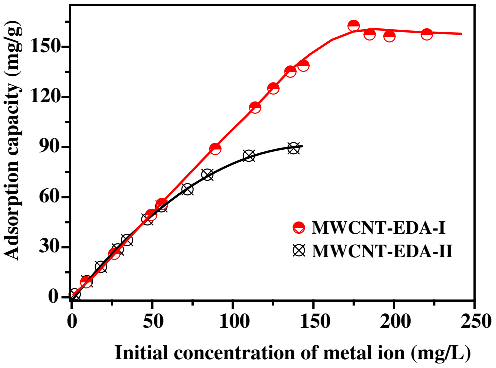

Fig. 5 The effect of Pb(II) initial concentration on the maximum adsorption quantities of MWCNTs-EDA-I and II (*n*=3)

increases with increasing pH values. As seen in Fig. 4a, the optimum pH for quantitative extraction (>95%) of Pb(II) occurs at pH>5. It is known that hydrolysis degree of the metal ions increases with increasing pH. In order to avoid hydrolyzation at higher pH, pH 5 was chosen as the enrichment acidity for further studies.

Different shaking time (ranging from 2 to 60 min) was also studied for the percentage extraction of Pb(II) by MWCNTs-EDA-I. From the results of adsorption of Pb(II) vs. the shaking time in minutes, it is evident that the percentage extractions of Pb(II) reached above 95% within 5 min (in Fig. A.4, Electronic supplementary material). The fast adsorption of Pb(II) is most probably due to the features of chelate amino units on the surface MWCNTs-EDA-I. Accordingly, the shaking time of 5 min was chosen as the adsorption equilibrium time.

Reasonably, the MWCNTs-EDA-I with more dispersed functional amino units should have a higher maximum Pb (II) adsorption capacity than the MWNCTs-EDA-II, as mentioned above. Therefore, the maximum adsorption capacities were determined for the two absorbents by batch static experiments (Fig. 5). The dried MWCNTs-EDA-I and II were each placed in a conical flask. A stock solution of Pb(II) was added to each flask and diluted to an equal volume. The acidity of each solution was adjusted to pH=5. The vessels were shaken for 4 h at room temperature in a mechanical vibrator. The concentrations of Pb(II) in solution were measured by FAAS until equilibrium was reached and the adsorption capacities of Pb(II) ions on the MWCNTs-EDA could be calculated. As shown in Fig. 5, the amount of Pb(II) adsorbed per unit mass of MWCNTs-EDA increased with the initial concentration of Pb(II). In order to reach saturation, the initial Pb(II) concentrations were increased until plateau values (maximum adsorption capacity values) were obtained. The average maximum adsorption capacities for MWCNTs-EDA-I and II were 157.19 and 89.16 mg/g, respectively. To evaluate the performance of MWCNTs-EDA-I, comparative information from investigations on extraction of Pb(II) by CNTs-based absorbents is given in Table 1 (Tuzen et al. 2008; Chen et al. 2009; Li et al. 2011). It is clearly seen that the optimized MWCNTs-EDA has superior adsorption capability on Pb(II).

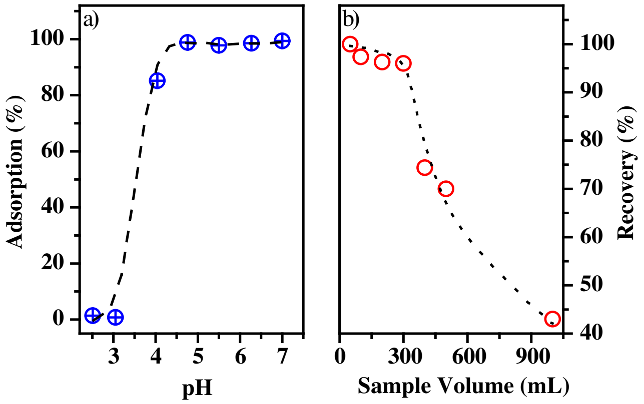

Fig. 4 **a** The effect of pH on absorption of 10 mg/L Pb(II) on MWCNTs-EDA-I; **b** effect of the sample volume on adsorption 5 μg Pb(II) in different volumes on MWCNTs-EDA-I

To obtain reliable and reproducible analytical results and a high concentration factor, it is very important to get satisfactory recoveries in as large as possible sample volumes. To determine the maximum sample volume, 5 μg/mL Pb(II) was added to different volumes of DDW at pH 5.0. Following the column procedure, the recovery of Pb(II) from different volumes were obtained. The effect of sample volume on the recoveries of the analytes is shown in Fig. 4b. The results showed that the maximum sample volume could be up to 300 mL while maintaining the recovery >95%. The elution condition was also studied by using various concentrations and volumes of the HNO_3 solution for desorption of retained Pb(II). The results showed that 5.0 mL of 1 mol/L HNO_3 was sufficient for complete elution for Pb(II). Therefore, an enrichment factor of 60 was obtained using 1 mol/L HNO_3 as eluent. In further experiments, 5.0 mL 1 mol/L HNO_3 was used as an eluent.

Table 1 Comparative data from some recent studies on preconcentraiton of Pb(II) using CNTs-based absorbents

Absorbents	Methods	Adsorption capacity (mg/g)	Reference
MWCNTs	FAAS	10.3	(Tuzen et al. 2008)
Pristine/oxide CNTs	AAS	1.0/15.6	(Li et al. 2002)
Oxide SWCNTs	ICP-MS	6.2	(Chen et al. 2009)
2-Aminobenzothiazole modified MWCNTs	ICP-OES	60.32	(Li et al. 2011)
Ethylenediamine modified MWCNTs	ICP-OES	54.48	(Zang et al. 2009)
MWCNTs-EDA-I	AAS	157.19	Herein

The effects of commonly coexisting ions on the Pb(II) adsorption of the MWCNTs-EDA-I were investigated. In these experiments, solutions of 1 mg/L of Pb(II) containing the added foreign ions were treated according to the recommended procedure. The tolerance limits was set to the amount of ions causing recoveries of the examined elements to be less than 95%. The excess of 500-fold K^+, Na^+, Ca^{2+}, Mg^{2+}, NH_4^+, 200-fold Al^{3+}, and 10-fold Zn^{2+}, Cd^{2+}, Mn^{2+}, Ni^{2+}, Cu^{2+} ions had no significant interferences in the analytical determination of Pb(II) (Table A.1 in Electronic supplementary material). However, it was found that Fe^{3+} in more than 4 mg/L has visible influence on Pb (II) ions (1 mg/L) adsorption on MWCNTs-EDA. This mainly comes from similar coordination characteristic of iron and lead ions, especially the chelating abilities with amidogen-N atoms. In order to improve ion selectivity of the MWCNTs-EDA, a further chemical modification or ion-imprinted technology could be adopted in the future research works. In general, the MWCNTs-EDA can give a considerable tolerable concentrations of co-existing metal ions for SPE of Pb(II).

The detection limit and analytical precision of the analytical method for trace amounts of Pb(II) were also evaluated. Under selected conditions, the recoveries of 20 ng/mL Pb(II) ions in 100 mL solutions, enriched and determined simultaneously 11 times, are in 95–100%. The precision of the method for a standard, evaluated as the relative standard deviation (R.S.D., n=11), was 2.6%. The limit of detection (3σ) (Long and Winefordner 1983), defined as the concentration of analyte giving signals equivalent to three times, the standard deviation of the blank plus the net blank intensity for 100 mL of sample volume, were 0.30 ng/mL.

3.3 Application of the method

Evaluating the toxic elements in the surface water has always been important in the environmental monitoring programs. Thus, in order to test the application and reliability of the method, the proposed procedure (MWCNTs-EDA-I used as extractant for preconcentration) has been applied to extract Pb(II) in the water samples from Huangpu and Nanxi rivers. The standard addition method was used, and the recovery of Pb(II) was >95% (Table 2). The treated sample solutions and standard solutions were introduced into the SPE column system in the same way as described previously. These results exhibit the suitability of MWCNTs-EDA-I for selective solid-phase extraction of trace amounts of Pb(II) in environmental water samples. The amount of Pb(II) in Huangpu River is close to the limitation of detection, obviously less than that in Nanxi River. This could be due to that a mass of urban sewage around Huangpu River result in high level organic contents. The organic complexes of lead are often formed and adsorbed on the sediment. On the contrary, the Nanxi River is located in a natural landscape district surrounded by meagerly populated mountains. There are less organic pollutions, resulting in more ionic lead than in Huangpu River. In this work, we only tested lead ions in surface water sample. The total Pb(II) could reasonably be concentrated after nitration by using the title absorbent.

4 Conclusions

We optimized EDA-grafted MWCNTs for SPE absorbents referring to developed synthetic methods. For comparison of the properties, two different approaches for oxidizing MWCNTs were employed. The results demonstrated that sonochemical oxidization provides higher degree of oxidation

Table 2 The results for the addition-recovery tests for trace amounts of Pb(II) in natural water (n=6)

Sample from	Pb(II) Added (μg/L)	Pb(II) Found (μg/L)	Recovery (%)
Nanxi River	0	3.98±0.04	–
	5.00	9.20±0.05	98.9
	10.00	16.53±0.05	113
Huangpu River	0	nd	–
	5.00	5.03±0.01	100
	10.00	9.98±0.06	99.8

nd not detected

onto the surface of MWCNTs and resulted in more EDA-grafting into the final absorbent. What is more, different from the reported MWCNTs-EDA (Zang et al. 2009), residue-free amidation reaction was employed in the modification. The optimized DEA-grafted MWCNTs obviously offer much better adsorption capacity and selectivity in solid-phase extraction of Pb(II). The much higher adsorption capacity could favor the applications in developing micro-preconcentration. Widely available organic ligands and advanced synthesis approaches should provide a world of possibilities in exploiting high-performance MWCNTs-supported SPE absorbents of heavy metal ions.

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