

PRE-CONCENTRATION AND DETERMINATION OF Pb(II) FROM WATER SAMPLES USING MODIFIED MULTIWALLED CARBON NANOTUBES

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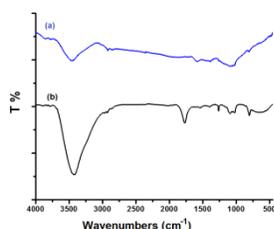
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Graphical abstract



Abstract

Pb(II) is a typically poisonous metal ion that can affect almost every organ and system in the body; it can accumulate in the body and cause kidney malfunctioning, hematological and brain damages. Recently, carbon nanotubes (CNTs), the nano-structured material, are applied for pre-concentration of heavy metal ions. This study investigates the pre-concentration of lead ion using oxidized multiwalled carbon nanotubes (MWCNT-COOH) via solid phase extraction method. MWCNT-COOH was prepared using as-synthesized MWCNT and the products were characterized by FTIR, FESEM, TEM and TGA. Various factors influencing the separation and pre-concentration were investigated namely the effects of pH (2-7) and the elution conditions (type, concentration and volume of eluent). The best extraction conditions were sample of pH 5 and 5 mL of 1M HNO₃ as eluent. The developed method was successfully applied to the determination of trace quantities of Pb(II) in water samples with good analyte recoveries (90-102.5%).

Keywords: Multiwalled carbon nanotubes, Solid phase extraction, Pre-concentration, Pb(II), Heavy metal ions

Abstrak

Pb(II) merupakan ion logam beracun yang memberi kesan terhadap anggota dan sistem tubuh; ia terkumpul di dalam badan dan menyebabkan kerosakan ginjal, hematologi dan kerosakan pada otak. Kebelakangan ini, tiub nano karbon (CNT), bahan berstruktur nano, digunakan bagi pra-pemekatan logam berat. Kajian ini menyelidiki pra-pemekatan ion plumbum dengan tiub nano karbon teroksida (MWCNT-COOH) dengan kaedah pengekstrakan fasa pepejal. MWCNT-COOH telah disediakan menggunakan MWCNT asli dan hasilnya dicirikan dengan FTIR, FESEM, TEM dan TGA. Berbagai faktor yang mempengaruhi pemisahan dan pra-pemekatan telah dikaji iaitu kesan pH (2-7) dan keadaan elusi (jenis, kepekatan dan isipadu pengelusi). Keadaan pengeskrakan terbaik telah diperolehi menggunakan pH 5 dan 5 mL larutan 1 M HNO₃. Kaedah yang dibangunkan telah berjaya diaplikasikan dalam penentuan kuantiti surihan Pb(II) di dalam sampel air dengan pulangan analit yang baik (90-102.5%).

Kata kunci: Karbon tiub nano berbilang dinding, Pengekstrakan fasa pepejal, Pra-pemekatan, Pb(II), logam berat

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1.0 INTRODUCTION

Heavy metals are major pollutants in marine, ground and industrial wastewater [1]. Heavy metals ions like mercury, lead, cadmium, nickel, chromium, copper and zinc are toxic even in extremely minute quantities present in air, water and food [2]. Flame atomic absorption spectroscopy (FAAS) is the most widely used technique for the analysis of metallic ions. This is attributed to the adequate sensitivity, ease of operation, and low initial and running cost of the instrument [3]. There are two main difficulties for the determination of traces of heavy metal ions in environmental samples: (a) the very low concentration of heavy metal ions that may be below the detection limit of many analytical techniques including FAAS, and (b) the interfering effects of the matrix. In order to achieve accurate, reliable, and sensitive results, pre-concentration and separation are needed. Solid-phase extraction (SPE) is a sensitive, fast, and economically viable pre-concentration method for trace analyte ions in various materials, including natural waters, ores, and biological samples. Among the separation-enrichment methods, SPE possesses several advantages: large pre-concentration factors, simplicity of phase separation, and suitability for automation [4-6].

Various solid phase adsorbents have been used for the separation and pre-concentration of trace amounts of heavy metal ions from environmental samples. Some of these adsorbents are suitable for pre-concentration of metal ions, but their methods of preparation are time consuming and involve rigid control of conditions. Carbon nanotubes (CNTs) are an allotrope of carbon. A carbon nanotube is a one atom thick sheet of graphite rolled up into a seamless cylinder with diameter of the order of a nanometer. It caused in an essentially one-dimensional nanostructure where the length-to-diameter ratio exceeds 1000. Such cylindrical carbon molecules have novel properties that make them potentially useful in a wide variety of applications in nanotechnology, electronics, optics and other fields of materials science. There are two main types of carbon nanotubes: single walled carbon nanotubes (SWCNTs) and multiwalled carbon nanotubes (MWNTs) depending on the carbon atom layers in the wall of the nanotubes [7, 8]. Recently, carbon nanotubes (CNTs), the nano-structure material, are applied for pre-concentration of heavy metals [9, 10], organics [11], and biological impurities [12] due to its large specific surface areas, outstanding thermal and chemical stabilities and ease of separation [13, 14].

In this article we report the application of MWCNTs for in-column pre-concentration of trace amounts of lead in water samples.

2.0 EXPERIMENTAL

2.1 Materials, Method and Instruments

Multiwalled carbon nanotubes (MWCNTs) (specific surface area $>233 \text{ m}^2 \text{ g}^{-1}$, purity $>95\%$, 10-20 nm outer diameter \times 50 μm in length) were purchased from Sun Nanotech (Jiangxi, China). A 1000.0 mg L^{-1} lead stock solution was purchased from Merck (Darmstadt, Germany), and 500.0 $\mu\text{g L}^{-1}$ working solutions were made by stepwise diluting the stock solution with ultrapure water. The solution pH values were adjusted with NaOH and/or HNO_3 (all from Sigma-Aldrich). The measurements of analyte ions were performed with Analytic Jena Vario 6 flame atomic absorption spectrometer (AAS). All measurements were carried out in air/acetylene flame. All pH measurements were performed with WTW pH meter. The IR spectrum was performed using a Perkin Elmer FTIR RX1 spectrum. FESEM images were obtained from JEOL/EQ JSM Instruments 6360. TGA were carried out using a SDTA 851 METTLER-TOLEDO TGA Instrument.

2.2 Adsorbent Preparation, Purification and Characterization

MWCNTs (1 g) was dispersed in a mixture of 75 mL of sulfuric acid (18 M) and 25 mL of nitric acid (16 M) (3:1 $\text{H}_2\text{SO}_4:\text{HNO}_3$) for 24 h to yield carboxylic acid functionalized MWCNTs. The mixture was then washed with distilled water and centrifuged until pH became 5-6 before being oven dried, hereafter referred to as MWCNTs-COOH. The FTIR spectra of MWCNTs and prepared adsorbent were recorded in solid state, by KBr pellet method using a FTIR spectrophotometer between 400 and 4000 cm^{-1} (Figure 1). FESEM and TGA of MWCNTs-COOH are shown in Figure 2 and Figure 3, respectively.

2.3 Column Preparation

MWCNTs-COOH (100 mg) was packed in a column with 60 mm in length and 9 mm in diameter, and sandwiched by two polypropylene frits at the ends to prevent loss of the adsorbent material during sample loading. Before use, 0.5 M HNO_3 and double-distilled deionized water were passed through the column to clean the adsorbent assembly.

2.4 Real Sample Pretreatment and Analysis

The proposed method was applied to the determination of lead in different water samples namely tap and lake water samples. The samples were immediately filtered through a cellulose filter membrane (pore size 0.45 μm), and were acidified to pH 2 for storage. Tap water samples were taken from our research laboratory without pretreatment. Before determination, the samples were adjusted according to optimized experiment conditions.

3.0 RESULTS AND DISCUSSION

3.1 Characterization of MWCNTs-COOH

The characterization of synthesized MWCNTs-COOH was performed using FTIR. The spectra of as-synthesized MWCNTs and MWCNTs-COOH are shown in Figure 1. FTIR spectroscopy was used to confirm the presence of desired functional groups in functionalized CNTs. The FTIR of MWCNTs (Figure 1(a)) showed the stretching vibrations of C-H group at 2918 cm^{-1} and the other peaks noted at 1612 and 1408 cm^{-1} are due to the stretching vibration of C=C and C-C groups, respectively. Comparison of the FTIR spectra of MWCNTs-COOH with MWCNTs showed Figure 1(b) a new peak in MWCNTs-COOH spectrum. In the MWCNTs-COOH spectrum, there are broad and strong absorbance peaks at 3424 and 1744 cm^{-1} , which corresponds to the O-H and C=O of COOH and indicated the carboxylic derivative of MWCNTs was prepared successfully.

Figure 2 shows the FESEM of as-synthesized and oxidized MWCNTs. Figure 2(a) showed that the as-synthesized MWCNTs are in the form of floss with a smooth surface. The oxidized MWCNTs in Figure 2(b) appear shorter than the as-synthesized MWCNTs. Moreover; the surface of the as-synthesized MWCNTs is smoother than the oxidized MWCNTs due to the damage to the surface caused by the acid treatment in the latter. After oxidation, the MWCNTs lost their well-aligned structure. High resolution TEM image of MWCNTs and oxidized MWCNTs are shown in Figure 2(c,d). TEM image of oxidized MWCNTs showed that the surfaces of MWCNTs are smooth and clean, and no obvious change of the surface structure and the framework of MWCNTs after functionalization with COOH.

The TGA was performed for the quantitative analysis of as-synthesized MWCNTs and MWCNTs-COOH. The weight loss curves of the as-synthesized MWCNTs and MWCNTs-COOH are shown in Figure 3. The MWCNTs do not decompose under nitrogen atmosphere up to $800\text{ }^{\circ}\text{C}$ with a heating rate of $5\text{ }^{\circ}\text{C min}^{-1}$. The MWCNTs-COOH loses 15% weight slowly under identical conditions due to the decomposition of carboxyl groups.

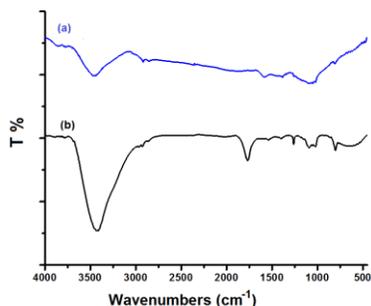


Figure 1 FTIR spectra of (a) as-synthesized MWCNTs, (b) MWCNTs-COOH

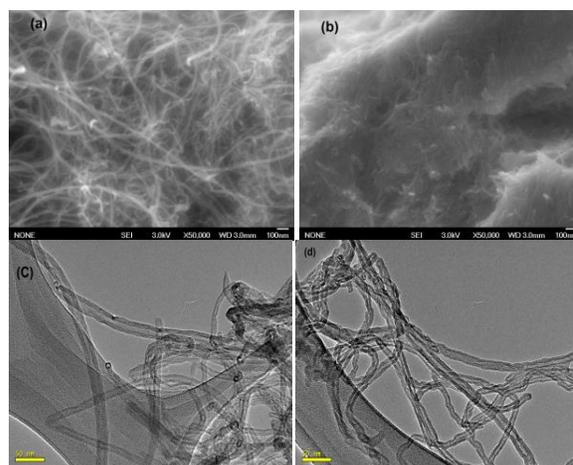


Figure 2 FESEM of (a) as-synthesized MWCNTs (b), MWCNT-COOH, TEM of (c) MWCNTs and (d) as-synthesized MWCNT

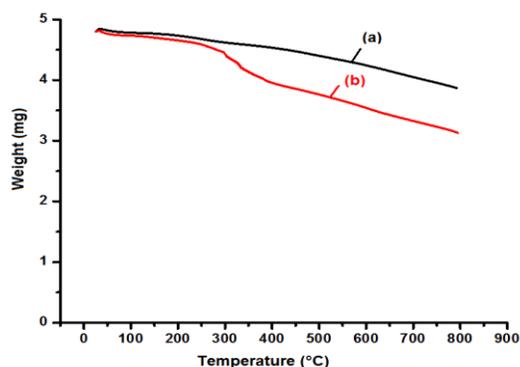


Figure 3 TGA weight loss curves of (a) MWCNTs and (b) MWCNTs-COOH

3.2 The Effect of pH

In the SPE studies, the pH of the aqueous solution is an important operational parameter for the adsorption process because it affects the solubility of the metal ions. The formation of metal complex and its chemical stability are the two important influence factors for the extraction of metal ions, and the pH of aqueous phase has a unique role on metal-chelate formation and subsequent extraction. Therefore, the influence of pH of the analyte solution on the extraction recovery of Pb(II) was studied within the pH range of 2.0–7.0. The results are shown in Figure 4. Since COO^- groups on MWCNTs-COOH are the sites responsible for metal ion adsorption it was apparent from the Figure 4 that the oxidized MWCNTs have better recovery compared to as-synthesized MWCNTs. The optimum pH for quantitative extraction of Pb(II) occurred at $\text{pH} > 5$. It is known that the degree of hydrolysis of the metal ions increases with increasing pH. In order to avoid hydrolysis at higher pH, pH 5 was chosen for further studies.

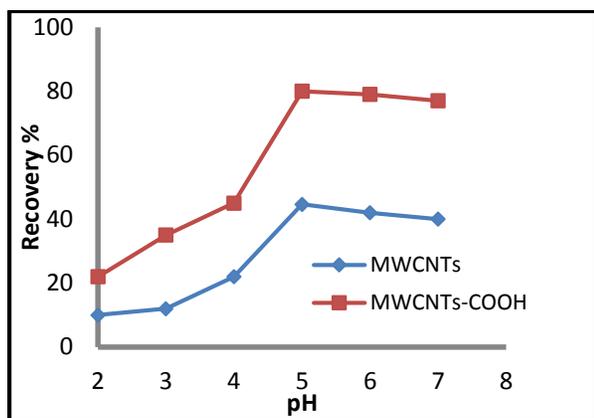


Figure 4 Effect of pH on the recovery of lead ions. (Conditions: pH varied from 2 to 7, concentration of lead 500 $\mu\text{g/L}$, volume of model solution; 50 mL, amount of adsorbent: 0.1 g)

3.3 The Effect of Type, Concentration and Volume of Eluent

In order to optimize the desorption of lead ions from MWCNTs-COOH, a series of eluents including HNO_3 , HCl and CH_3COOH at different concentrations were used. As shown in Table 1, it was found that HNO_3 (1 M) provided effective elution of lead ions from nanosorbent.

The effect of eluent volume on the recovery of lead ions was also studied. As Table 1 shows quantitative recovery could be obtained with 5 mL of HNO_3 (1 M). Therefore, volumes of 5 mL of eluent for desorption of the lead ions were used in the subsequent experiments.

Table 1 Effect of the type, concentration and volume of eluent for desorption of Pb(II) from MWCNTs-COOH. (Conditions: concentration of lead 500 $\mu\text{g L}^{-1}$, model solution volume; 50 mL, amount of adsorbent: 0.1 g and pH = 5)

Eluent	Concentration (M or mol L ⁻¹)	Volume (mL)	R ^a (%) \pm S ^b
HNO_3	1.0	10	82.2 \pm 0.02
HCl	1.0	10	50.6 \pm 0.009
CH_3COOH	1.0	10	44.2 \pm 0.008
HNO_3	1.5	10	80.3 \pm 0.037
HNO_3	0.5	10	57.8 \pm 0.03
HNO_3	1.0	7.5	95.8 \pm 0.029
HNO_3	1.0	5	98.1 \pm 0.09
HNO_3	1.0	2.5	56.1 \pm 0.04

^a Recovery.

^b Standard deviation (N = 3).

3.4 Application of the Method

In order to evaluate the application and reliability of the propose method, UTM lake water and Tap water

samples were analyzed using this procedure. The results are summarized in Table 2. The standard addition method was used and it was found that the excellent recoveries of analytes were obtained in a range 90%–102.5%.

Table 2 Results for the addition-recovery tests for the analyte ions in some real samples

	Added (mg/L)	Found (mg/L)	Recovery (%)
Tap Water	0	0.5	
	1	1.49	98
	2	2.45	90
Lake Water	0	0.8	
	1	1.74	92.5
	2	2.82	102.5

4.0 CONCLUSION

In this work, oxidized MWCNTs were used for solid phase extraction of lead ions from water samples. The result showed the oxidized MWCNTs could be employed as SPE material. The oxidized MWCNTs can easily adsorb Pb(II) at pH of above 5 and the method provided good recoveries and suitable for the determination of Pb(II) in water samples.

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