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Magnetic Multi-Walled Carbon Nanotubes Modified with Polythiophene as a Sorbent for Simultaneous Solid Phase Microextraction of Lead and Cadmium from Water and Food Samples

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Polythiophene (PT) coated magnetic multi-walled carbon nanotubes (MMWCNTs) as a magnetic sorbent was synthesized and characterized by FT-IR, SEM, XRD and VSM. The sorbent was applied for the simultaneous solid-phase microextraction of trace amounts of lead and cadmium ions from various matrices. The retained analytes were eluted using nitric acid solution (0.5 M) and quantified by flame atomic absorption spectrometry. The main factors affecting the extraction of lead and cadmium such as pH, type and concentration of eluent, amount of the sorbent, ionic strength and sample volume were investigated and optimized. Under the optimized conditions, the detection limits (based on $3S_b/m$) of 0.54 and 0.03 $\mu\text{g l}^{-1}$ and the enhancement factors of 197.6 and 195.5 were obtained for lead and cadmium, respectively. The relative standard deviations of 1.5% ($n = 6$) at 50.0 $\mu\text{g l}^{-1}$ of lead and 2.1% at 5.0 $\mu\text{g l}^{-1}$ of cadmium were achieved. The method was found to be effective, selective, rapid, and simple for the determination of trace amounts of lead and cadmium and was successfully applied to the determination of lead and cadmium in water, black tea, rice, and milk samples without evident interference from the complex matrix. Furthermore, the sorbent showed high capacity, and the precision and accuracy of the method were satisfactory. The validity of the method was examined through the recovery experiments and independent analysis by electrothermal atomic absorption spectrometry.

Keywords: Flame atomic absorption spectrometry, Lead and cadmium, Magnetic solid-phase microextraction, Multi-walled carbon nanotubes, Polythiophene

INTRODUCTION

In these decades, the safe concentrations of toxic heavy metals in the environment are a great concern owing to the increase in industrial activities as well as their cumulative nature. Lead and cadmium are among the most hazardous heavy metals, causing great problems on human health through the accumulation in several organs [1,2]. Lead is known as a carcinogenic agent with irreversible effects on the human body which causes a variety of diseases and undesired health consequences. Lead accumulates in the

vital organs of humans and animals. Its cumulative poisoning effects on human health are brain damage, anemia, and kidney malfunctioning [3]. Cadmium is also highly toxic even at low concentrations, causing damages to different parts of the body such as kidneys, liver, and lungs. It is noteworthy that the International Agency for Research on Cancer (IARC) has classified cadmium and its compounds as Group 1 of carcinogenic materials [4]. Thus, due to the existence of very low levels of lead and cadmium in environmental and biological samples and the necessities of their monitoring, the sensitive analytical techniques are required for their determination in different samples [5]. Among various techniques, inductively coupled plasma

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mass spectrometry (ICP-MS) [6] and electrothermal atomic absorption spectrometry (ETAAS) [7] have relatively good sensitivity for the direct determination of these elements at trace levels. However, these methods suffer from the drawbacks of spectral and non-spectral interferences in complex matrices, as well as being costly. Flame atomic absorption spectrometry (FAAS), as an available and manageable instrument, is an alternative method for the determination of these metal ions but suffers from the limitations of low sensitivity and matrix interferences [8]. To alleviate these problems, a sample preparation step including separation and preconcentration of analytes is required. Various methods have been reported for the separation and preconcentration of heavy metals including solid-phase extraction (SPE) [9-11], solid-phase microextraction (SPME) [12,13], chemical coprecipitation [14], cloud point extraction (CPE) [15,16] and liquid-liquid microextraction (LLME) [17]. Among them, SPME, a modified mode of conventional SPE, has attracted much attention for separation and preconcentration of metal ions from samples with complex matrices. The advantages of SPME are simplicity, rapidity, the possibility of achieving high enrichment factors, low cost and low consumption of organic solvent [18]. However, the common sorbents used in SPE and SPME suffer from the disadvantages of low selectivity toward target analytes, low sorption capacity, as well as low stability under extreme conditions. To overcome these problems, nanostructured sorbents are promising due to their high surface area, enhanced active sites, and abundant functional groups on their surfaces. Among nanostructured materials, carbon nanotubes (CNTs), containing carbon atom layers in their wall, are classified as multi-walled carbon nanotubes (MWCNTs) or single-walled carbon nanotubes (SWCNTs) [19] are interesting sorbents owing to their unique properties of extremely high surface to volume ratio, as well as excellent thermal and electrical conductivities [20,21]. However, they have the limitations of small size, hydrophilicity, and high dispersibility which make their separation from the aqueous solution difficult. Furthermore, their affinity and selectivity toward heavy metal ions are limited. The limitation of separation can be overcome through the combination of CNTs with magnetic nanoparticles (MNPs) [22], whereas the affinity and selectivity toward heavy metal ions can be

improved through modification of the surface of carbon nanotubes with organic units with different functional groups. Up to now, different chelating agents such as (3-mercaptopropyl) silanetriolate [23], 1-(2-pyridylazo)-2-naphthol [24], 8-aminoquinoline [25], diphenylcarbazine [26], methyl-2-[2-(2-[2-(methoxycarbonyl) phenoxy] ethoxyethoxy) ethoxy] benzoate [27], 2-(2-benzothiazolylazo)orcinol [28], cyano [29], poly(2-amino thiophenol) [30] and 1,10-phenanthroline [31] have been used for modification of MWCNT.

Polythiophene (PT), the polymerized thiophene synthesized from inexpensive monomers, is a conducting polymer with optical properties such as dramatic color shifts in response to changes in solvent, temperature, applied potential, and binding to other molecules. Polythiophene-coated Fe₃O₄ has been synthesized and used as the sorbent in the solid phase extraction of plasticizer and precious metal ions [20,21,32,33]. In 2014, Mehdinia *et al.* [34] fabricate graphene/Fe₃O₄@polythiophene nanocomposite and used it for magnetic solid-phase extraction of polycyclic aromatic hydrocarbons from environmental water samples.

In this study, for the first time, PT was immobilized on the surface of magnetized multi-walled carbon nanotubes and used as the sorbent for the simultaneous magnetic solid-phase microextraction (MSPME) of lead and cadmium. The presence of abundant sulfur-containing functional groups of polythiophene on the surface of magnetic multi-walled carbon nanotubes (MMWCNTs) leads to the fabrication of a potential sorbent with a high number of active sites, and ease of magnetic separation for the lead and cadmium. The extracted ions were quantified by flame atomic absorption spectroscopy (FAAS). The factors affecting the separation and preconcentration of analytes were optimized, and the capability of the method for extraction and determination of analytes from various matrices was investigated.

EXPERIMENTALS

Apparatus

An Analytik Jena novAA 300 (model 330, Germany) atomic absorption spectrometer, equipped with hollow cathode lamps and an air-acetylene flame was used for Pb and Cd measurements. Hollow cathode lamps of Pb and Cd were operated at the currents of 5.0 and 4.0 mA,

wavelengths of 283.3 and 228.8 nm and the spectral bandwidths of 0.5 and 0.5 nm, respectively. The eluent was introduced to the FAAS for quantification of analytes *via* a single-line flow injection system consisting of a rotary injection valve (Rheodyne, CA, USA), various loops, and a peristaltic pump (Ismatic, MS-REGLO/8-100, Zurich, Switzerland). A Metrohm pH meter (model 691, Switzerland) equipped with a combined glass-calomel electrode was used for the pH measurements. A strong neodymium-iron-boron (Nd₂Fe₁₂B) magnet (1.2 T, 10 cm × 5 cm × 2 cm) was applied for the magnetic separation.

Reagents and Materials

All the glassware used for the trace analysis was kept overnight in a 10% nitric acid solution and subsequently rinsed twice with double distilled water just before use. Double distilled water was used throughout the procedure and sample preparation. Iron(II) chloride tetrahydrate, iron(III) chloride hexahydrate, multi-walled carbon nanotubes (MWCNT), iron(III) chloride and thiophene were purchased from Sigma-Aldrich (St. Louis, MO, USA). Ethanol, hydrochloric acid, nitric acid, and ammonia were purchased from Merck Company (Darmstadt, Germany). Stock standard solutions (1000 mg l⁻¹) of Pb(II) and Cd(II) were prepared by dissolving the proper amounts of Pb(NO₃)₂ (Merck, Darmstadt, Germany) and Cd(NO₃)₂·4H₂O (Merck, Darmstadt, Germany) in 1.0 ml nitric acid (63% w/v) and diluting to the mark with double distilled water in 100 ml flask. Working solutions were prepared daily by serial dilutions of the stock solutions.

Preparation of the Sorbent

Synthesis of MMWCNTs nanocomposite. MMWCNT was prepared by chemical coprecipitation method as reported by Gong *et al.* [35] with minor modifications. Thus, the MWCNT was carboxylated through refluxing with concentrated nitric acid and stirring at 60 °C for 6 h followed by filtration, washing with double distilled water and ethanol and drying in an oven at 50 °C overnight. Then, 0.5 g of oxidized MWCNT was dispersed in 50.0 ml of water, added to a solution containing 2.0 g FeCl₃·6H₂O and 0.7 g FeCl₂·4H₂O and was heated for 15 min at 80 °C under nitrogen gas. Finally, 10.0 ml concentrated NH₃ was added dropwise to the mixture under vigorous stirring (1000 rpm)

using a mechanical stirrer. When the reaction was completed (about 30 min), the black precipitate was collected with the help of a magnet, washed with double distilled water and ethanol, dried in an oven at 60 °C and stored for further modification.

Modification of MMWCNT with Polythiophene

The MMWCNT was modified with polythiophene by a procedure similar to that reported by Mehdinia *et al.* [34] for the fabrication of graphene/Fe₃O₄@polythiophene nanocomposite; *i.e.*, 0.3 g of the prepared MMWCNT was suspended in 55.0 ml of dried CHCl₃ under the nitrogen atmosphere in an ultrasound bath for 30 min. Then, 2.0 g of anhydrous FeCl₃ (as the oxidant) was slowly added to the mixture and stirred mechanically for 30 minutes. After that, 0.25 g of thiophene was added to the reaction mixture and was mixed for 6 h with a mechanical stirrer at 5 °C. In the next step, 50.0 ml of ethanol (70%) was added to the mixture and left at room temperature for 12 h. Finally, the prepared sorbent of MMWCNT coated with polythiophene (MMWCNT@PT) was washed with 300.0 ml of 1.0 M HCl, followed by double distilled water until the solution became neutral. Afterward, the sorbent was rinsed with 100.0 ml of ethanol and dried at 50 °C for 24 h for further use. The synthesized MMWCNT@PT was characterized by Fourier-transform infrared (FT-IR) spectroscopy, scanning electron microscopy (SEM), X-ray diffraction (XRD), and vibrating sample magnetometer (VSM).

Preparation of Real Samples

Water samples. The water samples were collected in polyethylene bottles and after the collection was acidified to pH 1.0 with nitric acid. Then, the samples were filtered through a 0.45 μm Millipore filter and the pH was adjusted to 6.0. Then, 15.0 mg of sorbent was added to 150.0 ml of each sample and treated according to the developed procedure.

Black Tea and Rice Samples

The black tea and rice samples were purchased from the local market. Each sample was washed with double distilled water and dried at 110 °C in an oven. Afterward, the sample was ground and 10.0 ml of concentrated HNO₃ and 3.0 ml H₂O₂ (30% w/w) was added to 250.0 mg of each sample

and heated to dryness on a heater-stirrer. The residue was dissolved in 10.0 ml of double-distilled water, filtered, the pH was adjusted to 6.0 and diluted to a 50.0 ml in a volumetric flask [36].

Milk Samples

The pasteurized cow milk, and infant dry formula milk samples were purchased from a local supermarket in Yazd, Iran. 15.0 ml of cow milk or 1.0 g of infant dry formula milk sample was transferred to a PTFE digestion vessel; 10.0 ml concentrated HNO₃ was added and kept at room temperature for 24 h. Then, 2.0 ml hydrogen peroxide (30% w/w) was added and the mixture was placed in a water bath for half an hour. Afterward, it was cooled to room temperature and filtered into a 100.0 ml volumetric flask; the pH was adjusted to 6.0 and diluted to the mark with distilled water [37].

Extraction Procedure

The pH of 150 ml of the sample or standard solution containing not more than 30.0 and 3.0 µg of lead and cadmium, respectively, was adjusted to ~ 6.0 upon addition of diluted hydrochloric acid or sodium hydroxide solution. Then, 15.0 mg of the prepared sorbent of MMWCNT@PT was added, and the mixture was stirred thoroughly for 3 min for complete sorption of the metal ions. After that, a strong magnet was placed at the bottom of the beaker to collect the sorbent containing the analytes and the bulk aqueous phase was decanted. The analytes were desorbed with 750.0 µl of nitric acid (0.5 M), the sorbent was retained using a magnet, and the analytes in the supernatant solution were quantified with FAAS equipped with a single line flow injection system.

RESULTS AND DISCUSSION

In the initial experiments, it was observed that the prepared sorbent has a high affinity for the sorption of lead and cadmium from aqueous solution. This observation can be related to the interaction of sulfur atoms of polythiophene and analytes through hard-soft acid-base theory, as well as the cation-induced polarization and electrostatic force between the cations and the permanent quadruple of the π -electron-rich aromatic structure of

polythiophene and MWCNT. Based on this observation, a MSPME method for separation and preconcentration of lead and cadmium was designed. The experimental variables such as pH of the sample solution, nature, volume, and concentration of eluent, the extraction and desorption time, the amount of the sorbent, and sample volume affecting the extraction procedure were optimized using the univariable method.

Characterization of the Sorbent

The morphology of oxidized MWCNT, MMWCNT, and MMWCNT@PT nanostructure was investigated using SEM images as shown in Fig. 1a-c, respectively. The SEM micrographs depicted in Fig. 1a and b show that Fe₃O₄ nanoparticles have grown and well distributed on the MWCNT surface. The SEM images of Fig. 1b and c revealed that the size of MMWCNT before coating with PT is less than 50 nm while after coating with PT, it is about 50-60 nm indicating the formation of a thin layer of the polymer on the surface of MMWCNT.

The Fourier transform infrared spectra of oxidized MWCNT, MMWCNT, and the modified MMWCNT with polythiophene are shown in Fig. 2. In oxidized MWCNTs (Fig. 2a), the bands at 1630 and 1740 cm⁻¹ correspond to COO⁻ asymmetric and C=O stretching of the carboxylate group, respectively. The bands at 2923 and 2856 cm⁻¹ are due to the -CH stretching while the strong broad absorption band at 3432 cm⁻¹ can be ascribed to the -OH stretching vibration of the -COOH group. In Fig. 2b and c, the appearance of a band around 590 cm⁻¹ corresponds to the Fe-O-Fe stretching vibration, indicating that Fe₃O₄ NPs are successfully anchored onto the MWCNT. The advent of the absorption band at 793.5 cm⁻¹ and 440 cm⁻¹ corresponding to the C-S and C-S-C stretching vibration of thiophene, respectively, confirms the immobilization of polythiophene on the MMWCNT.

The prepared sorbent was characterized by powder XRD in the 2 θ region of 10-80°. According to the XRD pattern (Fig. 3A), the diffraction peak at 2 θ of 25.91 is attributed to CNTs. Likewise, all the characteristic diffraction peaks of the pure cubic spinel crystal of Fe₃O₄ at 2 θ of 30.21, 35.61, 43.33, 53.60, 57.29 and 62.89 are present in the MMWCNTs which confirmed the successful synthesis of MMWCNT nanocomposite.

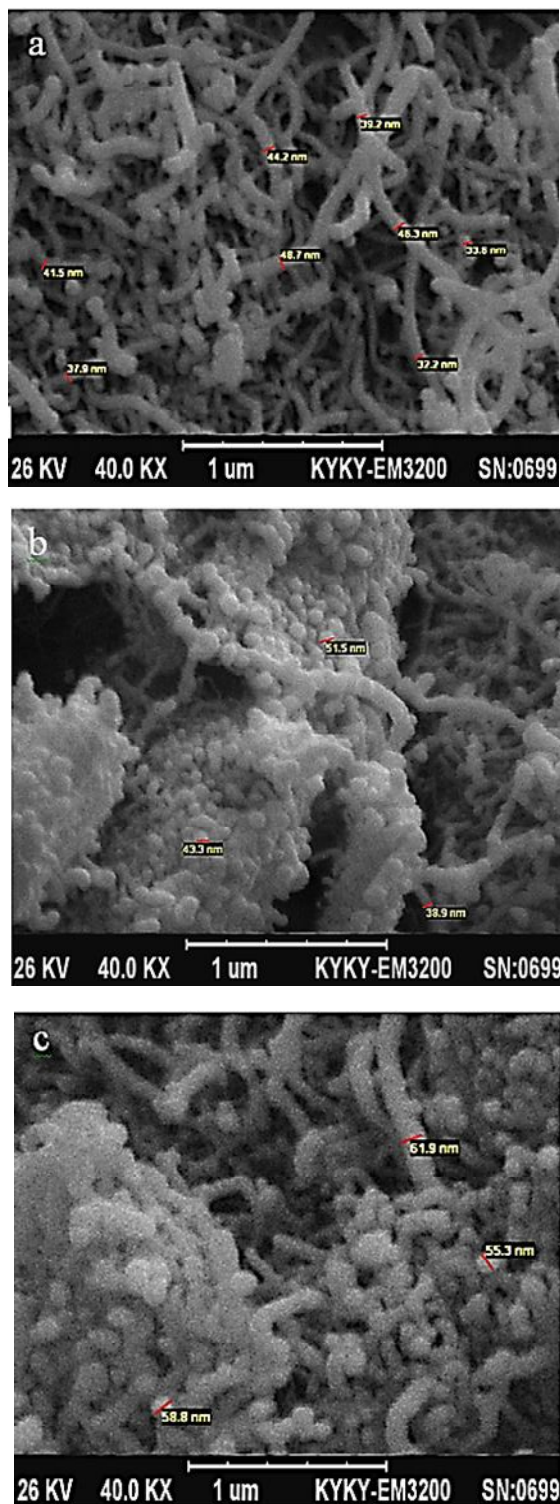


Fig. 1. The SEM images of oxidized MWCNT (a), MMWCNT (b), and MMWCNT@PT (c).

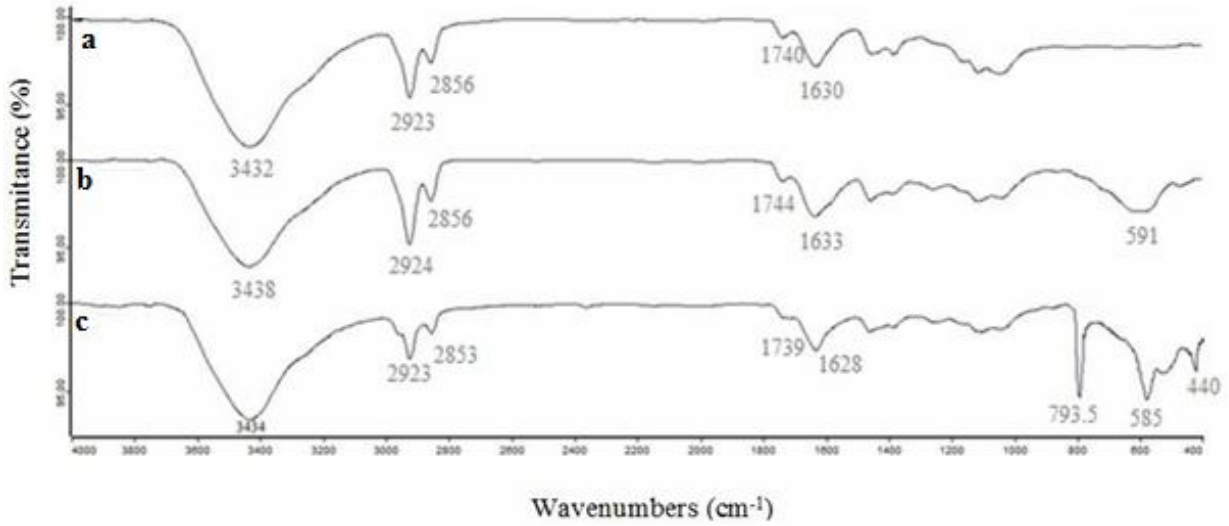


Fig. 2. FT-IR spectra of oxidized MWCNT (a), MMWCNT (b), and MMWCNT@PT (c).

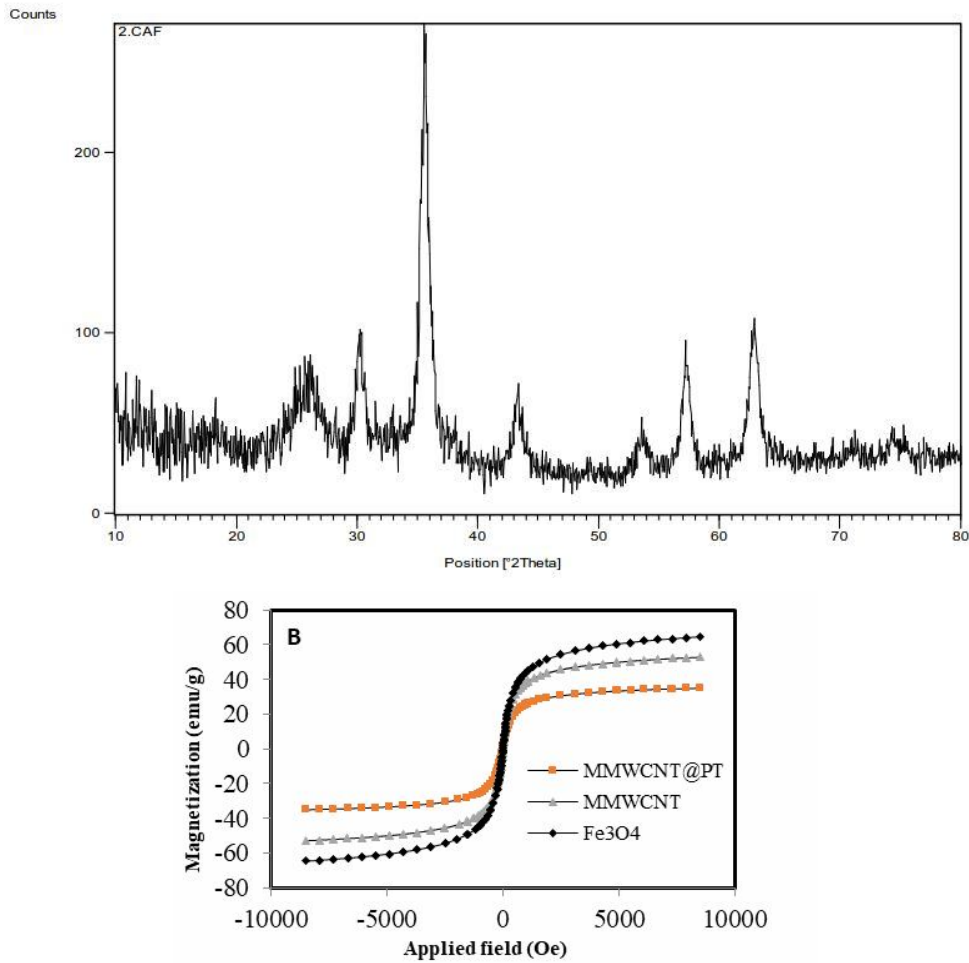


Fig. 3. XRD spectrum of MMWCNT@PT (A), and VSM of Fe₃O₄, MMWCNT, and MMWCNT@PT (B).

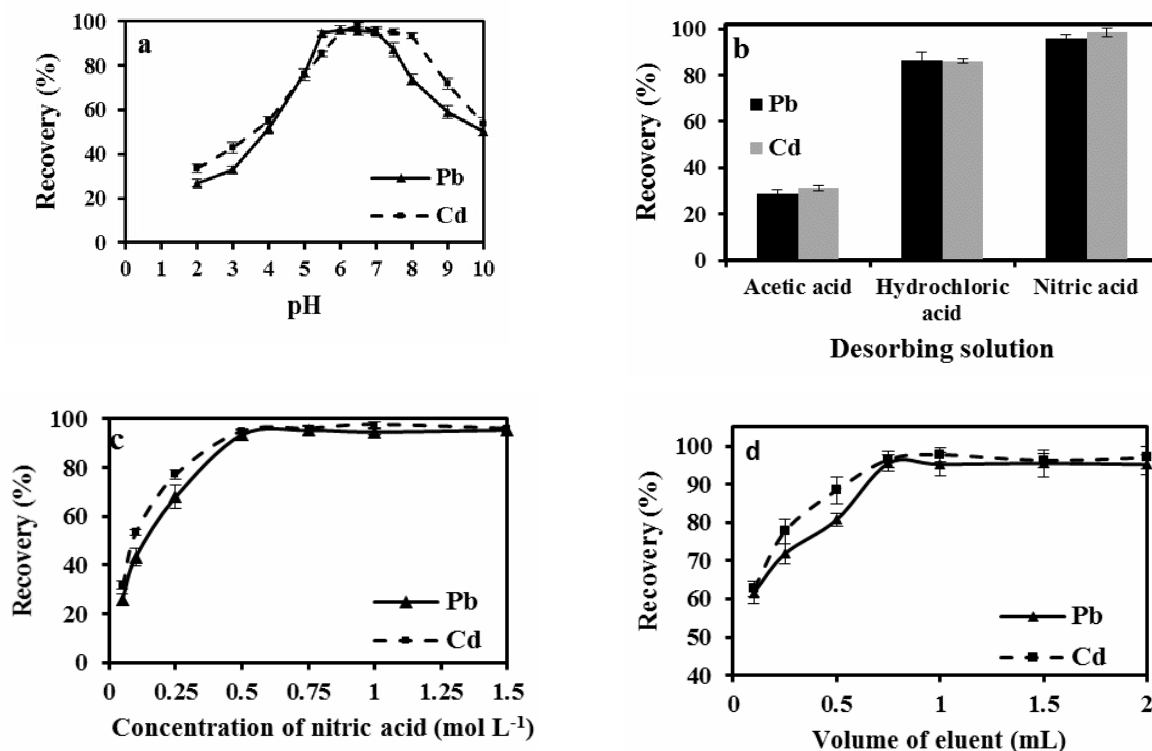


Fig. 4. The effect of pH (a), type of eluent (b), concentration of eluent (c), volume of eluent (d), and extraction time (e), on the extraction recovery of Pb(II) and Cd(II). Extraction conditions: sample solution, 100.0 ml of 40.0 $\mu\text{g l}^{-1}$ Pb(II) and 4.0 $\mu\text{g l}^{-1}$ Cd(II); sorbent, 15.0 mg.

Furthermore, the magnetic property of the MMWCNT@PT nanocomposites was considered through the vibrating sample magnetometer study. As shown in Fig. 3B, the absence of hysteresis loops in the field-dependent magnetization measurement indicates the superparamagnetic property of the nanocomposites. The saturation magnetizations of Fe_3O_4 , MMWCNT, and MMWCNT@PT were found to be 64.66, 52.87 and 35.05 emu g^{-1} , respectively. Furthermore, the results indicate that although the modification of Fe_3O_4 with MWCNT and polythiophene resulted in the reduction of the saturation magnetization of Fe_3O_4 , its saturation magnetization is still high enough to make feasible the rapid separation of the prepared sorbent from solution using an external magnet.

Effect of Sample pH

An optimum pH of the sample solution can improve the

efficiency of extraction and decrease the matrix interferences. Therefore, the effect of the sample pH on the extraction of Pb(II) and Cd(II) was studied by varying the pH in the range of 2.0-10.0. The pH of the solution was adjusted using 0.1 M of hydrochloric acid or sodium hydroxide solution. As shown in Fig. 4a, the optimum pH ranges for lead and cadmium were 5.5-7.0 and 6.0-8.0, respectively. The sharp decrease in the extraction efficiency at lower pH can be related to the competition of proton with analytes for interaction with sulfur atoms of polythiophene, whereas the decrease in the extraction efficiency at high pH may be due to the formation of hydroxide of the metal ions. Therefore, for the simultaneous extraction of both analytes, a pH of approximately 6.0 was selected for the subsequent experiments.

Effect of Desorbing Solution

The nature, concentration, and volume of the desorbing

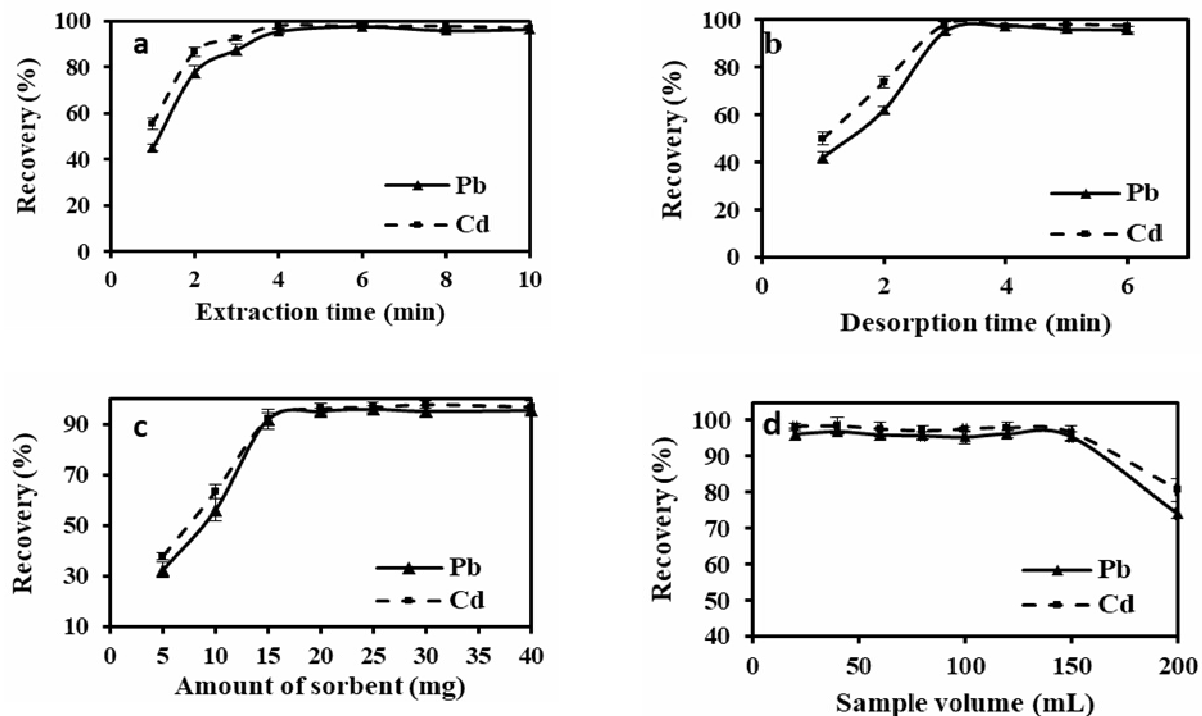


Fig. 5. The effect of extraction time (a), desorption time (b), amount of sorbent (c), and sample volume (d) on the extraction recovery of Pb(II) and Cd(II). Extraction conditions: analyte concentration, $40.0 \mu\text{g l}^{-1}$ Pb(II) and $4.0 \mu\text{g l}^{-1}$ Cd(II); pH = 6; desorbing solvent, $750 \mu\text{l}$ of 0.5 M nitric acid.

solution play an essential role in enhancement factors, as well as the quantitative extraction of analytes. The desorbing solution must have a high affinity toward the target analytes for their quantitative recovery in a minimum volume in a short time. To select the best eluent, 1.0 ml of different acid solutions including nitric acid, hydrochloric acid and acetic acid with a concentration of 1.0 M were examined based on the results of Fig. 4b. The highest desorption recovery was achieved with nitric acid and was selected as the desorbing sorbent. Then, the effect of the nitric acid concentration on the extraction efficiency of analytes was studied by changing its concentration in the range of 0.05-1.5 M. The results (Fig. 4c) indicate that the extraction efficiency increased with increasing the nitric acid concentration up to 0.5 M and then leveled off at higher concentration. Therefore, subsequent tasks were performed with 0.5 M nitric acid. In the next step, the effect of the volume of the desorbing solution in the range of 100-2000 μl on the analytes recoveries was studied, and a

volume of 750 μl was found to be sufficient for the quantitative recoveries and determinations of analytes (Fig. 4d). Thus, 750 μl of 0.5 M nitric acid was chosen as the desorbing solution in further experiments.

Effect of Extraction and Desorption Time

In an extraction procedure, the extraction and desorption time plays an important role in the speed of analysis and extraction efficiency. Therefore, the effect of the extraction time under the other optimized conditions was investigated by varying time in the range of 1.0-6.0 min. The results (Fig. 5a) indicate that the recovery of the analytes increased with an increase in the extraction time up to 3.0 min and then leveled off at higher extraction time. The effect of desorption time in the range of 1-10 min was also investigated. The results (Fig. 5b) revealed that 4 min is required for the quantitative desorption of the analytes from the sorbent. Therefore, an extraction time of 3 min and desorption time of 4 min was chosen for the subsequent

experiments. The short extraction time can be related to the large surface area between the sorbent and the aqueous phase.

Effect of the Amount of Sorbent

The effect of the sorbent amount on the recoveries of Pb(II) and Cd(II) was also studied by varying the mass of the sorbent within the range of 5.0-40.0 mg (Fig. 5c). It was observed that 15.0 mg of the sorbent was sufficient for the quantitative extraction of both analytes. The low consumption of sorbent can be related to the high capacity of the prepared nano-sized composite with a large surface to volume ratio.

Effect of Sample Volume

The effect of sample volume is another important aspect of the method development showing the capability of the method in the achievement of a high preconcentration factor. Thus, different volumes of the sample solution (20-200.0 ml) containing 10.0 µg of Pb(II) and 1.0 µg of Cd(II) were extracted under the optimized conditions (Fig. 5d). Based on the experimental results, the recoveries of analytes were constant and maximum up to a sample volume of 150.0 ml and then decreased by a further increase in the sample volume. By considering the maximum initial sample volume (150.0 ml) and the final desorbing solution volume (750 µl), a preconcentration factor of 200.0 was calculated for both analytes.

Sorbent Capacity

Sorbent capacity is one of the figures of merit of sorbent and is defined as the maximum amount of the analyte retained by one gram of the sorbent. To determine the sorbent capacity, 25.0 mg of the sorbent was added to 100.0 ml of the solution containing 4.0 mg of Pb(II) and 2.0 mg Cd(II) at pH 6.0. The mixture was stirred for 30 min to guarantee the achievement of equilibrium in the extraction system, the sorbent was retained with a magnet, and the amount of Pb(II) or Cd(II) in the supernatant solution was determined by FAAS. The capacity of the sorbent was calculated according to the following equation:

$$q_e = \frac{(C_i - C_e) \times V}{W}$$

where q_e is the adsorption capacity (mg g^{-1}), C_i and C_e are the initial and equilibrium concentrations (mg l^{-1}) of lead and cadmium ions, W (g) is the amount of the adsorbent and V (l) is the volume of the aqueous solution. The capacity of the sorbent was found to be 117.0 and 73.6 mg g^{-1} for Pb(II) and Cd(II), respectively.

Influence of Interfering Ions

The selectivity of the MSPME is a crucial factor that should be considered. Therefore, the selectivity of the developed method was examined by extracting the analytes from 100.0 ml of a solution containing 40.0 and 4.0 $\mu\text{g l}^{-1}$ of Pb(II) and Cd(II), respectively, in the presence of various cations and anions commonly present in the real samples or forming the complex with thiophene. The tolerance limit of each ion was taken as the maximum concentration of the ion causing a $\pm 5\%$ error in the extraction recovery of the analytes. The results of this study are summarized in Table 1, indicating that at the given mole ratio, the examined ions do not interfere with the extraction and determination of analytes. Thus, the method has a good selectivity for the determination of Pb(II) and Cd(II) in various matrices.

Reusability Studies

The reusability and regeneration of the sorbent were assessed through performing 12 consecutive adsorption-desorption cycles under the optimized conditions. The results showed that polythiophene induced a good stability to MMWCNT and the sorbent was reusable in the repetitive operation process without any significant loss in sorption capacities or recoveries of the studied ions.

Analytical Performance

Under the optimized conditions, the analytical performance of the developed method was investigated for Pb(II) and Cd(II). The results are summarized in Table 2. For a sample volume of 150.0 ml, the method showed linearity in the concentration ranges of 2.0-200.0 and 0.2-20.0 $\mu\text{g l}^{-1}$ of Pb(II) and Cd(II), respectively. The equations of the calibration curves were $A = 0.00199C + 0.0003$ and $A = 0.02356C + 0.0056$ with a determination coefficient (R^2) of 0.9992 and 0.9994 for Pb(II) and Cd(II), respectively. In these equations, A is the absorption of the

Table 1. Tolerance Limits of Foreign Ions for the Determination of Lead and Cadmium (n = 3)

Ion	Mole ratio		Recovery (%)	
	Pb	Cd	Pb	Cd
Na ⁺	5000	5000	96.2 ± 4.3	99.7 ± 4.3
K ⁺	5000	5000	101.8 ± 3.1	99.2 ± 3.5
Ca ²⁺	10000	10000	98.5 ± 3.4	96.7 ± 3.8
Mg ²⁺	1000	1000	98.3 ± 2.5	98.7 ± 2.6
Ba ²⁺	1000	1000	99.0 ± 3.1	98.5 ± 2.5
Ag ⁺	50	30	95.8 ± 3.8	99.1 ± 3.1
Pd ²⁺	100	50	97.2 ± 4.1	97.7 ± 3.8
Cu ²⁺	200	200	96.5 ± 3.1	97.9 ± 4.2
Ni ²⁺	1000	1000	101.5 ± 3.8	101.8 ± 2.5
Zn ²⁺	1000	1000	103.2 ± 3.1	98.7 ± 2.8
Co ²⁺	500	500	97.0 ± 3.8	99.7 ± 4.3
Hg ²⁺	200	100	98.0 ± 3.1	99.5 ± 2.5
As ³⁺	1000	1000	102.0 ± 2.4	100.5 ± 3.3
Cr ³⁺	500	1000	101.8 ± 3.1	99.2 ± 3.5
NO ₃ ⁻	1000	1000	98.5 ± 3.4	96.7 ± 3.8
Cl ⁻	1000	500	98.3 ± 2.5	98.7 ± 2.6
Br ⁻	1000	1000	103.2 ± 3.1	98.5 ± 2.5
PO ₄ ³⁻	200	200	98.5 ± 3.8	99.1 ± 3.1
SO ₄ ²⁻	500	500	104.1 ± 4.1	97.7 ± 3.8
CO ₃ ²⁻	1000	1000	96.5 ± 3.1	97.9 ± 4.2
F ⁻	1000	1000	101.5 ± 3.8	101.8 ± 2.5

analyte in the extract and C is its concentration ($\mu\text{g l}^{-1}$) in the initial solution. The limits of detection and quantification of Pb(II) and Cd(II), defined as $3S_b/m$ and $10S_b/m$, respectively, (where S_b is the standard deviation of the blank and m is the slope of the calibration curve) were

0.54 and $1.82 \mu\text{g l}^{-1}$ for lead 0.03 and $0.11 \mu\text{g l}^{-1}$ for cadmium. The relative standard deviations (RSD) of six replicate extractions and measurements at $50.0 \mu\text{g l}^{-1}$ concentration level for Pb(II) and Cd(II) were 1.5 and 2.1%, respectively.

Table 2. Analytical Performance Characteristics of MSPME Method for Determination of Lead and Cadmium Ions

Parameter	Figure of merit	
	Pb	Cd
Equation	$A = 0.00199C + 0.0003$	$A = 0.02356C + 0.0056$
r^2	0.9992	0.9994
Linear range	2-200	0.2–20
EF	197.6	195.5
PF	200	200
LOD ($\mu\text{g l}^{-1}$)	0.54	0.03
LOQ ($\mu\text{g l}^{-1}$)	1.82	0.11
RSD% (n = 6)	1.5	2.1

EF: enhancement factor; PF: preconcentration factor; LOD: limit of detection; LOQ: limit of quantification; RSD: relative standard deviation.

Table 3. Determination of Lead and Cadmium in Water Samples (n = 3)

Sample	Added ($\mu\text{g l}^{-1}$)		Found ($\mu\text{g l}^{-1}$) ^a		Recovery (%)		GF-AAS ($\mu\text{g l}^{-1}$) ^a	
	Pb	Cd	Pb	Cd	Pb	Cd	Pb	Cd
Tap water	0	0	3.71 ± 2.16	N.D			3.56 ± 2.25	N.D
	20	10	23.81 ± 2.39	9.78 ± 1.96	100.5	97.8		
River water (Karoon)	0	0	5.42 ± 2.69	N.D			5.70 ± 3.18	N.D
	20	10	25.23 ± 1.98	10.24 ± 3.41	99.0	102.4		
Well water	0	0	6.14 ± 1.28	0.69 ± 2.86			6.21 ± 2.32	0.75 ± 3.24
	20	10	25.83 ± 0.58	11.04 ± 2.62	98.4	103.5		
Sea water (Persian Gulf)	0	0	17.55 ± 1.99	4.12 ± 1.45			17.92 ± 3.41	4.18 ± 4.12
	20	10	36.86 ± 1.32	14.43 ± 1.25	96.6	103.1		

Table 4. Determination of Lead and Cadmium in Food Samples

Sample	Added ($\mu\text{g g}^{-1}$)		Found ($\mu\text{g g}^{-1}$) ^a		Recovery (%)		GF-AAS ($\mu\text{g g}^{-1}$) ^a	
	Pb	Cd	Pb	Cd	Pb	Cd	Pb	Cd
Black tea	0	0	5.62 ± 0.89	0.53 ± 1.88			5.58 ± 2.37	0.56 ± 5.35
	10	2	15.66 ± 1.27	2.54 ± 1.96	100.4	100.5		
Rice	0	0	N.D	0.45 ± 2.20			N.D	0.43 ± 4.65
	10	2	9.80 ± 1.02	2.37 ± 2.11	98.0	96.0		
Infant dry formula milk ^b	0	0	1.35 ± 2.22	0.03 ± 3.30			1.34 ± 3.73	0.03 ± 6.66
	10	2	11.14 ± 1.07	1.98 ± 2.02	97.9	97.5		
Infant dry formula milk ^c	0	0	3.86 ± 2.07	0.02 ± 3.57			3.82 ± 4.70	0.02 ± 5.00
	10	2	13.90 ± 3.59	1.95 ± 1.53	100.4	96.5		
Cow's milk ($\mu\text{g l}^{-1}$)	0	0	60.68 ± 2.47	2.55 ± 3.92			61.21 ± 4.28	2.61 ± 4.00
	10	2	71.16 ± 1.40	4.49 ± 3.30	104.8	97.0		

^aAverage and relative standard deviation of three determinations. ^bShad noush Company. ^cPuyan Company.

The enhancement factors, defined as the ratio of the slope of the calibration curve with and without preconcentrations, were found to be 197.6 for Pb and 195.5 for Cd. The closeness of the enhancement factors to the preconcentration factor (200.0) indicates that the extraction of analytes is almost quantitative. The extraction recovery was calculated by dividing the enhancement factor of each analyte to the preconcentration factor and were found to be 98.8 and 97.7 for Pb(II) and Cd(II), respectively.

Validation and Application of the Method

The feasibility of the method was assessed through the application of the method to the determination of Pb(II) and Cd(II) in tap water, well water, river water (Karooon), seawater (Persian Golf), black tea, rice, and milk samples. The accuracy of the method was evaluated by the recovery experiment as well as comparing the results with data obtained from an independent analysis using electrothermal atomic absorption spectrometry (ETAAS). As demonstrated

in Tables 3 and 4, the recoveries of the spiked samples are almost quantitative (96.0-104.8%) and at the 95% confidence level, there is no significant difference between the results obtained by the developed method and those obtained by ETAAS analysis. Thus, the developed procedure is reliable for the extraction and determination of lead and cadmium in a wide range of samples examined.

Comparison of the Method with Other SPE Methods Combined with FAAS

The merit of the sorbent was considered by comparing the analytical performance of the developed method with some recently reported SPE procedure using nanocomposite sorbent combined with FAAS for determination of lead and cadmium. As Table 5 shows, with the exception of the references [30,43] the prepared sorbent has an excellent capacity, low detection limit with comparable relative standard deviation. Furthermore, with a 150.0 ml sample volume, the enhancement factor of the developed method is

Table 5. Characteristic Performance Data of the Proposed Method and other SPE Methods Using Nanocomposite Sorbent for FAAS Determination of Lead and Cadmium

Sorbent	Analyte	LOD ($\mu\text{g l}^{-1}$)	RSD (%)	EF	Sample volume (ml)	Capacity (mg g^{-1})	Ref
TiO ₂ NPs modified with alizarin red S	Pb	0.30	1.9	100.0	200.0	19.2	[1]
	Cd	0.11	2.1	96.0		10.7	
Multi-walled carbon nanotube modified BTAO	Pb	2.6	<5.0	-	500	4.0	[28]
	Cd	1.2	<5.0	-		4.6	
TiO ₂ NPs modified with 2- mercaptobenzothiazole	Pb	1.38	4.83	-	250.0	3.17	[38]
	Cd	0.12	3.54	-		2.5	
Nano alumina coated SDS-PAN	Pb	0.17	3.2	-	500.0	16.4	[39]
	Cd	0.15	2.8	-		11.1	
DES modified magnetic nanoparticles	Pb	0.4	1.8	99.0	60.0	25.0	[40]
	Cd	0.1	2.1	97.0		23.7	
Sulfur-nanoparticle-loaded alumina	Pb	0.6	4.8	175.0	250.0	4.69	[41]
	Cd	0.3	2.4	63.0		0.85	
Multi-walled carbon nanotube modified polypyrrole	Pb	1.1	5.9	-	200	25.0	[42]
	-	-	-	-		-	
Multi-walled carbon nanotube modified poly(2-amino thiophenol)	Pb	1.0	3.2	304.0	2400.0	186.4	[30]
	Cd	0.3	2.4	282.0	2200.0	178.7	
mGO/SiO ₂ @coPPy-Th	Pb	0.65	<6.0	36.0	250.0	230.0	[43]
	Cd	0.21	<6.0	40.0		80.0	
Magnetic multi-walled carbon nanotube modified polythiophene	Pb	0.54	1.5	198.0	150.0	117.0	This work
	Cd	0.03	2.1	196.0		73.6	

LOD: limit of detection; RSD: relative standard deviation; EF: enhancement factor; BTAO: 2-(2-benzothiazolylazo) orcinol; SDS-PAN: sodium dodecyl sulfate 1-(2-pyridylazo)-2-naphthol; mGO/SiO₂@coPPy-Th: SiO₂-coated magnetic graphene oxide modified with pyrrole-thiophene copolymer.

higher than that reported by the other methods, making it suitable for extraction and determination of lead and cadmium at trace levels. It should be noted that the enhancement factor reported by reference [30] is higher

than that obtained by the developed method, but they used a much higher sample volume (2200 in comparison to 150.0 ml used in this procedure).

CONCLUSIONS

In the present work, a new MMWCNT modified with polythiophene sorbent was synthesized and used for the separation and preconcentration of lead and cadmium. The developed MSPME method proved to be effective for the separation and preconcentration of low amounts of Pb(II) and Cd(II) from water, and food samples such as black tea, rice, and milk prior to their determination by FAAS. The presence of many sulfur functional groups in polythiophene and the high specific surface area of MMWCNT cause the sorbent to have the excellent capacity as well as a good selectivity toward the analytes. The method also has the advantage of the ease of separation of sorbent by an external magnetic field improving the labor and time consumption of extraction. The other advantages of the method are low detection limit, high enhancement factor, good accuracy and precision, simplicity, and relatively low cost.

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