Synthesis, characterization and application of ethylenediamine-modified multiwalled carbon nanotubes for selective solid-phase extraction and preconcentration of metal ions

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ABSTRACT

A new method that utilizes ethylenediamine-modified multiwalled carbon nanotubes as a solid-phase extractant has been developed for simultaneous preconcentration of trace Cr(III), Fe(III) and Pb(II) prior to the measurement by inductively coupled plasma optical emission spectrometry. Identification of the surface modification was characterized and performed on the basis of transmission electron microscopy, Fourier transform infrared spectra and elemental analysis. The separation/preconcentration conditions of analytes were investigated, including the pH value, the shaking time, the sample flow rate and volume, the elution condition and the interfering ions. The maximum adsorption capacity of the adsorbent at optimum conditions was found to be 39.58, 28.69 and 54.48 $mg\,g^{-1}$ for Cr(III), Fe(III) and Pb(II), respectively. The detection limits of the method were under 0.35 $ng\,mL^{-1}$ and the relative standard deviations were lower than 3.5% ($n = 11$). The method was validated using a certified reference material, and has been applied for the determination of trace Cr(III), Fe(III) and Pb(II) in biological and natural water samples with satisfactory results.

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1. Introduction

The determination of metal ions at trace level is very important in the content of environmental protection, food and agricultural chemistry as well as high purity materials. However, the direct determination of metal ions in complex matrices is limited due to their usually low concentrations and matrix interferences. In trace analysis, therefore, a preconcentration and/or separation is necessary to improve sensitivity and selectivity of determination.

Recently, Solid-phase extraction (SPE) is the most common technique used for preconcentration of analytes in environmental water because of its advantages of high enrichment factor, high recovery, rapid phase separation, low cost, low consumption of organic solvents and the ability of combination with different detection techniques in the form of on-line or off-line mode [1,2].

In SPE procedure, the choice of appropriate adsorbent is a critical factor to obtain full recovery and high enrichment factor [3,4]. Since carbon nanotubes (CNTs) were discovered by Iijima [5], they have come under intense multidisciplinary study because of their unique physical and chemical properties and their possible applications.

CNTs include single-walled carbon nanotubes (SWCNTs) and multiwalled carbon nanotubes (MWCNTs) dependent on the number of layers comprising them. Due to their unique characteristic and strong adsorption ability [6,7], MWCNTs and oxidized-MWCNTs have been used as adsorbent for preconcentration of many kinds of pollutants such as bisphenol A, 4-n-nonylphenol and 4-tert-octylphenol [2], pesticides [8], sulfonamides [9], phenols [7], herbicides [10], diazinon [11], dichlorodiphenyltrichloroethane [12], tetracyclines [13], organometals [14] and metal ions [15–19]. However, the selectivity of the raw or oxidized-MCWNTs for SPE is quite limited, especially for metal ions [20]. MWCNTs modified with some organic compounds are expected to be more selective than untreated and oxidized-MWCNTs for the solid-phase extraction of metal ions. However, to the best of our knowledge, few such studies have been reported so far.

In this work, we report the synthesis, characterization and application of ethylenediamine-modified multiwalled carbon nanotubes (MWCNTs-EDA) as selective sorbent in SPE for separation and preconcentration of Cr(III), Fe(III) and Pb(II). The new adsorbent of MWCNTs-EDA has a high adsorption capacity for SPE of Cr(III), Fe(III) and Pb(II) present in the water samples. Parameters that can affect the adsorption and elution efficiency of the metal ions were studied in batch and column modes. Then, the method was validated by analyzing the standard reference material (GBW 08301, river sediment) and applied to the analysis of water samples with satisfactory results.

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2. Experimental

2.1. Chemicals and reagents

Reagents of analytical and spectral purity were used for all experiments and doubly distilled deionized water was used throughout. Standard labware and glassware used were repeatedly cleaned with HNO_3 and rinsed with double distilled water, according to a published procedure [21].

Standard stock solutions of Cr(III), Fe(III) and Pb(II) (1 mg mL^{-1}) were prepared by dissolving spectral pure grade chemicals $CrCl_3 \cdot 6H_2O$, $FeCl_3 \cdot 6H_2O$ and $Pb(NO_3)_2$ (The First Reagent Factory, Shanghai, China) in double distilled water with the addition of hydrochloric acid (The First Reagent Factory, Shanghai, China) and further diluted daily prior to use. MWCNTs used in the experiment were bought from Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences (Chengdu, China). The lengths of MWCNTs range from 10 to 50 μm and outer diameters are in the range of 15–65 nm. The special surface area and thermal conductivity of the MWCNTs are 40–300 m^2 g^{-1} and ~2000 W (mK)$^{-1}$ (Watt per meter-Kelvin), respectively. Ethylenediamine (EDA) (The First Reagent Factory, Shanghai, China) and N,N′-dicyclohexylcarbodiimide (DCC) (Sinopharm Chemcial Reagent Co. Ltd., Shanghai, China) were used in this work. The standard reference material (GBW 08301, river sediment) was provided by the National Research Center for Certified Reference Materials (Beijing, China).

2.2. Instruments and apparatus

An Iris Advantage ER/S inductively coupled plasma emission spectrometer, Thermo Jarrel Ash (Franklin, MA, USA) was used for all metal ions determination. The instrumental parameters were those recommended by the manufacturer. The wavelengths selected were as follows: Cr 283.563, Fe 259.940, and Pb 216.999 nm. A pHs-3C digital pH meter, Shanghai Lei Ci Device Works (Shanghai, China) was used for the pH adjustments. Infrared spectra (4000–400 cm^{-1}) in KBr were recorded on a Nicolet NEXUS 670 fourier transform infrared (FT-IR) spectrometer, Nicolet (Madison, WI, USA). The transmission electron microscopy (TEM) images were obtained using a high resolution transmission electron microscopy (JOEL JEM2010 HRTEM) at 200 kV. A VarioEL element analyzer, Elementar Analysen-systeme GmbH (Hanau, Germany), was used for elemental analysis. An YL-110 peristaltic pump, General Research Institute for Non-ferrous Metals (Beijing, China) was used in the column process. A PTFE (polytetrafluoroethylene) column (50 mm × 9.0 mm i.d, Tianjin Jinteng Instrument Factory, Tianjin, China) was used.

2.3. Sample preparation

River water was collected from Yellow River, Lanzhou, China. The water samples were filtered through a 0.45 μm PTFE millipore filter, and acidified to a pH of about 2 with concentrated HCl prior to storage for use.

Balsam pear leaves were obtained from Anning village, Lanzhou, China. Balsam pear leaves were dried in an oven at 80 °C to constant weight. 1.0 g balsam pear leaves' sample was weighted and transferred into a digestion tube, and then 5 mL of concentrated HNO_3 was added into it. The tube was left at room temperature for one night. Then it was placed in a digester block and heated slowly until the temperature was up to 165 °C. This temperature was maintained until the evolution of the brown fumes ceased. After the tube was cooled down, 1.3 mL perchloric acid was added into it. Then the temperature was raised to 210 °C until evolution of white fumes began. The volume was adjusted to 100 mL with double distilled water when the tube was cooled down [22]. The certified reference material (GBW 08301, river sediment) was digested according to literature [23].

2.4. Synthesis

2.4.1. Synthesis of carboxylic derivative of multiwalled carbon nanotubes (MWCNTs-COOH)

MWCNTs were first purified with HCl (10%) for 24 h so as to remove the metal ions and other impurities sorbed on it. Then 5.0 g of purified MWCNTs was suspended in 400 mL of concentrated HNO_3 and refluxed for 12 h with vigorous stirring. The product (MWCNTs-COOH) was filtered through a 1.2-μm filter, washed with deionized water to neutral and dried under vacuum at 80 °C for 8 h.

2.4.2. Synthesis of MWCNTs-EDA

For the synthesis of MWCNTs-EDA, a 4.0 g amount of MWCNTs-COOH was suspended in 150 mL of EDA under stirring and heating, then 5.0 g of DCC was added into the suspension and refluxed for 48 h [24]. The product (MWCNTs-EDA) was filtered off, washed with ethanol and dried in an oven at 80 °C for 8 h. The synthesis route of MWCNTs-EDA is illustrated in Fig. 1.

2.5. Procedures

2.5.1. Batch method

A series of standards or sample solutions containing Cr(III), Fe(III) and Pb(II) was transferred into a 25 mL beaker, and the pH value was adjusted to the desired value with 0.1 mol L^{-1} HCl and 0.1 mol L^{-1} $NH_3 \cdot H_2O$. Then the volume was adjusted to 10 mL with double distilled water. 20 mg of MWCNTs-EDA was added, and the mixture was shaken vigorously for 10 min to facilitate adsorption of the metal ions onto the adsorbents. The concentrations of the metal ions in the solution were directly determined by inductively coupled plasma optical emission spectrometry (ICP-OES).

2.5.2. Column SPE procedure

50 mg of MWCNTs-EDA was packed in the PTFE column plugged with a small portion of glass wool at both ends. Prior to use,
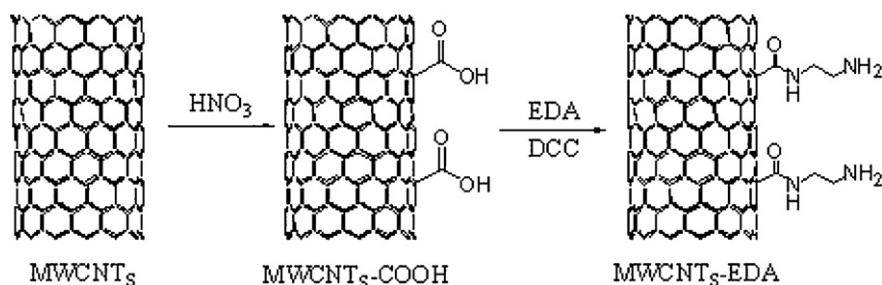

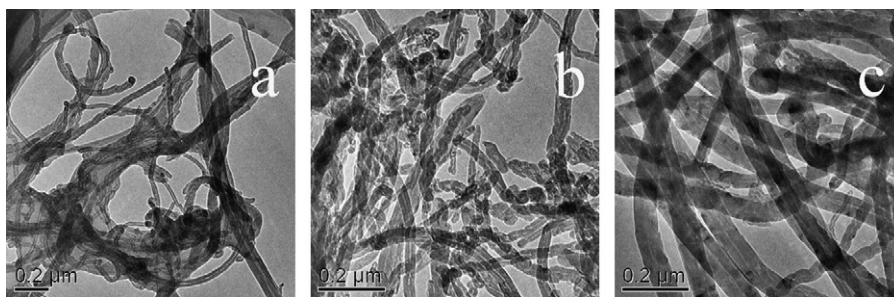**Fig. 1.** Synthesis route of MWCNTs-EDA.

Fig. 2. TEM images of MWCNTs (a), MWCNTs-COOH (b) and MWCNTs-EDA (c).

0.5 mol L^{-1} HCl and doubly distilled deionized water were successively passed through the microcolumn in order to equilibrate, clean and neutralize it. Portions of aqueous standard or sample solutions containing Cr(III), Fe(III) and Pb(II) were prepared, and the pH value was adjusted to the desired pH value with 0.10 mol L^{-1} of HCl or 0.10 mol L^{-1} NH$_3$·H$_2$O. Each solution was passed through the column at a flow rate of 4.0 mL min^{-1} by a peristaltic pump. Afterwards, the metal ions retained on column were eluted with 1.0 mol L^{-1} HCl and the analytes in the elution were determined by ICP-OES.

3. Results and discussion

3.1. Characteristic of the raw MWCNTs, MWCNTs-COOH and MWCNTs-EDA

TEM was conducted to characterize the raw MWCNTs, MWCNTs-COOH and MWCNTs-EDA. The representative TEM images were shown in Fig. 2. The raw MWCNTs are highly entangled by van deer Waals force to form a dense, robust, network structure (see Fig. 2a). In contrast, the observed length of MWCNTs-COOH materials (see Fig. 2b) was relatively shorter and their dispersing property was better than MWCNTs in ethanol. When MWCNTs-COOH was modified by EDA (see Fig. 2c), it was obvious that the diameter of MWCNTs-EDA (50–80 nm) appeared wider than those of MWCNTs and MWCNTs-COOH (15–65 nm). The result indicated that EDA was grafted on the MWCNTs surface.

The modified MWCNTs were also confirmed by FT-IR analysis, as shown in Fig. 3. Comparison of the FT-IR spectra of MWCNTs-COOH with MWCNTs, a new bang (1723 cm^{-1}) appeared in MWCNTs-COOH due to C=O stretching vibration of the carboxylic acid group, which indicated the carboxylic derivative of MWCNTs was prepared successfully. When MWCNTs-COOH was modified by EDA, several new peaks appeared in the spectrum. According to the literature [25,26], the new peaks can be assigned as follows: the peak at 1655 cm^{-1} is due to C=O stretching vibration. The peak at 1563 cm^{-1} is caused by C–N stretching vibration and N–H bending vibration.

Elemental analysis indicated 56.49% carbon, 6.560% nitrogen and 1.957% hydrogen in MWCNTs-EDA. It could be calculated that 1 g MWCNTs contained 0.141 g EDA and 0.0376 g NH$_2$-groups.

Consequently, the above experimental results suggest that MWCNTs are successfully modified by EDA.

3.2. Effect of pH

The acidity of a solution has two effects on metal adsorption. Firstly, protons in acid solution can protonate binding sites of the chelating molecules. Secondly, hydroxide in basic solution may complex and precipitate many metals. Therefore, pH of a solution is the first parameter to be optimized. The reaction between Cr(III), Fe(III) and Pb(II) and the adsorbent (MWCNTs-EDA) can be influenced by changes of pH value. In order to determine this parameter, the effect of the pH on Cr(III), Fe(III) and Pb(II) adsorption onto MWCNTs-EDA was investigated over the range from 1 to 7 using the batch procedure. The adsorption experiments were in triplicates. It can be seen from Fig. 4, the adsorption quantity of Cr(III), Fe(III) and Pb(II) increases with the increase in pH value in the studied pH ranges. Below pH 2.0, the adsorption quantity of investigated metal ions was very low which is attributed to the protonation of the adsorbent, but the adsorption rate is increasing rapidly above pH 2.0; above pH 4.0, the increasing rate is relatively very slow, the adsorption capacity is near the maximum capacity. At pH 4.0 it was possible to carry out the determination of Cr(III), Fe(III) and Pb(II). So, pH 4.0 was chosen as the optimum pH for further studies.

3.3. Effect of shaking time

The shaking time is an important factor in determining the possibility of application of MWCNTs-EDA for the selective extraction of metal ions. In this work, different shaking time (range from 2 to 40 min) was studied for the percentage extraction of Cr(III), Fe(III) and Pb(II) by MWCNTs-EDA. As shown in Fig. 5, the adsorption of Cr(III), Fe(III) and Pb(II) was over 95% sorption during the first 2 min. It indicated that kinetics of equilibrium is very fast.
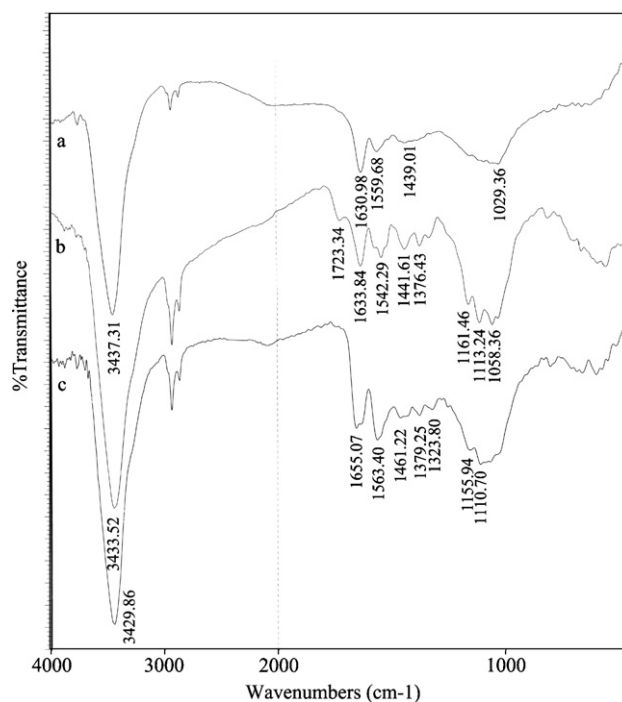

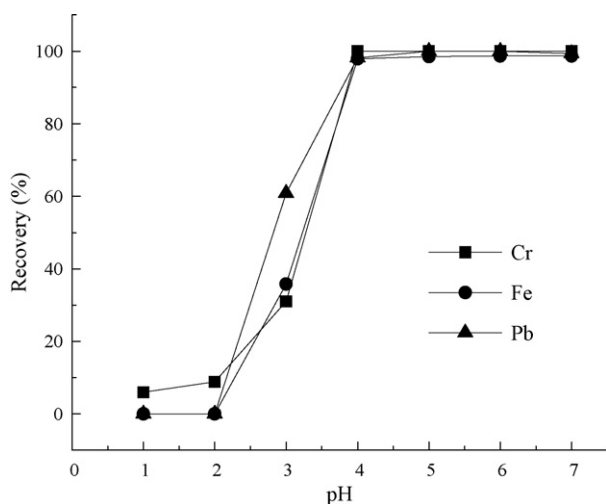**Fig. 3.** FT-IR spectra of MWCNTs (a), MWCNTs-COOH (b) and MWCNTs-EDA (c).

Fig. 4. Effect of pH on adsorption of 1.0 μg mL^{-1} Cr(III), Fe(III) and Pb(II) on MWCNTs-EDA. Other conditions: shaking time 10 min, temperature 25 °C.

Fig. 6. Effect of solution flow rates on adsorption of Cr(III), Fe(III) and Pb(II). Other conditions: 50 mg of MWCNTs-EDA, volume 50 mL, pH 4.0, and temperature 25 °C.

3.4. Effect of flow rate

In a SPE system, the flow rate of sample solution not only affects the recoveries of analytes, but also controls the analysis time. Therefore, the effect of the flow rate of sample solution was examined under the optimum conditions (pH, eluent, etc.) by passing 50 mL of sample solution through the microcolumn with a peristaltic pump. The flow rates were adjusted in a range of 0.5–6.0 mL min^{-1}. As shown in Fig. 6, it was found that the retention of the studied ions was practically not changed up to 4.0 mL min^{-1} flow rate. The recoveries of the analytes decrease slightly when the flow rate is over 4.0 mL min^{-1}. Thus, a flow rate of 4.0 mL min^{-1} is employed in this work.

3.5. Elution condition, maximum sample volume and enrichment factor

The elution condition was studied by using various concentrations and volumes of HCl for the desorption of retained Cr(III), Fe(III) and Pb(II). The obtained results showed that 2.0 mL of 1.0 mol L^{-1} HCl was sufficient for complete elution for all metal ions. So, 2.0 mL of 1.0 mol L^{-1} HCl was used as eluent in further experiments.

To obtain reliable and reproducible analytical results and a high concentration factor, it is very important to get satisfactory recov-
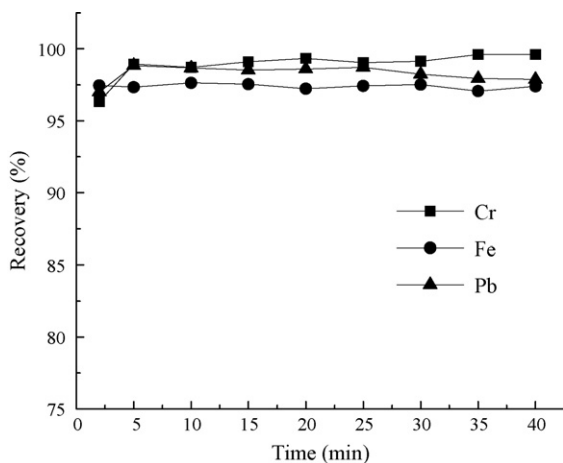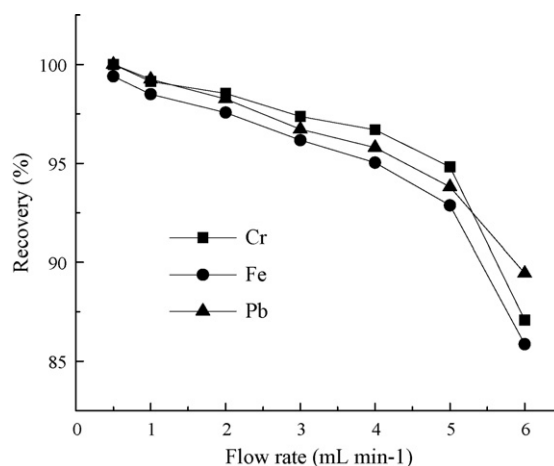
eries for all the compounds studied in as large a volume of sample solutions as possible. So it is necessary to obtain the maximum volume in the SPE. To determine the maximum volume, different volumes of purified water at pH 4.0 were spiked with the three metal ions at 1.0 μg mL^{-1} concentration levels. Following the experimental procedure, the recoveries of the three analytes at different volumes were obtained. The effects of sample volumes on the recoveries of the three analytes are shown in Fig. 7. The results showed that the maximum sample volume could be up to 400 mL with the recovery >95%. Therefore, 400 mL of sample solution was adopted for the preconcentration of analytes from sample solutions. And a high enrichment factor of 200 was obtained because 2.0 mL of 1.0 mol L^{-1} HCl was used as eluent in these experiments.

3.6. Adsorption capacities

The capacity study was adopted from the paper recommended by Maquieira et al. [27]. 10 mL of Cr(III) and Pb(II) sample solutions of a series of concentrations (10–300 μg mL^{-1}) and 10 μg mL^{-1} of Fe(III) of a series of volumes (50–400 mL) were adjusted to the appropriate pH. The proposed separation and preconcentration procedures (batch method) described above were applied. A breakthrough curve was gained by plotting the concentration (μg mL^{-1}) or volume (mL) vs. the micrograms of Cr(III), Fe(III)

Fig. 5. Effect of shaking time on adsorption of 1.0 μg mL^{-1} Cr(III), Fe(III) and Pb(II) on MWCNTs-EDA. Other conditions: pH 4.0, temperature 25 °C.
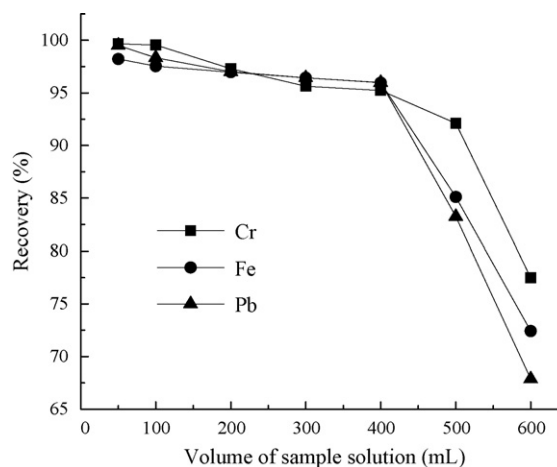

Fig. 7. Effect of the sample volume on adsorption of 1.0 μg mL^{-1} Cr(III), Fe(III) and Pb(II). Other conditions: 50 mg of MWCNTs-EDA, pH 4.0, and temperature 25 °C.
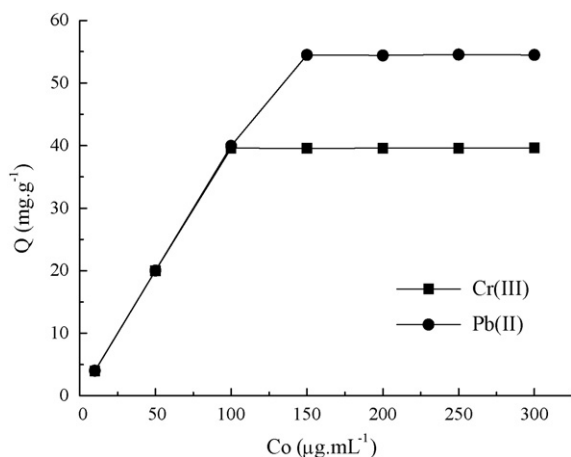
Fig. 8. Effect of initial concentration (C_0) of Cr(III) and Pb(II) on the adsorption quantity(Q) of MWCNTs-EDA. pH 4.0; sample volume 10 mL; temperature 25 °C.

and Pb(II) adsorbed per gram of MWCNTs-EDA (Figs. 8 and 9). From the breakthrough curve, the maximum adsorption capacities of MWCNTs-EDA for Cr(III), Fe(III) and Pb(II) are found to be 39.58, 28.69 and 54.48 mg g^{-1} at pH 4.0, respectively. However, Cr(III), Fe(III) and Pb(II) ions were adsorbed poorly on untreated and oxidized-MWCNTs at pH 4. The results showed that MWCNTs-EDA had a high adsorption capacity for Cr(III), Fe(III) and Pb(II).

3.7. Effects of coexisting ions

The effects of common coexisting ions on the adsorption of Cr(III), Fe(III) and Pb(II) on MWCNTs-EDA were investigated. In these experiments, solutions of 1.0 μg mL^{-1} of Cr(III), Fe(III) and Pb(II) containing the added interfering ions were treated according to the recommended procedure. The tolerance limit was set as the amount of ions causing recoveries of the examined elements to be less than 90%. The results showed that in excess of 2000-fold K(I), Na(I), Ca(II), Mg(II), NH$_4^+$; 100-fold Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II) ions had no significant interferences in the preconcentration and determination of the analyses. This is due to the low adsorbing capacity or rates for interfering ions. It can be seen that the presence of major coexisting ions has no obvious influences on the determination of Cr(III), Fe(III) and Pb(II) under the selected conditions.
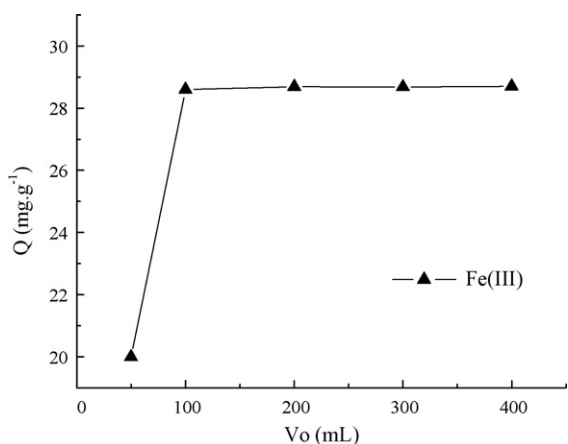

Fig. 9. Effect of initial volume (V_0) of Fe(III) on the adsorption quantity(Q) of MWCNTs-EDA. pH 4.0; sample concentration 10 μg mL^{-1}; temperature 25 °C.

Table 1
Analysis results for the determination of Cr(III), Fe(III) and Pb(II) in standard reference material (GBW 08301, river sediment) and biological samples.

Ion	Found by present method[a] (μg g^{-1})	Certified value (μg g^{-1})
Cr(III)	89 ± 1.7	90 ± 8.0
Fe(III)	38.8 ± 2.5	39.4 ± 0.12
Pb(II)	78 ± 3.1	79 ± 6.0
Balsam pear leaves		
Cr(III)	0.39 ± 0.20	0.40 ± 0.15
Fe(III)	3.60 ± 0.12	3.56 ± 0.17
Pb(II)	0.61 ± 0.09	0.60 ± 0.11

[a] The value following "±" is the standard deviation ($n = 3$).

Table 2
Analytical results for the determination of Cr(III), Fe(III) and Pb(II) in Yellow River samples.

Ion	Added (μg L^{-1})	Found[a] (μg L^{-1})	Recovery (%)	RSD (%)
Yellow River water				
Cr(III)	0	3.39 ± 0.17		
	5	8.41 ± 0.08	100.2	3.8
	10	13.27 ± 0.14	99.1	2.2
Fe(III)	0	5.82 ± 0.11		
	5	10.78 ± 0.20	99.6	1.7
	10	15.80 ± 0.15	99.8	2.5
Pb(II)	0	6.77 ± 0.18		
	5	11.70 ± 0.06	99.4	4.1
	10	16.58 ± 0.13	98.9	3.6

[a] The value following "±" is the standard deviation ($n = 5$).

3.8. Detection limits and precision

The detection limits (evaluated as the concentration corresponding to the three times the standard deviation of 11 runs of the blank solution) of the method were found to be 0.24, 0.19, and 0.33 ng mL^{-1} for Cr(III), Fe(III) and Pb(II), respectively. The relative standard deviations (RSDs) of the eleven replicate determinations were lower than 3.5% (Cr(III): 2.7%; Fe(III): 3.0%; Pb(II): 1.9%), which indicated that the method had good precision for the analysis of trace Cr(III), Fe(III) and Pb(II) in solution samples.

3.9. Application of the method

The proposed method has been applied to the determination of trace Cr(III), Fe(III) and Pb(II) in standard material (GBW 08301, river sediment), balsam pear leaves and Yellow River water samples. The results were listed in Tables 1 and 2. The analytical results for the standard material were in good agreement with the certified values. The analytical results for balsam pear leaves were in agreement with the electrothermal atomic absorption spectrometry (ET-AAS) method. For the analysis of natural Yellow River water and tap water samples, the standard addition method was used, the recoveries of analytes were in the range of 98–101%. These results indicated the suitability of MWCNTs-EDA for selective SPE and determination of trace Cr(III), Fe(III) and Pb(II) in environmental samples.

4. Conclusions

Thus, a selective and sensitive method for the determination of trace levels of Cr(III), Fe(III) and Pb(II) was developed using EDA modified MWCNTs as a solid-phase extractant. The most important characteristic of MWCNTs-EDA is its excellent selectivety towards Cr(III), Fe(III) and Pb(II) over other ions. In addition, the preparation of EDA modified MWCNTs is relatively simple and rapid. As far as we know, this is the first time that the oxidative surface modified

MWCNTs have been used as adsorbent for the SPE of Cr(III), Fe(III) and Pb(II) from aqueous solutions before they are analyzed by ICP-OES. The results show that the modified MWCNTs have high analytical potential for preconcentration of trace metal ions from water samples. In this work, we have preliminarily demonstrated that as promising adsorbents, the modified MWCNTs have great potential for SPE of some metal ions.

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