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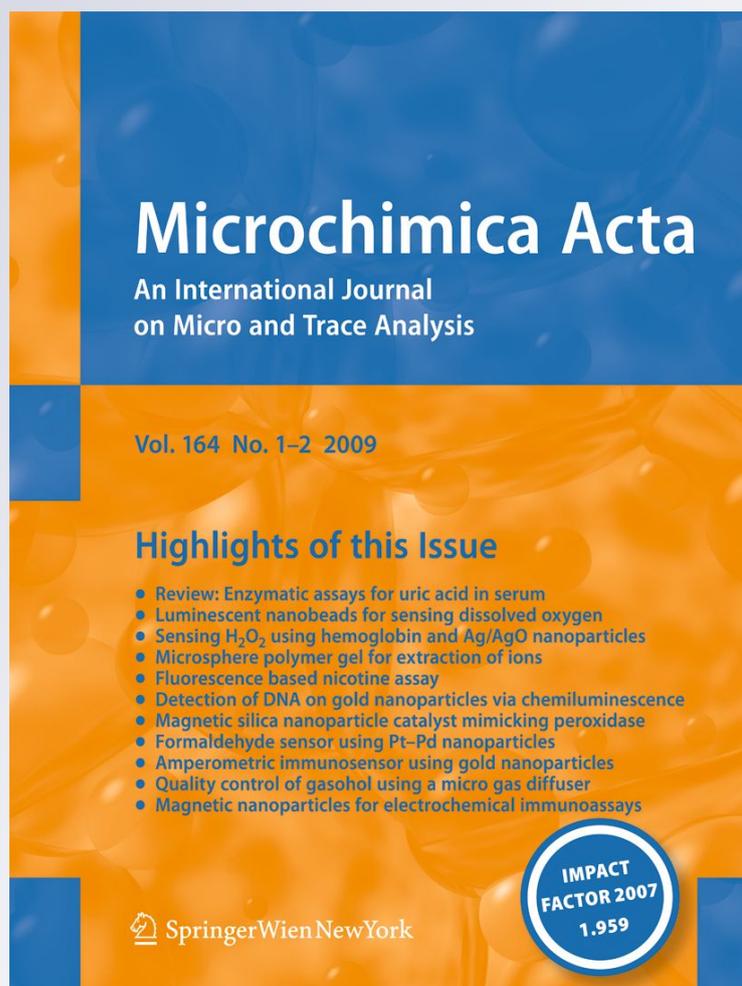
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Novel phenyl-iminodiacetic acid grafted multiwalled carbon nanotubes for solid phase extraction of iron, copper and lead ions from aqueous medium

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Abstract We have covalently grafted phenyl-iminodiacetic acid groups onto multi-walled carbon nanotubes via a diazotation reaction. The resulting material was characterized by FT-IR and UV–vis spectroscopy, by TGA, XPS and SEM. It is shown to be a valuable solid-phase extraction adsorbent for the preconcentration of trace quantities of Fe (III), Cu(II) and Pb(II) ion from aqueous solution prior to their determination by ICP-OES. Various factors affecting the separation and preconcentration were investigated. The enrichment factor typically is 100. Under optimized experimental conditions, the maximum adsorption capacities for Fe(III), Cu(II) and Pb (II) are 64.5, 30.5 and 17.0 mg g⁻¹, respectively, the detection limits are 0.26, 0.15 and 0.18 ng mL⁻¹, and the relative standard deviations are <2.5% (*n*=6). The new adsorbent shows superior reusability and stability. The procedure was successfully applied to the determination of trace quantities of Fe(III), Cu(II) and Pb (II) in water samples.

Keywords Carbon nanotube · SPE · Diazonium reaction · Heavy metals

Introduction

Carbon nanotubes (CNTs) have attracted increasing attention owing to their remarkable properties and widespread applications [1–3]. So far, further developments in the chemical functionalization of CNTs offer new possibilities for a variety of analytical applications [4, 5]. As opposed to the un-treated CNTs, the surface of modified CNTs can be bonded with functional groups, such that they become compatible in different solvents [6, 7]. These modified CNTs have been well demonstrated in their utilization as catalyst supports [8], chemical sensors [9, 10], and delivery vehicles for proteins and anticancer drugs [11]. Recently, due to highly promising sorption characteristics, modified CNTs in solid-phase extraction (SPE) field are of considerable interest, which have generated various novel extractants with superior sensitivities and stabilities, especially for toxic metal ions [12, 13]. For instance, Yan's group utilized L-cysteine to modify multiwalled carbon nanotubes (MWCNTs) resulting in a novel extractant for preconcentration of Cd(II) [14]. Unlike pristine MWCNTs, the sorption of Cd(II) onto the modified MWCNTs is not influenced by ionic strength in a wide range. Similar strategy also has been used by Chang and his coworkers to exploit ethylenediamine-grafted MWCNTs extractant [15]. The new extractant shows higher adsorption capacities for SPE of Cr(III), Fe(III) and Pb(II).

Similarly as described above, functionalizations of CNTs for SPE extractants mostly start from oxidation that typically involves treatment with oxidizing agents to introduce carboxylic groups [16, 17]. Of course, further

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derivatizations by either amidation or esterification can make numerous possible derivatives. However, one of the main drawbacks of acid-oxidation method is CNTs fragmentation (shortening) and defect generation in the graphitic network that destroyed the inherent large area surface. Meanwhile, time-consuming and harsh reaction conditions are not facile and environmentally friendly. The radical addition with aryl diazonium salts has been demonstrated to be a versatile route to functionalize CNTs. This modification technique favors introducing various functional moieties by using different aniline precursors, which could facilitate the further functionalizations [18]. Moreover, the mechanism of the reaction ensures uniformly grafted molecules loading on the surface of CNTs in the mild mediums, such as water [19], ionic liquids [20], molten urea [21], and even “solvent free” [22]. Most crucially, the modification being with such more dispersed molecule layers on the surface of CNTs without skeleton damage might open a possible opportunity to endow CNTs as a prior candidate for SPE materials.

In this work, we have developed a mild radical additions approach to anchor phenyl-iminodiacetic acid groups (PIDA), a superior chelating agent for heavy metals [23, 24], onto the surface of MWCNTs. The new grafted MWCNTs (PIAD-MWCNTs) was evaluated as extractant for SPE of toxic heavy metals from aqueous medium. Compared with pristine MWCNTs, the PIAD-MWCNTs presents better dispersibility and higher sorption affinities for Cu(II), Fe(III) and Pb(II) [25]. The parameters influencing the sorption capabilities and elution efficiencies of Cu(II), Fe(III) and Pb(II) were evaluated statically and dynamically. The results demonstrate PIAD-MWCNTs is suitable for preconcentration of Cu(II), Fe(III) and Pb(II) from aqueous medium. The method was successfully applied to determinate the trace amounts of heavy metals from natural water samples.

Experimental

Materials and reagents

All reagents used were of at least analytical reagent grade and doubly distilled water (DDW) was carried out throughout. The main range of diameter, length and specific surface area of the pristine MWCNTs (Chendu Organic Chemicals Co. Ltd., China Academy of Sciences, Chendu, China, <http://www.cioc.ac.cn>) are 8 nm, 30 μm , and 500 $\text{m}^2 \text{g}^{-1}$, respectively. 1,4-benzenediamine, sodium dodecyl benzenesulfonate (SDBS) and sodium chloroacetate (Aladdin Reagent Inc, Shanghai, China, <http://www.sigmaaldrich.com>) were used without further purification. All metal stock solutions (1000 mg L^{-1}) (the National Research Center for Certified Reference Materials) were

further diluted to the desired concentrations prior to use according to standard method.

Instrumentations and apparatus

An Optima 2100 DV inductively coupled plasma optical emission spectrometer (ICP-OES) (PerkinElmer, Franklin, MA, USA) was used for metal ions determination. The wavelengths of Cu(II), Fe(III) and Pb(II) were 327.39, 238.21 and 220.23 nm, respectively, which recommended by the manufacturer. The pH values were measured with a PHS-25 digital pH meter (Shanghai Leici Instrument Factory, China). Infrared spectra (4000–400 cm^{-1}) in KBr were recorded on a Nicolet NEXUS 670 FT-IR spectrometer (Nicolet, Madison, WI, USA). X-ray photoelectron spectroscopy (XPS) was performed by using a Axis Ultra DLD spectrometer (Kratos Analytical. Ltd., UK) to investigate the functional groups on the surface of PIDA-MWCNTs. A model PSPE01 portable solid-phase-extractor (Green empire environmental protection S&T Co. Ltd., Shanghai, China) was used as solid-phase extraction system.

Sample preparation

River water sample was collected from backward position of Huangpu River, Shanghai, China. The water samples were filtered through a 45 μm PTFE membrane (Millipore) filter and were maintained around pH 2.0 for storage. Tap water sample taken from our research laboratory were analyzed without pretreatment.

Synthesis of PIDA-MWCNTs

Phenyl-amino-functionalized MWCNTs (PA-MWCNTs)

The preparation of PA-MWCNTs was performed by sonicating 300 mg pristine MWCNTs dispersed in 250 mL 1 wt% aqueous SDBS surfactant. Following addition of 756 mg 1,4-benzenediamine (7.0 mmol), 483 mg sodium nitrite (7.0 mmol) and 6 mL HCl solution (20%, 6.4 M, 19.2 mmol), the reaction was heated in an oil bath at 60 °C for 2 h. The mixture was then allowed to cool to room temperature, and filtered through a 45 μm PTFE membrane (Millipore). The resulting solid was sonicated in DMF and filtered again. The process was repeated until the DMF was colorless after sonication. After being washed by ethanol and DDW, the product was dried under vacuum (at 80 °C) over night.

Phenyl-iminodiacetic-acid functionalized MWCNTs (PIDA-MWCNTs)

The 100 mg PA-MWCNTs was dispersed into 300 mL anhydrous ethanol under sonication for 30 min. Following

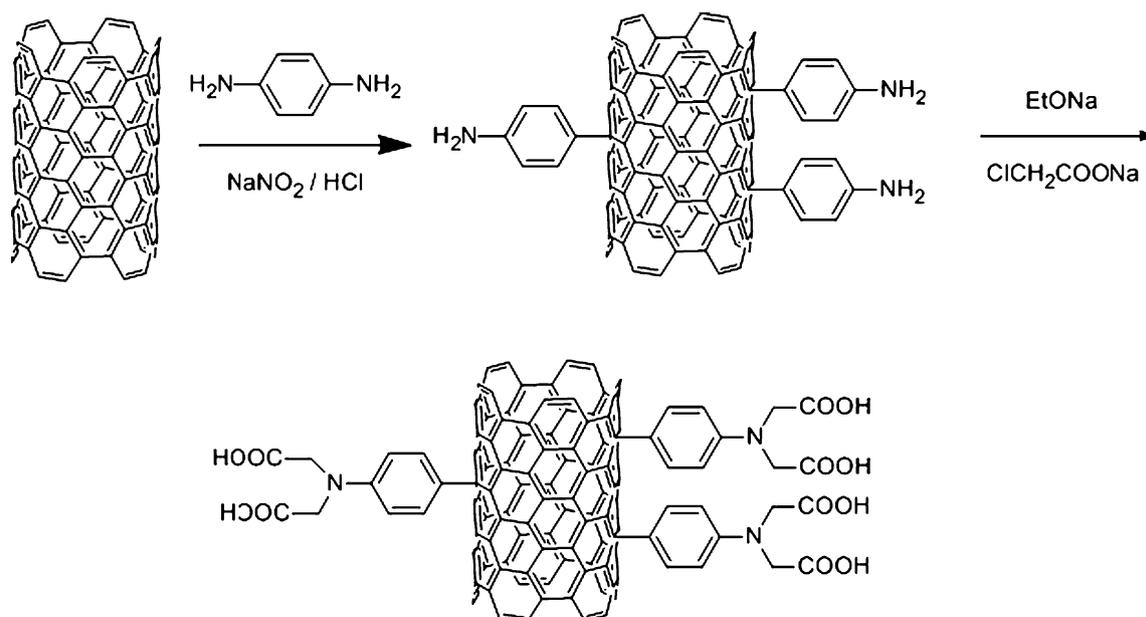


Fig. 1 The synthesis route of PIDA-MWCNTs

addition of 0.5 g sodium alcoholate, the mixture was heated at 78 °C for 45 min. 1.5 g sodium chloroacetate was added and stirred for another 12 h. The suspension was filtered and washed with DMF several times until it's colorless. After washed with ethanol, DDW and acetone, the final product was dried under vacuum (at 80 °C) over night. The synthesis route of PIDA-MWCNTs is illustrated in Fig. 1.

Batch method procedure

A portion of standard or sample solutions containing Cu (II), Fe(III) and Pb(II) were transferred into a 10 mL triangular flask; and the pH values were adjusted to the desired values with 0.1 mol L⁻¹ hydrochloric acid and 0.1 mol L⁻¹ aqueous ammonia. Then the volume was adjusted to 10 mL with DDW. 10 mg of PIDA-MWCNTs was added; and the mixture was shaken vigorously for 15 min to facilitate adsorption of the metal ions onto the PIDA-MWCNTs. After filtered, the concentration of the metal ions in the solution was determined by ICP-OES. The extractant was then eluted with HCl at optimum concentration and volume. Then the desorbed metal ions were measured by ICP-OES.

Column SPE procedure

The dynamic capacity is an important parameter for the PIDA-MWCNTs in on-line application. The column SPE procedure was used to simulate the on-line test. 30 mg of PIDA-MWCNTs was packed in the polytetrafluoroethylene (PTFE) column (50 mm×9.0 mm i.d.) plugged with a small portion of glass wool at both ends. Before use, 5 mL of 0.5 mol L⁻¹ HCl

and DDW were successively passed through the micro-column in order to equilibrate, clean and neutralize it. Portions of aqueous standard or sample solutions containing Cu(II), Fe(III) and Pb(II) were prepared; and the pH values were adjusted to the desired pH values with 0.10 mol L⁻¹ of HCl or 0.10 mol L⁻¹ aqueous ammonia. Considering of saving time in the actual application, an overall considered flow rate of 4.0 mL min⁻¹ was adopted. Afterwards, the metal ions retained on column were eluted with 2 mol L⁻¹ HCl solution and the analytes in the elution were determined by ICP-OES.

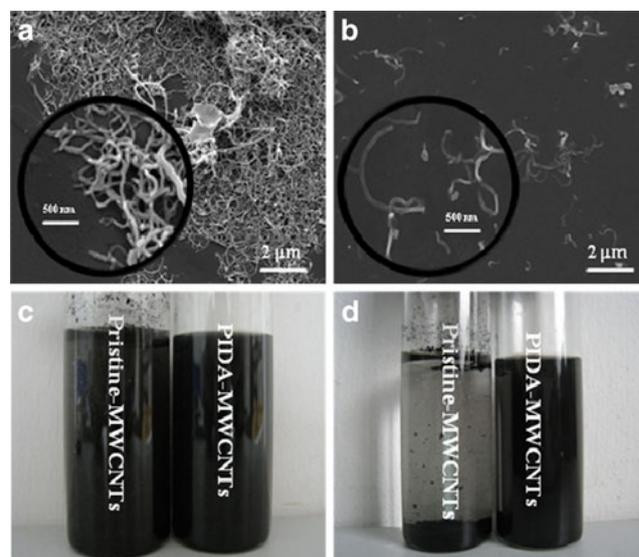


Fig. 2 Representative SEM image of pristine MWCNTs (a); PIDA-MWCNTs (b); the photographs of pristine MWCNTs and PIDA-MWCNTs dispersed in water after 15 min ultrasonication (c); and 24 h (d)

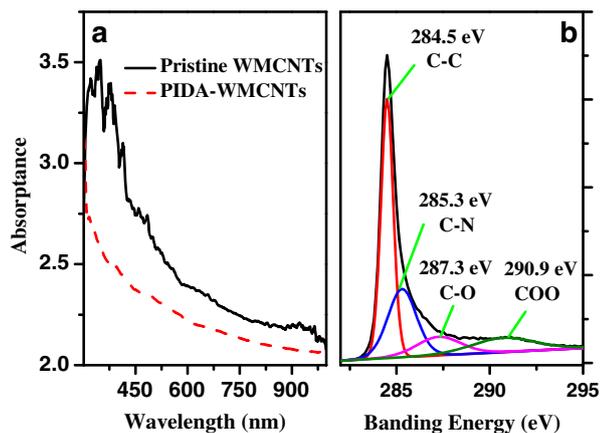


Fig. 3 The UV/vis spectrum of pristine MWCNTs and PIDA-MWCNTs (a); the XPS spectra for PIDA-MWCNTs (b)

Results and discussion

Characterization of PIDA-MWCNTs

The dispersibility is an intuitive proof whether the modification is carried out successfully. So the representative SEM images and photographs (Fig. 2) were taken to estimate the dispersibility of the modified CNTs. The dispersibility of PIDA-MWCNTs has been enhanced obviously, which contributed to the introduction of hydrophilic carboxylic groups. The UV-vis spectrum (Fig. 3a) confirms the existence of van hove singularities in MWCNTs before the functionalization, which obviously disappeared after functionalization (Fig. 3b), agreeing with dispersibility test [26]. The FT-IR spectra of the pristine MWCNTs, PA-MWCNTs and PIDA-MWCNTs are presented in Fig. 4. Amine groups were introduced on the surface of MWCNTs with the radical addition, as indicated by the presence of characteristic absorptions at 1579 and 1508 cm^{-1} for stretching vibrations of N-H and C-N, respectively. The disappearance of stretch at 1579 cm^{-1}

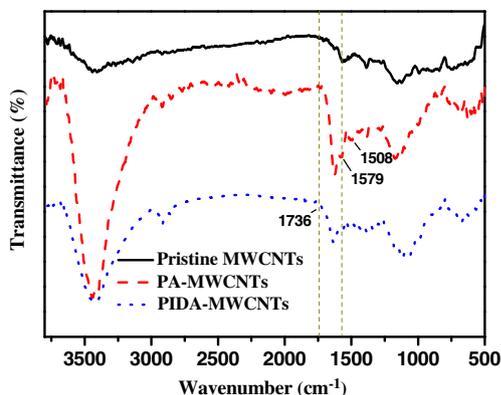


Fig. 4 The FT-IR spectra of pristine MWCNTs, PA-MWCNTs and PIDA-MWCNTs

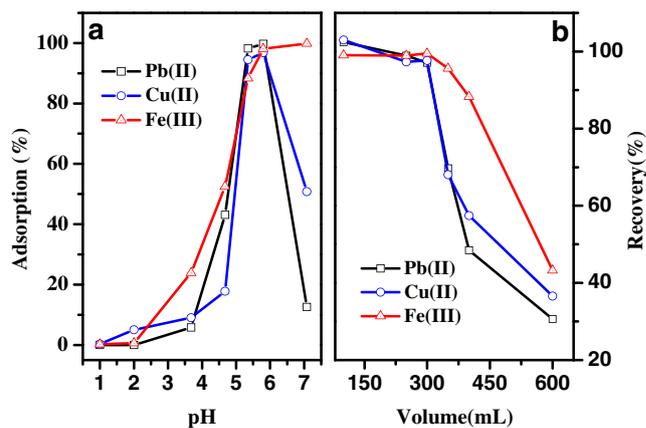


Fig. 5 The effect of pH on adsorption of 10 mg L⁻¹ Fe(III), Cu(II) and Pb(II) on PIDA-MWCNTs (a); effect of the sample volume on adsorption 5 μg Fe(III), Cu(II) and Pb(II) in different volumes on PIDA-MWCNTs (b)

from amino group and new stretch at 1736 cm^{-1} attributed to C=O stretch vibration suggest that carboxylic groups were bonded to MWCNTs covalently [15, 27, 28]. The XPS spectrum was also employed to investigate the organic groups on the surface of the PIDA-MWCNTs (Fig. 3b), the peak of typical graphitic carbon attributed to C1s spectra was found at 284.5 eV, other three peaks in the shoulder of the main peak with higher binding energies at 285.3, 287.3 and 290.9 eV could be assigned to C-N, -C-O and -COO species, respectively [14].

Evaluation of adsorption

Effect of pH

The pH condition is important during the adsorption process. According to the recommended procedure (batch method), eight metals ions, including Cr(III), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II) were determined in the pH range between 1 and 7 in order to find the optimal pH and the adsorption affinity. The adsorptions were carried out in

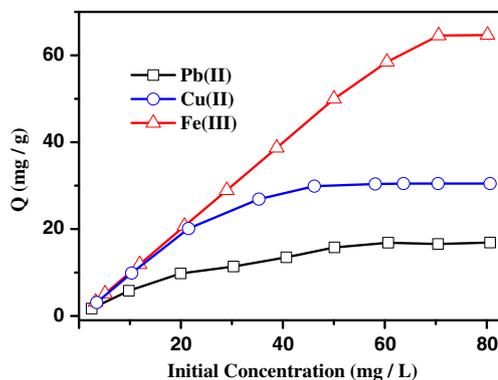


Fig. 6 The adsorption capacity of Fe(III), Cu(II) and Pb(II) on PIDA-MWCNTs

Table 1 Effects of matrix components on the recoveries of Fe (III), Cu(II) and Pb(II) ($n=3$)

Ion	Concentration (mg L ⁻¹)	Added as	Adsorption (%)		
			Fe(III)	Cu(II)	Pb(II)
Ca(II)	5000	CaCl ₂	100.8±1.1	99.7±1.8	99.3±2.4
Na(I)	20,000	Na ₂ SO ₄	100.2±0.8	101.3±1.2	99.7±1.6
K(I)	5000	KCl	100.7±0.6	100.4±0.9	99.9±1.1
Mg(II)	5000	Mg(NO ₃) ₂	100.1±0.6	100.4±0.9	99.3±1.7
Co(II)	10	Co(NO ₃) ₂	99.1±1.6	97.2±1.4	96.9±2.1
Cd(II)	10	Cd(NO ₃) ₂	98.4±1.4	98.2±1.6	97.5±1.1
Cr(III)	10	Cr(NO ₃) ₃	97.1±1.6	96.2±1.4	96.5±2.4

*Mean ± standard deviation

triplicates. Finally, Fe(III), Cu(II) and Pb(II) were found to be highly extracted by PIDA-MWCNTs. As shown in Fig. 5a, the quantitative extractions (> 95%) of Fe(III), Cu(II) and Pb(II) occurred at pH from 5 to 6. In this work, pH 5.5 was selected. In addition, Cd(II), Zn(II), Ni(II), Cr(II) and Co(II) could be also adsorbed to an extent in a range of 10–30% at the same pH, but they do not interfere enrichments and determination of Fe(III), Cu(II) and Pb(II) [29].

Effect of shaking time

The effect of shaking time for the adsorption rate was also investigated. Different shaking time from 1 to 50 min were carried out for the extraction percentage of Fe(III), Cu(II) and Pb(II) by using the PIDA-MWCNTs. The results suggested that the adsorptions of Fe(III), Cu(II) and Pb(II) were over 90% sorption during the first 15 min. It indicated that the adsorption equilibrium is relatively quick. Accordingly, the shaking time of 15 min was chosen as the adsorption equilibrium time.

Adsorption capacity

The adsorption capacity is an important factor because it determines how much extractant is required to quantitatively concentrate the analytes from a solution. The adsorption capacity was tested following the batch procedure, 10 mg extractant was equilibrated with 10 mL of various concentration of each Fe(III),Cu(II) and Pb(II) at pH 5.5 for 15 min. In order to reach saturation, the initial concentrations increased till the plateau values were

obtained. The amount (Q in mg g⁻¹) of metal ions adsorbed per gram of extractant versus the initial concentration (C₀ in mg L⁻¹) is illustrated in Fig. 6. The Q was calculated by the equation, $Q=(C_0-C_e) V/M$, where C_e is the equilibrium concentration of Fe(III), Cu(II) and Pb(II) in mg L⁻¹, M the mass of the material in g and V the volume of solution in L. The maximum adsorption capacities of Fe(III), Cu(II) and Pb(II) were calculated to be 64.6, 30.5 and 16.8 mg g⁻¹, respectively.

Effects of potentially interfering ions

The effects of potentially interfering ions on the adsorption were investigated. The solutions of 0.5 mg L⁻¹ of Fe(III), Cu(II) and Pb(II) containing the added interfering ions were treated according to the recommended procedure. The tolerance limits were set as the amount of ions causing adsorption of the examined elements to be less than 95%. As shown in Table 1, most of the ions do not interfere the determinations of Fe(III), Cu(II) and Pb(II). It indicates that the PIDA-MWCNTs can give considerable tolerances of co-existing metal ions for SPE of Fe(III), Cu(II) and Pb(II).

Evaluation of SPE

Effect of elution condition on recoveries

The effect of elution was investigated by using various concentrations and volumes of HCl solutions. As shown in Table 2, 3 mL of 2 mol L⁻¹ HCl was sufficient for the

Table 2 Elution recoveries (%) for Fe(III), Cu(II) and Pb(II) adsorbed on PIDA-WMCNTs ($n=3$)

Optimization of eluent concentration (the volume of HCl was 10 mL)						
Concentration (mol L ⁻¹)	0.1	0.5	1.0	1.5	2.0	2.5
Recovery (%)	43.2	75.1	88.9	97.5	100.8	99.7
Optimization of eluent volume (the concentration of HCl was 2 mol L ⁻¹)						
Volume (mL)	1	2	3	4	5	6
Recovery (%)	82.5	94.2	99.4	100.4	100	99.5

Table 3 The results for the addition-recoveries tests for trace amounts of Fe(III), Cu(II) and Pb(II) in natural water ($n=6$)

Ion	Added ($\mu\text{g L}^{-1}$)	Found ($\mu\text{g L}^{-1}$)	Recovery (%)
Huangpu River Water			
Fe(III)	0	2.21 \pm 0.25	–
	5	7.39 \pm 0.18	103.6
	10	12.19 \pm 0.23	99.8
Cu(II)	0	3.30 \pm 0.17	–
	5	8.28 \pm 0.13	99.6
	10	13.24 \pm 0.20	99.4
Pb(II)	0	6.10 \pm 0.22	–
	5	11.15 \pm 0.31	101.0
	10	16.13 \pm 0.12	100.3
Tap water			
Fe(III)	0	10.12 \pm 0.15	–
	5	15.37 \pm 0.31	105.0
	10	20.26 \pm 0.26	101.4
Cu(II)	0	4.15 \pm 0.11	–
	5	9.21 \pm 0.25	101.2
	10	14.83 \pm 0.20	96.6
Pb(II)	0	1.10 \pm 0.16	–
	5	6.02 \pm 0.28	98.4
	10	10.89 \pm 0.30	97.9

complete elution of Fe(III), Cu(II) and Pb(II). Therefore, 3 mL of 2.0 mol L⁻¹ HCl was used as eluent. Meanwhile, in order to obtain a high concentration factor, it is important to get satisfactory recoveries for all the analytes in largest possible volume of sample solution. It is necessary to know the maximum sample volume in the SPE process. Following the column procedure, different volumes of purified water at pH 5.5 were spiked with Fe(III), Cu(II) and Pb(II) at 5 μg , the recoveries of the three analytes at different volume were obtained. The effect of sample volume on the recoveries of the analytes is shown in Fig. 5b. The results showed that the maximum sample volume could be increased up to 300 mL with the recovery >95%. Thus, a high enrichment factor of 100 was obtained.

Table 4 Comparative data of the analytical performance of presented method with those in the literatures

Extractant	Method	Element	Enrichment factor	D.L.(ng mL ⁻¹)	RSD (%)	Reference
MWCNTs	AAS	Pb, Cu Mn, Fe(III)	20	3.5–8.0	<2.5	[32]
APDC-MWCNTs	FAAS	Cu, Co, Pb	80	0.3–0.6	<5	[33]
IDA-MWCNTs	FAAS	V, Cr, Co, Cu, As, Cd and Pb	66–101	0.4–3.4	<4	[34]
ABTZ-MWCNTs	ICP-OES	Pb	100	0.27	1.6	[35]
EDA-MWCNTs	ICP-OES	Cu, Cr, Pb	200	0.19–0.33	3.5	[15]
PIDA-MWNTs	ICP-OES	Cu, Pb, Fe(III)	100	0.15–0.26	< 2.5	This work

Analytical precision and detection limits

Using the optimized experimental conditions described above, six portions of 50 ng mL⁻¹ standard solutions were enriched and analyzed simultaneously. The relative standard deviations (R.S.D.s) of the method were 1.8% for Cu(II), 1.5% for Pb(II) and 2.5% for Fe(III). It indicates that the method has a good precision for the determinations of trace Fe(III), Cu(II) and Pb(II) from aqueous media. The limits of detection (LOD) based on three times of the standard deviation [25, 30] was calculated to be 0.26 ng mL⁻¹ Fe(III), 0.15 ng mL⁻¹ Cu(II) and 0.18 ng mL⁻¹ Pb(II).

Application of the method

In order to examine the application and reliability of the method, two water samples (Huangpu River and tap water) were analyzed and the results summarized in Table 3. The standard spiked experiments were adopted and the recoveries of Fe(III), Cu(II) and Pb(II) were more than 95%. The results indicate that the proposed method is reliable. In addition, the resulting higher amount of Fe(III) in tap water would be related to the ferruginous running water pipe.

Comparison with other methods

Comparative information from some studies on preconcentration of heavy metals by different sorbents based on CNTs is given in Table 4. The PIDA-MWCNTs have relatively superior performances, which is reasonably contributed from dispersed carboxylic groups on the surface. It is possible for the PIDA-MWCNTs to be used as a candidate extractant for SPE of heavy metals in trace level.

Conclusion

We have developed a novel PIDA-grafted MWCNTs SPE extractant. A mild and facile diazonium functionalization was used to graft 1, 4-benzenediamine onto the surface of MWCNTs for further introducing multi-carboxylic groups.

Different performance tests indicate the modified MWCNTs offer much better adsorption capacity and compatibility for SPE of Fe(III), Cu(II) and Pb(II). The results demonstrate that it is a possible candidate as an extractant for on-line preconcentration of Fe(III), Cu(II) and Pb(II) in environmental samples. Moreover, this work reveals that the radical addition could be an efficient way for CNTs modification to fabricate superior SPE extractants of heavy metals. Ongoing studies focusing on modification using more special chelates and application of ion-imprinted technology [31] will predictably help to enrich the species of toxic metal SPE extractants based on CNTs.

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