

Modified multiwall carbon nanotubes supported on graphite as a suitable solid nano-sorbent for selective separation and preconcentration of trace amounts of cadmium and lead ions

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Abstract The present work demonstrates the application of modified multiwall carbon nanotubes (MMWCNTs) as a new selective and stable solid sorbent for the preconcentration of trace amounts of Cd(II) and Pb(II) ions in aqueous solutions. Multiwall carbon nanotubes are oxidized with concentrated HNO_3 and modified with cyanuric-SH. Cd(II) and Pb(II) ions are quantitatively retained by the modified multiwall carbon nanotubes. The adsorbed ions are then eluted from the modified MWCNTs with 3.0 mL of 0.050 mol L^{-1} HNO_3 solution and flame atomic absorption spectrometry (FAAS) is used to measure the eluted Cd(II) and Pb(II) ions. The linear range for the determination of Cd(II) is maintained between 0.3 and $2,000 \text{ ng mL}^{-1}$, while for Pb(II) it remains within $1.0\text{--}2,000 \text{ ng mL}^{-1}$ (in initial solution) with detection limits of 0.1 ng mL^{-1} Cd(II) and 0.3 ng mL^{-1} Pb(II) in the initial solutions. The enrichment factor of the modified solid phase is determined as 660 for Cd(II) and Pb(II) ions. The sorption capacity of the modified MWCNTs for Cd(II) and Pb(II) are 11.2 and 18.6 mg g^{-1} , respectively. The relative standard deviations for separation and measurement of the ions in ten 100-mL solutions containing 50 ng mL^{-1} Cd(II) and Pb(II) and in 500-mL solutions containing 5.0 ng mL^{-1} Cd(II) and Pb(II) were 4.2 and 4.5 % for Cd(II) and 3.4 and 3.5 % for Pb(II), respectively. Finally, the proposed method will be employed for the separation and determination of Cd(II)

and Pb(II) in different real samples to confirm its accuracy and validity.

Keywords Cd(II) and Pb(II) preconcentration · Cyanuric-SH · Modified multiwall carbon nanotubes · Atomic absorption spectrometry · Solid-phase microextraction

Introduction

Determination of trace metals by flame atomic absorption spectrometry (FAAS) has a number of advantages such as high selectivity, high speed, and fairly low operational cost. Despite its significant analytical chemical capacities for metal determination at low concentration levels, FAAS often requires a suitable pretreatment step (preconcentration and separation) of the sample to facilitate the desired sensitivity and selectivity [1, 2]. Solid-phase extraction (SPE) is a common technique for the separation and preconcentration of metal ions in environmental samples [3–5] due to its simplicity, rapidity, minimal cost, low consumption of reagents, and ability to combine via different detection techniques in the form of online or off-line modes [6]. Several methods based on SPE sorbents have been used for the preconcentration of different metals ions. Not only should the sorbent phase achieve fast and quantitative sorption, but it should also consist of a stable and insoluble porous matrix that has suitable active groups (to interact with analyte) and a high sorption capacity, an accessible surface area, and a good reusability. As yet, many sorbents, such as modified activated carbon [7, 8], modified resin [9], and nanometer-sized materials [10–14], have been employed as the solid phase. Among these sorbents, nanometer-sized materials have attracted more attention

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due to their special properties. One of their most interesting properties is the presence of most atoms on the surface of the nanoparticles. The unsaturated surface atoms can then bind with other atoms possessing strong chemical activities to yield a high sorption capacity.

Carbon nanotubes (CNTs) form an allotrope of carbon. A carbon nanotube is a one-atom-thick sheet of graphite rolled up into a seamless cylinder with diameters in the order of 1 μm . 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. Recently, different preconcentration methods have been developed by sorption on multiwall carbon nanotubes (MWCNTs) because they have a large specific surface area and an excellent adsorption capacity [15]. The hexagonal arrays of atoms on the surface of graphene sheets of carbon nanotubes (CNTs) have a strong interaction with other molecules or atoms, which makes CNTs a promising sorbent material as a substitute for activated carbon [16]. Recently, such materials have won a lot of attention (owing to their exceptional chemical and physical properties) and found applications for preconcentration purposes over a short period of time (in fact, only since 2004). However, when using CNTs as mini-column packing materials, they tend to offer a flow resistance in the flow system and thus deteriorate the overall separation and preconcentration performance of the flow system due to the very small size of the CNTs.

Cadmium and lead ions are two toxic metal ions without a known positive physiological role in the human body. Depending on the type of exposure, these elements have been implicated in different destructive effects in the kidneys, lungs, and bones [17]. Cadmium accumulates in the liver and the kidneys, with its half-life in the latter organ ranging between one and four decades. Tobacco smoking and special diets are the main sources of cadmium intake in people. High levels of cadmium have also been found to be associated with damages in the central nervous system and injuries in the immune system or to cause fertility disorders and different types of cancer [18]. In addition, certain studies indicate a possible role for cadmium in coronary diseases [19].

Lead(II) is a highly poisonous metal ion affecting almost every organ and system in the body. The main target for lead toxicity is the nervous system, both in adults and in children. Long-term exposure of adults can result in decreased performance in some tests that measure functions of the nervous system. Lead, even at very low concentrations, is a well-known toxic element to animals and humans. Determination of trace amounts of lead in environmental samples is of great importance due to its high tendency for accumulation, toxicity, and persistent character in living organisms [20, 21].

Moreover, Cd(II) and Pb(II) determination in environmental samples is an important screening procedure for

environmental pollution and occupational exposure studies. The goal of the present study is to explore the performance of a new modified multiwall carbon nanotube (MMWCNTs) as a new sorbent for the preconcentration of Cd(II) and Pb(II) ions from water samples prior to their determination by FAAS. Modification of MWCNTs is performed by thiolated cyanuric acid, (3-(4,6-bis(2-mercaptoethylthio)-1,3,5-triazin-2-ylamino)propyl) silanetriol). The applicability of the proposed method for the analysis of different samples will be explored and it will be shown that the MMWCNTs have a high capacity that does not decline even after regeneration for several times.

Experimental

Apparatus

An atomic absorption spectrometer, Perkin-Elmer (Model 380), was used. The measurements were performed using Cd and Pb Perkin-Elmer hollow cathode lamps operating at 228.8 and 217.0 nm, with current intensities of 6 and 10 mA, respectively. The bandwidths for Cd and Pb were 0.7 nm in all cases. The flame composition was acetylene with a flow rate of 1.5 L min^{-1} and air with a flow rate of 3.5 L min^{-1} . A Teflon column (80 \times 10 mm) was used as the column for preconcentration. All glassware and columns were washed with nitric acid (1:1) before use. A schematic diagram of the preconcentration system is shown in Fig. 1. The hardware of the system was composed of a 32-channel I/O card (PCL-720, Advantech, Taiwan) which has a power relay module to convert the output of the I/O card to 220 V AC. A peristaltic pump (Ismatec, ISM 404, Switzerland) with three 220 V AC electrical valves, a silicon rubber tubing pump (2.06 mm i.d.), and a PC computer Pentium II (233 MHz) were used. The mini-column was made by packing Teflon tubes (3 mm i.d.) with MMWCNTs. A small amount of glass wool was plugged at the ends of each column to prevent material loss.

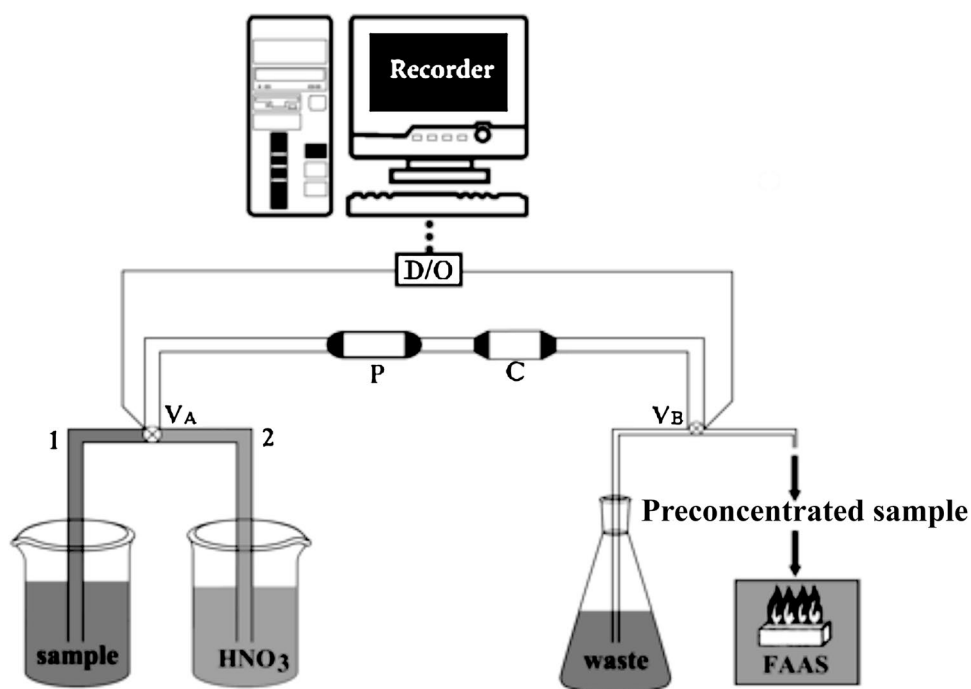
A Metrohm (Switzerland), Model 827, pH meter with a glass electrode was used to read pH levels of aqueous solutions. AFM was performed in ambient conditions using Bruker Nano Instrument (Germany). Fourier transform-IR spectrum was recorded using a JASCO FT-IR (680 plus) spectrometer using KBr pellets.

Chemicals

All solutions were prepared with doubly distilled water and the chemicals used were of analytical grade.

A stock solution of Cd(II), 1,000 mg L^{-1} , was prepared by dissolving 274.5 mg Cd $(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Merck) in water in a 100-mL volumetric flask. A stock solution of Pb(II),

Fig. 1 Schematic diagram of the preconcentration system.
P pump, *C* microcolumn, *D/O* analog to digital converter, *V_A* Valve A, *V_B* valve B



1,000 mg L⁻¹, was also prepared by dissolving 160 mg Pb(NO₃)₂·4H₂O (Merck) in water in a 100-mL volumetric flask. Universal buffer solutions (pH 3.0–9.0) were made of a mixture of acetic acid, boric acid, phosphoric acid, and sodium hydroxide and/or hydrochloric acid (0.05 mol L⁻¹) in water. A spectrally pure graphite powder (particle size <50 nm) was purchased from Merck and multiwall carbon nanotubes (>90 % MWCNTs basis, $d \times l = (110\text{--}70\text{ nm}) - (5\text{--}9\text{ mm})$) were obtained from Fluka.

Preparation of cyanuric-SH

To prepare modified MWCNTs, cyanuric-SH was synthesized according to the method reported in the literature [22]. For this purpose, amino-functionalized silica (1.0 g) was refluxed with 0.29 g (1.57 mmol) cyanuric chloride in dry toluene (30 mL) for 24 h. The solid was filtered and washed off with dry toluene and dried at room temperature under vacuum. Then, 0.25 mL (3.46 mmol) of 1,2-ethanedithiol and 1.0 g of SiO₂-pyridine-NH-cyanuric-Cl were refluxed in 30 mL of dry toluene for 24 h. The mixture thus produced was filtered, washed off with ethanol, and dried at room temperature. The cyanuric-SH was characterized by elemental analysis (CHNS) (C: 9.19 %, H: 1.79 %, N: 5.03 %, S: 1.23 %).

Preparation of activated MWCNTs

To create binding sites with –COOH groups at the surface of modified multiwall carbon nanotubes, MWCNTs were

oxidized with concentrated HNO₃ as described in the literature [23]. The treatment was carried out by dispersion of 2.0 g of MWCNTs into 50 mL of 3.0 mol L⁻¹ HNO₃ for 15 h in a flask and then refluxed for 15 h. The MWCNTs were subsequently washed with water, centrifuged (3,500 rpm), and dried at room temperature.

Preparation of MWCNTs

The stable suspension of activated MWCNTs was obtained by ultrasonication 200 mg of the MWCNTs in 5.0 mL of water. To the suspension 500 mg of cyanuric-SH was then added and the mixture was stirred for 30 min. The mixture thus produced was centrifuged (3,500 rpm) and washed with water several times to remove any free cyanuric-SH. To prevent flow resistance at the surface of the nanoparticles in the flow system, different amounts of graphite powder (previously mixed with 50 mL of 2.0 mol L⁻¹ HNO₃ for 2 h and washed several times with water) were mixed well with the modified MWCNTs and the mixtures were used as the sorbent for preconcentration and analysis. It was observed that when more of the modified MWCNTs were used than the graphite powder, a flow resistance was created in the flow system, deteriorating the overall separation and preconcentration performance. An MWCNTs to graphite powder (w/w) ratio of 1:1 was therefore selected and 300 mg of the modified MWCNTs was mixed well with 300 mg of the graphite. A Teflon column was packed with 110 mg of the sorbent (height of packing being about 40 mm) and used as the operational column. The column

could be used repeatedly up to 30 times after washing with distilled water.

Procedure

The method was tested with the model solution before its application to real samples. For this purpose, 50 mL of the Cd(II) and Pb(II) solution buffered (universal buffer, 0.05 mol L⁻¹) at pH 6.0 was passed through the column at a flow rate of 1.0 mL min⁻¹ by opening position 1 of the electrical valves A and B (Fig. 1). After finishing the sample solution, position 1 of the valves was close to open position 2. Then, a volume of 3.0 mL of 0.050 mol L⁻¹ nitric acid was passed through the column at a flow rate of 1.50 mL min⁻¹ to elute the adsorbed Cd(II) and Pb(II) ions. The eluent was collected and the Cd(II) and Pb(II) ions were measured using the flame atomic absorption spectrometry. The percentages of the metal ions adsorbed on the column were calculated from the amount of Cd(II) and Pb(II) ions in the starting sample and the amount of the metal ions eluted from the column.

Determination of Cd(II) and Pb(II) in real samples

Water and wastewater samples were collected in prewashed (with detergent, doubly distilled water, dilute HNO₃, and deionized water, respectively) 1.5-L polyethylene bottles, acidified to 0.5 % with nitric acid, and subsequently stored at 4 °C in a refrigerator. The samples were filtered through a Millipore cellulose nitrate membrane of a pore size of 0.45 µm before analysis. To apply the proposed method, 1,000 mL of each of the water samples was taken in a beaker, and the pH of the samples was adjusted to pH 6.0 with the buffer solution. Then, Cd(II) and Pb(II) ions were separated and FAAS was used to measure the quantity of each using the recommended procedure.

Radiator manufacturing wastewater was collected from Arak, Iran, and immediately filtered through a Millipore membrane filter (0.45 µm pore size), acidified to pH 2.0 with HNO₃, and stored in precleaned polyethylene bottles. The pH of the sample was adjusted to 6.0 and the Cd(II) and Pb(II) content was analyzed using the recommended procedure.

About 2.0 g of rice (taken from Lenjan, Isfahan, Iran) was powdered. Then, 15 mL of concentrated HNO₃ was added to 1.00 g of the powder in a 100-mL beaker and the mixture was kept overnight. To this beaker 6.0 mL of concentrated HNO₃ plus 4.0 mL of concentrated HClO₄ was subsequently added and the mixture was slowly heated to evaporate to near dryness on a hot plate at about 130 °C for 4 h. The residue was dissolved in 0.5 mol L⁻¹ HNO₃ and filtered using a Millipore membrane filter (0.45 µm pore size). The clear solution obtained was diluted to 50 mL

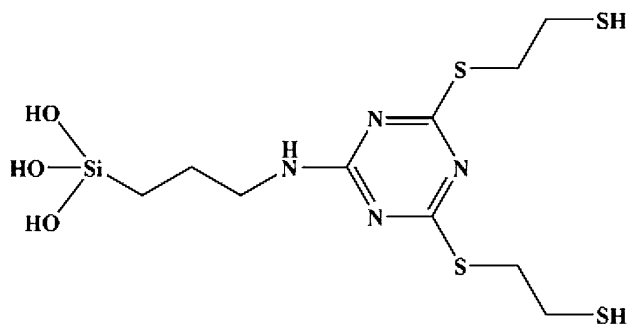


Fig. 2 Structure of cyanuric-SH

with the buffer solution (pH 6.0)³⁰ and subjected to analysis for its Cd(II) and Pb(II) content using the recommended procedure.

Results and discussion

Selection of the adsorbent

Cyanuric-SH is a molecule with -SH and -NH functional groups (Fig. 2). This type of ligand has a strong affinity to remove Cd(II) and Pb(II) from the matrix solution depending on the pH of the sample solution. Cyanuric-SH has silanol groups that can interact with -COOH groups of activated MWCNTs and is capable of being strongly adsorbed at the surface of MWCNTs. In addition, the presence of MWCNTs provides more sites for both the chemical adsorption of the ligand (the modifier) and the relatively homogeneous distribution of cyanuric-SH at the surface of the solid base. Since the -COOH group of MWCNTs reacts with the -OH group of silanol, other functional groups such as -SH and -NH will remain intact. This will cause these functional groups to be free to interact with the metal ions, yielding a better preconcentration.

Figure 3 shows the AFM images of the unmodified MWCNTs (Fig. 3a) and cyanuric-SH-modified MWCNTs (Fig. 3b). As shown in Fig. 3b, cyanuric-SH covered the surface of the MWCNTs. FT-IR spectra (in the range of 4,000–400 cm⁻¹) of the modified MWCNTs with cyanuric-SH clearly show (Fig. 4) absorption bands at around 3,437 cm⁻¹, which are characteristic of the stretching vibration of the hydroxyl functional group (O–H) on the surface of MWCNTs or those of adsorbed water in the sample and the -NH group in cyanuric-SH. The absorption band at 1,730 cm⁻¹ corresponds to the stretching vibration of carbonyl group (C=O), while that of the carboxylate group (C=O) is observed at around 1,378 cm⁻¹. Stretching vibrations of the C=C group are located at 1,629 cm⁻¹. The absorption band at around 1,111 cm⁻¹ is assigned

Fig. 3 AFM images of unmodified MWCNTs (a) and modified MWCNTs (b)

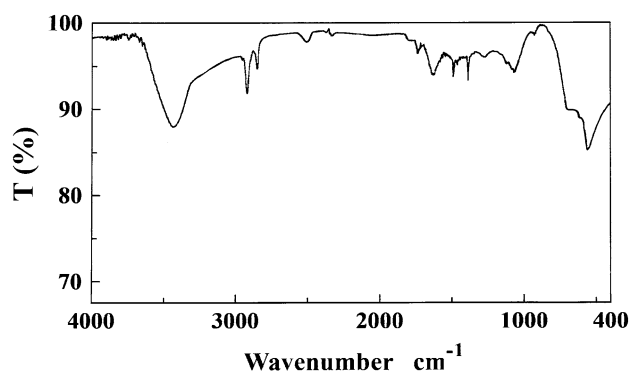
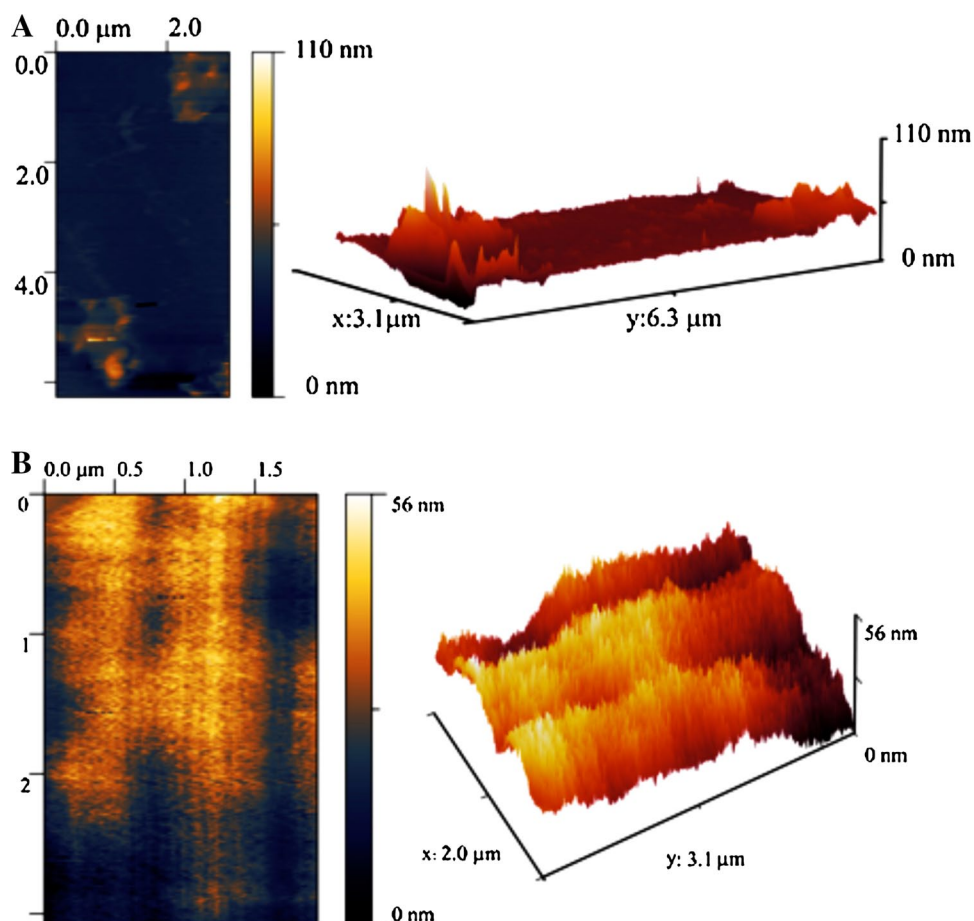


Fig. 4 FT-IR spectra of the modified MWCNTs with cyanuric-SH

to the stretching vibration of the C–C–C group and that at around $1,102\text{ cm}^{-1}$ is due to the stretching vibration of Si–O–Si units of silica. The bands at $2,920\text{--}2,940$ and $2,842\text{--}2,867\text{ cm}^{-1}$ are assigned to the stretching modes of the --CH_2 groups. The presence of these bands, the N–H deformation peak at $1,543\text{--}1,562\text{ cm}^{-1}$, implies that the silica surface is successfully modified by the amine spacer groups. Peaks in the $1,500\text{--}1,700\text{ cm}^{-1}$ range belong to the

skeletal vibration of the cyanuric ring. The S–H vibration band appears weakly at $2,572\text{ cm}^{-1}$.

In this study, cyanuric-SH-modified MWCNTs were used as a strong sorbent for the separation and preconcentration of Cd(II) and Pb(II) ions. However, when using MWCNTs as a mini-column packing material, it tended to create a flow resistance in the flow system and thus deteriorated the overall separation and preconcentration performance of the flow system due to the small size of the MWCNTs. Therefore, different graphite to MMWCNTs (w/w) ratios were investigated to find that a 1/1 (w/w) graphite to MMWCNTs ratio would give a suitable mixture as the mini-column packing material to avoid this resistance. Investigations revealed that graphite was not able to adsorb Cd(II) and/or Pb(II) ions when the target ion concentrations were $<5.0\text{ }\mu\text{g mL}^{-1}$ (with a flow rate of 1.5 mL min^{-1}). To check the influence of the amount of graphite on the adsorption ability of the sorbent to separate trace amounts of Cd(II) and Pb(II) ions, different amounts of the target ions were passed through a column containing a fixed amount (500 mg) of graphite. The results are presented in Fig. 5. These results confirm that MMWCNT has the main active solid phase to adsorb Pb(II) and Cd(II)

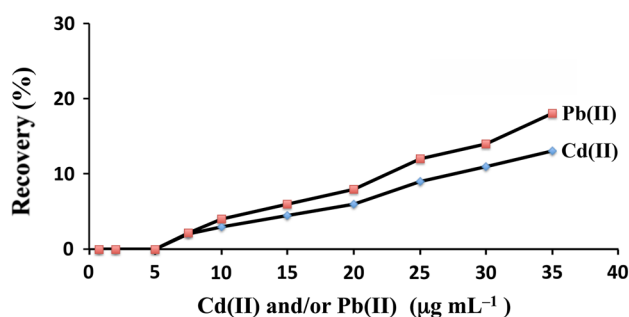


Fig. 5 Adsorption of the target ions by graphite. Conditions: sample volume containing Pb(II) and/or Cd(II), 250 mL; solution pH, 6.0; sample flow rate, 1.5 mL min⁻¹; HNO₃ (as an eluent), 0.10 mol L⁻¹; eluent volume, 5.0 mL; and eluent flow rate, 1.5 mL min⁻¹

ions at ultra trace levels, whereas graphite has no considerable effect on the recovery percentage of the target ions. To get the best conditions and good selectivity of MMWCNTs for preconcentration of Cd(II) and Pb(II), the effects of such experimental conditions as pH of the sample solution; type, concentration, and volume of the eluent; and the flow rate of the eluent on separation efficiency were studied and optimized.

Influence of variables

Different factors affecting the experimental results including pH of the sample solution, sample solution flow rate, elution flow rate, elution concentration, and elution volume were studied. For this purpose, a Teflon column packed with 110 mg of the sorbent (height of packing being about 40 mm) was used as the operational column.

The effect of sample solution pH on the preconcentration step of Cd(II) and Pb(II) was studied. For this purpose, experiments were conducted to determine the effects of sample solution pH on the separation of 50 μg Cd(II) and Pb(II) ions from 1,000-mL solutions in the pH range of 3.0–9.0 (using dilute HCl and/or NaOH solution). The pH of the eluent solution was also investigated for Cd(II) and Pb(II) concentration using FAAS (Fig. 6). The results showed that the suitable pH levels for the adsorption of Cd(II) and Pb(II) on MMWCNTs were about 7.0 and 6.0, respectively. This is due to the fact that the formation constants of Cd(II)–cyanuric-SH complex and Pb(II)–cyanuric-SH complex decrease in acidic solutions due to the protonation of the cyanuric-SH compound. Therefore, a buffer solution with pH 6.0 (0.05 mol L⁻¹) was used for the preconcentration step of both ions.

More experiments were carried out to choose a proper eluent for the adsorbed Cd(II) and Pb(II) ions after their extraction (50 μg Cd(II) and Pb(II)) from 1,000-mL solution, using MMWCNTs. The ions were eluted with

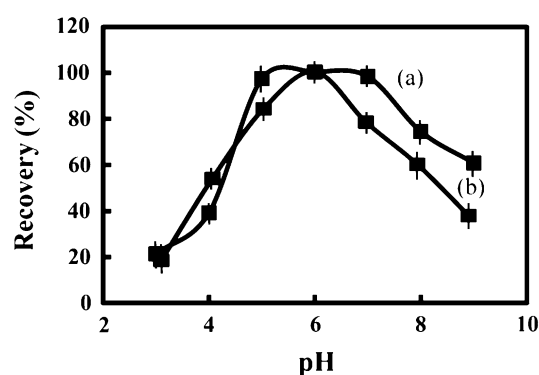


Fig. 6 Effect of pH on the retention of a Cd(II) and b Pb(II) in the column. Conditions: sample volume, 50 mL; sample flow rate, 0.5 mL min⁻¹; eluent volume, 3.0 mL; eluent flow rate, 0.5 mL min⁻¹; and HNO₃ concentration, 0.05 mol L⁻¹

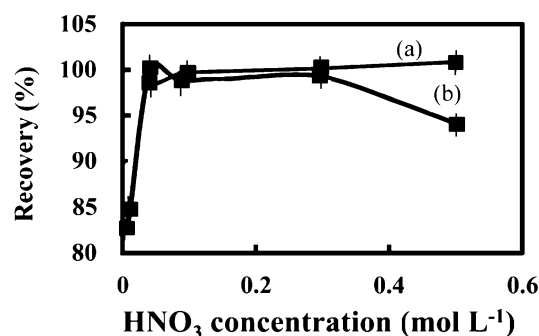


Fig. 7 Effect of the eluent concentration on the retention of a Cd(II) and b Pb(II) in the column. Conditions: pH, 6.0; sample volume, 50 mL; sample flow rate, 0.5 mL min⁻¹; eluent volume, 3.0 mL; and eluent flow rate, 0.5 mL min⁻¹

different types, volumes, and concentrations of HNO₃, HCl, and H₃PO₄. Among the three different acid solutions, 0.050 mol L⁻¹ nitric acid was found to be capable of recovering more than 98 % of Cd(II) and Pb(II) ions from MMWCNTs, while other acids such as 0.050 mol L⁻¹ HCl and H₃PO₄ were not able to complete the elution of Cd(II) and Pb(II) ions (Fig. 7).

The influence of HNO₃ volume (between 2 and 5.0 mL 0.05 mol L⁻¹ HNO₃) on the complete recovery of the metal ions after their preconcentration from 50.0 mL of 50 ng mL⁻¹ Cd(II) and Pb(II), and from 500 mL of 5.0 ng mL⁻¹ Cd(II) and Pb(II) was investigated. The results showed that Cd(II) and Pb(II) recovery percentages were maximized by up to 100 % in all the experiments when 3.0 mL of 0.05 mol L⁻¹ HNO₃ was used. Higher volumes of HNO₃, however, did not affect the recovery percentages. Therefore, 3.0 mL of 0.05 mol L⁻¹ HNO₃ was selected as the optimum eluent volume.

Experiments were carried out to determine the influence of eluent flow rate (HNO₃, 0.05 mol L⁻¹) in the range of

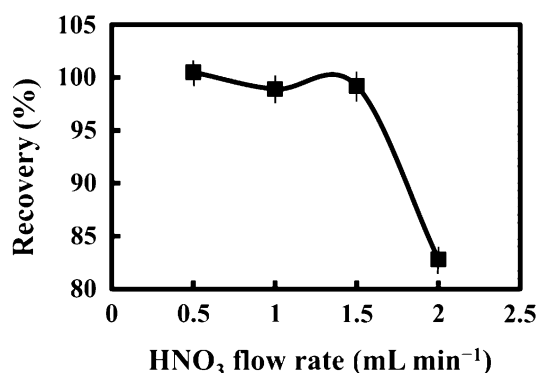


Fig. 8 Effect of eluent flow rate on the removal of Cd(II) and Pb(II) from the column. Conditions: pH, 6.0; sample volume, 50 mL; sample flow rate, 1.0 mL min⁻¹; eluent concentration, 0.05 mol L⁻¹; and eluent volume, 3.0 mL

0.5–2.0 mL min⁻¹ after preconcentration of 50.0 mL of 50 ng mL⁻¹ Cd(II) and Pb(II). The results showed that the recovery percentages of Cd(II) and Pb(II) were retained at their maximum values when using an elution rate of up to 1.5 mL min⁻¹ (Fig. 8), whereas higher flow rates decreased the recovery percentage. Therefore, 1.5 mL min⁻¹ was selected as the elution flow rate for further study.

The influence of sample flow rate on the adsorption of Cd(II) and Pb(II) into the column was also investigated using 50 mL of 50.0 ng mL⁻¹ Cd(II) and Pb(II) solutions. The solutions were passed through the modified column at flow rates between 0.50 and 3.0 mL min⁻¹. Then, the adsorbed Cd(II) and Pb(II) ions were washed using 3.0 mL of 0.05 mol L⁻¹ nitric acid solution. The Cd(II) and Pb(II) ion contents were measured using FAAS. The results showed that Cd(II) and Pb(II) recoveries remained at their maximum levels with increasing sample solution flow rates from 0.1 to 1.0 mL min⁻¹. However, the recovery values for Cd(II) and Pb(II), respectively, decreased to 98.8 ± 1.5 and 98.6 ± 1.6 % for 1.5 mL min⁻¹, and to 95.2 ± 1.5 and 95.0 ± 1.5 % for 2.2 mL min⁻¹. Higher flow rates did not give enough time for the reaction to reach equilibrium with the modified MWCNTs. Therefore, a sample flow rate of 1.0 mL min⁻¹ was used for further study.

Sorbent capacity

The maximum capacity of the 110 mg sorbent was determined by adding the solid phase to 50 mL of the aqueous solution containing 250 mg L⁻¹ Cd(II) and Pb(II) while stirring it for 20 min. The mixture was then passed through a filter paper and washed three times with water (each, 5 mL H₂O). The metal ions retained on the filter were determined using FAAS. The results revealed that the maximum capacity of the solid phase was 0.10 mmol of Cd g⁻¹ and 0.09 mmol of Pb g⁻¹, equal to 11.2 mg of Cd(II) and

18.6 mg of lead(II) ions per g of the solid phase. It is, therefore, necessary to select a sample volume with an appropriate amount of the solid phase to avoid column saturation.

Preconcentration factor

To explore the preconcentration factor from water sample, 1,000 mL of the sample containing 0.06–2.0 ng mL⁻¹ of Cd(II) and Pb(II) was passed through the column under the optimum conditions. The results showed that when Cd(II) and Pb(II) concentrations decreased to <0.1 and 0.3 ng mL⁻¹, respectively, the recovery levels also decreased and the column failed to recover the metal ions quantitatively from the sample solution.

The breakthrough volume of the sample solution was studied by passing different volumes (100, 250, 500, 750, 1,000, 1,500, 2,000, and 2,500 mL) of the sample solution containing 0.50 µg of Cd(II) and/or Pb(II) ions according to the recommended procedure. Based on the results obtained, it can be said that sample volume had no effect on the adsorption of Pb(II) and Cd(II) ions for volumes up to 2,000 mL (the breakthrough volume) for which target ion extraction exceeded 98.8 %. For higher volumes, however, a decline was observed in the recovery percentage. Thus, the preconcentration factor defined as the ratio of the volume of the standard solution (2,000 mL) to the volume of the eluting solution (3.0 mL) for the analytes was 660.

Detection limit, precision, reproducibility, and reusability

The detection limit of the proposed method for the determination of Cd(II) and Pb(II) ions under optimum experimental conditions was determined as 0.1 ng mL⁻¹ for Cd(II) and 0.3 ng mL⁻¹ for Pb(II).

The precision of the method was evaluated by separation and measurement of the ions in ten 100-mL solutions containing 50 ng mL⁻¹ Cd(II) and Pb(II) and in 500-mL solutions containing 5.0 ng mL⁻¹ Cd(II) and Pb(II). The results showed that the relative standard deviations were 4.2 and 4.5 % for Cd(II) and 3.4 and 3.5 % for Pb(II).

The reproducibility of the sorbent was investigated by separation and measurement of the ions in a 500-mL solution containing 5.0 ng mL⁻¹ Cd(II) and Pb(II) with ten replicates of solid sorbents (with the same size) prepared at different times. The relative standard deviations were found to be 3.9 % for Cd(II) and 3.8 % for Pb(II).

Reusability of the modified activated carbon was investigated using the same solid phase for sorption–desorption of Cd(II) and Pb(II) ions 40 times. The data indicated that the maximum change in the performance (i.e., recovery of target metal ions) of the solid would be <2 % even after 30 times. This finding indicates that a negligible amount of

Table 1 Comparison studies of the proposed method with those previously reported in literature based on flame atomic absorption spectrometry

Sorbent	Detected ion	Limit of detection (ng mL ⁻¹)	Interfering ions	Preconcentration factor	Real sample	Refs.
Activated carbon loaded with xylenol orange	Pb	0.4	Not studied	200	Water and wastewater	[8]
Carbon active modified with methyl thymol blue	Cd	1>	Cu, Hg	1,000	Water	[24]
Activated carbon loaded with xylenol orange	Cd	0.3	Cu	200	Water and wastewater	[25]
Polychlorotrifluoroethylene	Pb	7.2	Cu, Hg	Not reported	Water	[26]
2-[(Isopropoxycarbonylthio)disulfanyl]ethanethioate(IIDE)-modified silica gel	Pb	7.5	Not studied	200	Water	[27]
Amino thioamidoanthraquinone silica	Pb	22.5	Cu, Ni, Co, Fe	Not reported	Water	[28]
Silica gel modified with <i>p</i> -dimethylaminobenzaldehyde	Pb	1.1	Cr, Cu, Ni, Zn	125	Water	[29]
MWCNT modified with tris(2-aminoethyl)amine	Pb	0.32	Hg, Cu	60	Water	[30]
2-Aminothiophenoltrimethoxysilane	Pb	4.12	Not reported	Not reported	Water and wastewater	[31]
1-(2-Pyridyl Azo)2-Naphthol (PAN) complex on a Octadecyl bonded silica cartridges	Pb	50	Not studied	36	Water and wastewater	[32]
Oxidized MWCNTs	Pb	2.6	Not reported	44.2	Water and wastewater	[33]
Oxidized MWCNTs	Cd	11.4	Not reported	51	Water	[34]
MWCNTs modified with diphenylcarbazine	Cd	4	Not reported	360	Water	[35]
Amberlite XAD-1180 modified with thio-salicylic	Cd, Pb	1.1, 3.2	Mn, Co, Ni, Cu, Fe	143, 143	Water	[36]
2-Aminoacetylthiophenol modified with polyurethane foam	Cd,Pb	4.8, 6.6	Not reported	250, 167	Water	[37]
MWCNTs modified with iron phosphate	Cd	0.13	Not reported	31.2	Water and soil	[38]
Amberlite XAD-2 modified with 3-(2-nitrophenyl)-1 <i>H</i> -1,2,4-triazole-5(4 <i>H</i>)-Thione	Cd,Pb	0.22, 0.16	Ni, Cu	60, 60	Water and food	[39]
Nanoporous silica modified with diphenylcarbazine	Cd	0.15	Cu, Fe	294	Water, soil and ore	[40]

Table 1 continued

Sorbent	Detected ion	Limit of detection (ng mL ⁻¹)	Interfering ions	Preconcentration factor	Real sample	Refs.
Nano-alumina modified with sodium dodecyl sulfate-1-(2-pyridylazo)-2-naphthol	Cd, Pb	0.15, 0.17	Cu, Sn, Zn, Hg	250, 250	Water and food	[41]
MWCNTs modified with iminodiacetic acid	Cd, Pb	0.4, 0.7	V, Cr, Co, Cu, As	101, 66	Food	[42]
MWCNTs modified with poly(2-amino thiophenol)	Cd, Pb	0.3, 1.0	Al, Cr, Cu, Ni, Mn	284, 304	Water and food	[43]
MWCNTs modified with tartrazine	Cd, Pb	0.8, 6.6	Ca, Cu, Ni, Co, Fe	40, 40	Water	[44]
Sulfur-nanoparticle-loaded alumina	Cd, Pb	0.3, 0.63	Zn, Cu	83, 83	Marine	[45]
Silica gel modified with aminothioamidoanthraquinone	Cd, Pb	1.1, 22.5	Cu, Ni, Co	85, 85	Water	[46]
MWCNTs modified with L-alanine	Cd	1.03	Co, Cr, Hg, Ni	Not reported	Sediment	[29]
MWCNTs modified with 8-hydroxquinoline	Cd, Pb	1.0, 5.2	Co, Ni, Fe, Cu, Zn	336, 336	Water	[47]
Fe ₂ O ₃ nanoparticles modified with thiol	Cd, Pb	0.1, 0.4	Cu, Hg	151, 116	Water	[48]
Modified hollow fiber	Cd, Pb	0.1, 0.9	Cu, Fe, Zn	30, 30	Diesel and gasoline	[49]
MWCNTs modified with 4-(4-isopropylbenzylideneamino)thiophenol	Cd, Pb	1.6, 5.6	Ni, Zn, Fe	178, 178	Water and food	[50]
2-Acetylbenzothiazole modified mesoporous silica	Cd, Pb	20, 40	Hg, Cu	210, 210	Water	[51]
Silica gels modified with thiourea	Cd, Pb	0.81, 0.57	Hg, Cu, Zn	275, 275	Water and food	[52]
Silica disk modified with 2-mercaptobenzoimidazole	Cd, Pb	0.14, 0.18	Cu, Fe, Hg	245, 211	Water	[53]
Poly 1,8-diaminonaphthalene-MWCNTs	Cd, Pb	0.09, 0.7	Not reported	101.2, 175.2	Water	[54]
1-(2-Pyridylazo)-2-naphthol	Cd, Pb	0.04, 0.32	Not reported	180, 180	Foods and water	[55]
Nano-TiO ₂ modified with 2-mercaptobenzo-thiazole	Cd, Pb	0.12, 1.38	Hg, Cu	162, 180	Water and ore	[56]
Fe ₃ O ₄ -surfactant	Cd, Pb	0.15, 0.74	Co, Zn	Not reported	Water and soil	[57]
Ionic imprinted polymers	Cd, Pb	0.15, 0.5	Zn, Ni, Hg	152, 120	Food	[58]
MWCNT modified Cyanuric-SH	Cd, Pb	0.1, 0.3	No interference	660, 660	Water and wastewater	Present work

cyanuric-SH leaches from the surface of MMWCNTs during 30 times use of the column. Beyond this, however, the column needs to be refreshed with new sorbent materials.

In addition, no change was observed in the recovery of the target metal ions of the MMWCNTs after 5 months of storage.

Table 2 Result obtained for determination of Cd(II) and Pb(II) ions in different water samples ($n = 3$)

Sample	Proposed method, Cd(II)/ ng mL ⁻¹	Alternative method ^a , Cd(II)/ ng mL ⁻¹	Proposed method, Pb(II)/ ng mL ⁻¹	Alternative method ^a , Pb(II)/ ng mL ⁻¹
Tap water	0.3 ± 0.1	0.3 ± 0.1	<Limit of detection	<Limit of detection
Wastewater (I)	1.2 ± 0.1	1.1 ± 0.1	7.3 ± 0.2	7.5 ± 0.5
Wastewater (II)	1.8 ± 0.1	1.7 ± 0.1	17.2 ± 0.4	–
Zayandeh-Roud river water	<Limit of detection	<Limit of detection	5.3 ± 0.1	5.4 ± 0.3
NIST 1640a ^b	4.0 ± 0.1	–	12.2 ± 0.2	–
Radiator manufacturing wastewater	7.4 ± 0.3	7.2 ± 0.5	567.0 ± 8.9	572.2 ± 13.7
Rice sample	2.3 ± 0.2	1.9 ± 0.5	9.7 ± 0.5	10.0 ± 0.7

±Values are RSDs based on three replicate analyses

^a Samples were tenfold preconcentrated by evaporation at vacuum and then analyzed using ICP-OES

^b NIST 1640a SRM water sample contains 3.96 ± 0.07 ng mL⁻¹ Cd(II) and 12.01 ± 0.04 ng mL⁻¹ Pb(II)

Table 1 compares the values for limit of detection, relative standard deviation, and preconcentration factor obtained for the proposed method and those reported for solid-phase extraction methods for Cd(II) and Pb(II) [8, 24–58] based on different sorbents such as MWCNTs and other nanoparticles. The proposed method is also compared in the same table with respect to quantitative adsorption sample, limit of detection, and selectivity with the SH-based adsorbents in solid-phase separation of Cd and Pb ions.

Interference study

Matrix effect is an important problem in the separation and determination of metal ions in real samples. To assess the suitability of the proposed method in preconcentration (separation) and analysis of Cd(II) and Pb(II) in real samples, the interference of several cations and anions in the separation and measurement of Cd(II) and Pb(II) was examined under the optimized conditions. Various salts and metal ions were added individually to 100 ng mL⁻¹ of Cd(II) and Pb(II) solution, and the proposed method was applied for the preconcentration and determination of Cd(II) and Pb(II) ions. The results showed that 100,000-fold of alkali and alkaline earth, chloride, nitrate, hydrogen carbonate, and sulfate; and 5,000-fold Zn(II), Fe(II), Ni(II), Fe(III), Mn(II), Cu(II), Al(III), Mo(VI), Co(II), Cr(III), and Ag(I) did not affect the selectivity of the method for Cd(II); neither did 100,000-fold of alkali and alkaline earth, nitrate, hydrogen carbonate, chloride, carbonate and sulfate; 5,000-fold of Fe(II), Ni(II), Zn(II), Mn(II), Mo(VI), Co(II), Ag(I), Al(III), and Cr(III); and 300-fold of Cu(II) for the separation of Pb(II). However, more than 50-fold of Hg(II) was found to interfere for both Cd(II) and Pb(II). On the other hand, the tolerance limit for Hg(II) increased at 500-fold in the presence of 0.01 mol L⁻¹ NaCl in the buffer solution.

The results confirm that the modified solid phase is highly selective for the preconcentration of Cd(II) and Pb(II).

Real sample analysis

To validate the proposed method, different water samples including river water from the Zayandeh-Roud river (Isfahan, Iran), industrial wastewater (Mobarak Steel Complex, Isfahan, Iran), tap water after filtering the samples with a Millipore cellulose nitrate membrane of pore size 0.45 μm, radiator manufacturing wastewater, rice sample solution, and CRM (NIST 1640a) were selected. For preconcentration, the pH of the samples was adjusted to 6.0 with the buffer solution before analysis. In addition, the recovery experiments of different amounts of Cd(II) and Pb(II) were carried out. The results show that the new solid phase is capable of separating and preconcentrating Cd(II) and Pb(II) ions from water at trace levels (Table 2). The results of the water samples were also compared with those obtained from an alternative method (ICP-OES) after tenfold preconcentration of the samples using evaporation of the solvent in vacuum. The results confirm the accuracy and sensitivity of the proposed method for separation and detection of ultra trace amounts of Cd(II) and Pb(II).

Conclusion

This study demonstrated the suitability of the modified MWCNTs sorbents for the separation and preconcentration of ultra trace amounts of Cd(II) and Pb(II) ions. The procedure was also found to be economical for the preparation of MWCNTs due to its simplicity and sorbent reusability. Cadmium and lead ions were completely removed at pH 6.0. The adsorbed Cd(II) and Pb(II) ions were recovered

with 0.050 mol L⁻¹ nitric acid. The figures of merit of the proposed method vs. the same reported methods for Cd(II) and Pb(II) separation are presented in Table 1. As can be seen, the proposed method offers a suitable preconcentration factor and a low limit of detection. In addition, the preconcentration factor of the new sorbent is higher than those reported for Cd(II) and Pb(II) separation (660 for Cd(II) and Pb(II)). The tolerance limit of such interfering ions as Ag(I), Hg(II), and Fe(III) for the separation of Cd(II) and Pb(II) ions was found to be relatively high. The method can, therefore, be successfully employed for the preconcentration and determination of ultra trace amounts of cadmium and lead ions in different water samples using the modified MWCNTs and FAAS. The method was also used for the separation and determination of Cd(II) and Pb(II) ions in water, wastewater, and CRM water samples with a good accuracy and high recovery percentage.

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