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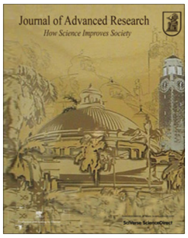

ORIGINAL ARTICLE

Pseudo-stir bar hollow fiber solid/liquid phase microextraction combined with anodic stripping voltammetry for determination of lead and cadmium in water samples

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ABSTRACT

A new procedure is presented for the determination of low concentrations of lead and cadmium in water samples. Ligand assisted pseudo-stir bar hollow fiber solid/liquid phase microextraction using sol–gel sorbent reinforced with carbon nanotubes was combined with differential pulse anodic stripping voltammetry for simultaneous determination of cadmium and lead in tap water, and Darongar river water samples. In the present work, differential pulse anodic stripping voltammetry (DPASV) using a hanging mercury drop electrode (HMDE) was used in order to determine the ultra trace level of lead and cadmium ions in real samples. This method is based on accumulation of lead and cadmium ions on the electrode using different ligands; Quinolin-8-ol, 5,7-diiodo quinoline-8-ol, 4,5-diphenyl-1H-imidazole-2(3H)-one and 2-{[2-(2-Hydroxy-ethylamino)-ethylamino]-methyl}-phenol as the complexing agent. The optimized conditions were obtained. The relationship between the peak current versus concentration was linear over the range of 0.05–500 ng mL^{-1} for Cd (II) and Pb (II). The limits of detection for lead and cadmium were 0.015 ng mL^{-1} and 0.012 ng mL^{-1}, respectively. Under the optimized conditions, the pre-concentration factors are 2440 and 3710 for Cd (II) and Pb (II) in 5 mL of water sample, respectively.

Introduction

In 1974, USA Congress passed the Safe Drinking Water Act. This law requires environmental protection agency of USA (EPA) to determine safe levels of chemicals in drinking water which do or may cause health problems. These levels, based just on possible health risks and representation, are called Maximum Contaminant Level Goals (MCLGs).

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Lead is a metal found in natural deposits as ores containing different elements. Since lead contamination generally occurs from corrosion of homemade lead pipes, it cannot detect or removed directly by the water system. The MCLG for lead has been set by EPA at zero, since the action level for lead has been set at 15 μg L^{-1} because EPA believes, which present technology and resources, this is the minimum amount to which water systems can advisedly be required to check this contaminant should it occur in drinking water at their customers home taps [1,2]. Cadmium is a metal found in natural deposits as ores including different elements.

Cadmium has the potential to cause the following effects from a lifetime exposure at levels above the Maximum Contaminant Level (MCL); kidney, liver, bone and blood damage. Some cadmium compounds are able to leach through soils to ground water. When cadmium compounds do graft to the sediments of rivers, they can be more easily bio-accumulated or re-dissolved when sediments are disturbed, like during deluge. Its tendency to accumulate in aquatic life is large in some species, low amount in others. The MCLG for cadmium has been set at 5.0 μg L^{-1} [2]. This has prompted the development of methods for the determination of lead and cadmium trace levels in the water matrices. Although they can be detected by various analytical techniques, their concentrations in uncontaminated natural waters including seawater are so low that their determination is difficult. So, a sample treatment method for pre-concentration of these analytes before their detection is necessary.

Solid phase microextraction (SPME) is a solvent free process, developed by Arthur and Pawliszyn [3]. This technique is fast, portable, easy to use and has been applied for determination of heavy metals [4]. However, SPME suffers from some drawbacks: its fiber is fragile and has limited lifetime and desorption temperature, and also sample carry-over is a problem [5]. Recently Malik and co-workers established a suitable method using sol–gel technology to overcome some important drawbacks of conventional SPME coatings such as; working temperature problems, inconstancy and swelling in organic solvents [6]. More recently, Es'haghi and coworkers introduced a new method named hollow fiber solid phase microextraction (HF-SPME) and have benefited from the more advantages over the conventional SPME technique such as elimination the possibility of sample carry-over and high reproducibility [7–10]. In their investigations, the solid phase sorbents that were constructed based on sol–gel reinforced with nanoparticles containing carbon nanotubes have been consumed.

Carbon nanotubes (CNTs) are a kind of interesting carbon material first found in 1991 by Iijima [11]. The internal pores of the CNTs are large enough to allow molecules to penetrate. Large sorption surface is also available on the outside and in the interstitial spaces within the nanotube bundles. All these indicate that CNTs have strong physical adsorption ability to wide range of compounds. Moreover, the hardness and adherence of the CNT into the sol–gel composites are important parameters for practical use. In HF-SPME the CNT-reinforced sol was supported by a macro-porous polypropylene tube as a disposable SPME fiber that protected the composite network structure.

In this study we examined the application of ligand effect as stripping agent to improve the extraction and determination of lead and cadmium using HF-SPME. We also optimized the chemical and electroanalytical parameters, to improve the sensitivity. The success of the improved method is demonstrated by its application to the determination of lead and cadmium in uncontaminated Darongar river water samples (Dargaz, Iran). A new class of ligand assisted composite sorbent made of sol–gel derived multiwalled carbon nanotubes were used for the determination of analytes in aqueous solutions. Compared with conventional methods, the new technique was fast and highly affordable.

Experimental

Reagents

Lead nitrate, cadmium nitrate, ethanol, nitric acid, acetic acid, hydrochloric acid, trifluoroacetic acid, Tris(hydroxymethyl)aminomethane (TRIS), Tetraethyl orthosilicate (TEOS), ammonium hydroxide, acetone and 1-octanol were purchased from Merck. Analytes, solvents, salts, acids, and bases were of analytical grade. Quinolin-8-ol (L_1) was purchased from ScharlauChemie S.A. (Barcelona, Spain), 5,7-diiodo quinoline-8-ol (L_2) was obtained from Sigma Aldrich (Chemie GmbH, Germany), and 4,5-diphenyl-1H-imidazole-2(3H)-one (L_3) and 2-{[2-(2-Hydroxy-ethylamino)-ethylamino]-methyl}-phenol (L_4) were synthesized in our laboratory. The hollow fiber polypropylene membrane support Q3/2 Accurel PP (200 μm thick wall, 0.6 mm inner diameter and 0.2 μm average pore size) was purchased from Membrana (Wuppertal, Germany) (see Fig. 1). The multi-walled carbon nanotubes (MWCNTs) were purchased from the Research Institute of the Petroleum Industry (Tehran, Iran). The mean diameter of the MWNTs was 10–15 nm, the length was 50–100 nm and purity > 98%.

Apparatus and voltammetry procedure

All of the voltammetry measurements were obtained by μAuto lab type(III) with polarography stand Metrohm Model 757 VA computrace (Switzerland), containing usual three electrode arrangements such as hanging mercury drop electrode (HMDE) as a working electrode, Ag/AgCl (saturated KCl) as a reference electrode and carbon electrode as an auxiliary/counter electrode. The voltammograms of Pb^{2+} and Cd^{2+} ions were obtained in DPASV mode. The volume of the solution introduced in the voltammetric cell has been 11.0 mL. The

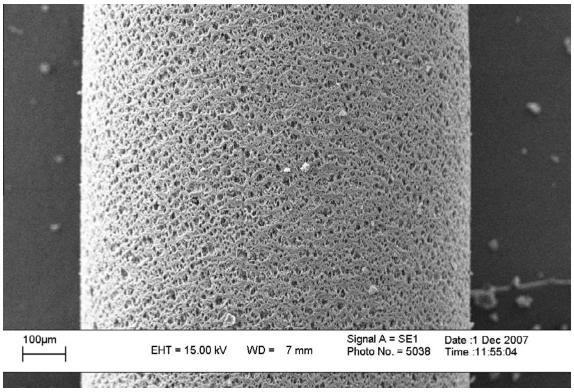

Fig. 1 Scanning electron microscopy polypropylene hollow fiber structure.

solutions were de-aerated by ultrapure N_2 gas for 100 s. The voltammetry experimental variables such as deposition potential, deposition time, scan rate of electrode potential and stirring speed of the solution were optimized. At very long deposition time, deposited metals may saturate the surface of electrode. The study revealed that current for analyzed metals was linearly proportional to deposition time up to 60 s. No more increase in peak currents was observed for the cations under study. Therefore, 60 s was selected for simultaneous determination of Pb and Cd. The influence of deposition potential on intensity currents of Pb and Cd standard solution was examined over the potential range from −0.2 to −0.8 V at a deposition time of 60 s. It was observed that the best current signal value obtained at a deposition potential of −0.8 V, and it was used for the further studies. The further DPASV optimized conditions were as follows: operational mode differential pulse, equilibration time 5 s, pulse amplitude 0.05005 V, pulse time 0.04 s, sweep rate 0.0149 V S^{-1}, stirring rate 2000 rpm, voltage step time 0.4 s and voltage step 0.005951 V. A digital pH meter (Metrohm Instruments Model 744) with a glass electrode was used for all pH measurements. Stirring of the solutions was carried out by a Biocate STUART CB302 magnetic stirrer (Ukraine).

Sol–gel preparation

The nanocomposites were prepared by both acidic and basic catalyzed conditions. The method with basic conditions showed better results and were used for this work. The sol–gel solution was prepared as follows: first to initiate the hydrolysis, 640 μL of TEOS, 130 μL of TRIS aqueous solution (5%) as base catalyst and 500 μL of EtOH were added into a polypropylene micro-centrifuge vial and the mixture stirred and heated at 70 °C for 2–3 h until a homogeneous solution is formed. After this time, 20 μL of concentrated ammonium hydroxide was added to the micro-centrifuge vial. The mixture was centrifuged at 3000 rpm for 5 min. The top clear solution was removed and the synthesized gel at the bottom of the tube was washed sequentially twice with deionized water and once with ethanol to remove the un-reacted reactant and surplus catalyst. The produced gel was placed to a clean vial and dispersed in 1 mL 1-octanol and then used for metal extraction study.

Carbon nanotube functionalization

Functionalization of CNTs is often discussed in articles reporting dispersion and interaction of CNTs with different materials, but it is difficult to compare data between articles because there are several different procedures and many adaptations. The addition of functional groups on CNTs is commonly made by immersing it in sulfuric acid (H_2SO_4) and nitric acid (HNO_3) in the range 3:1. This method inserts carboxyl groups on the surface of nanotubes. In this work, CNTs were functionalized as follows; 1.0 g of raw MWCNT was dispersed in to a flask containing 100 mL mixture of concentrated H_2SO_4/HNO_3 (3:1 v/v) and the mixture was refluxed at 80 °C for 6 h. After cooling, the MWCNTs were washed by deion-

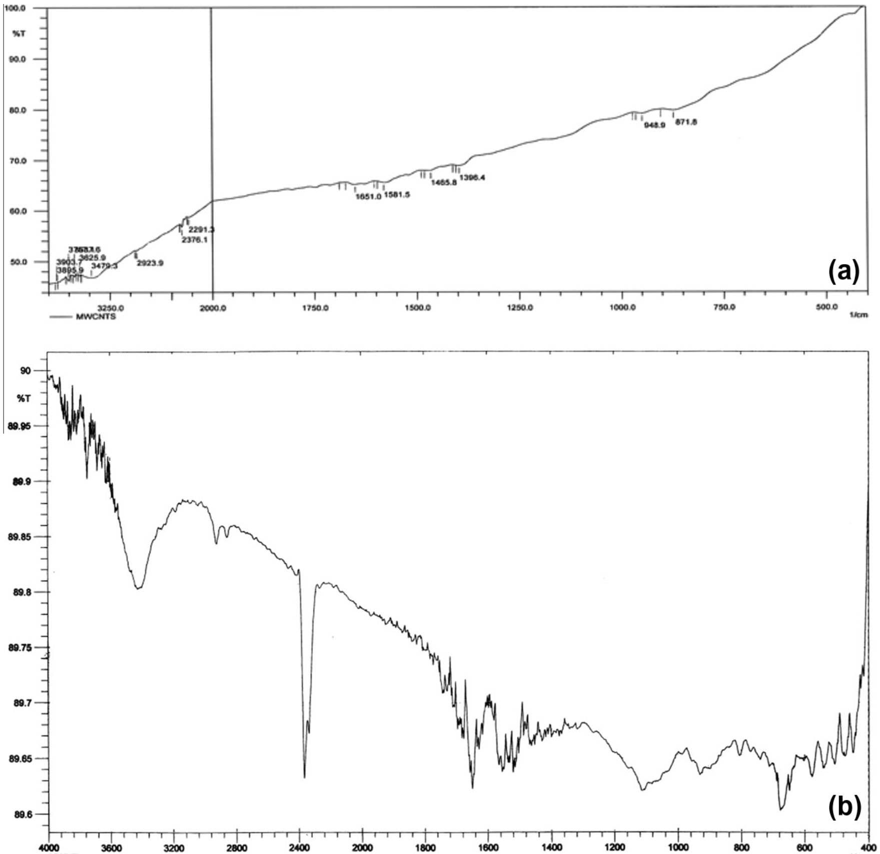

Fig. 2 (a) FT-IR spectra of untreated MWCNTs, (b) FT-IR spectra of acid-functionalized MWCNTs.

ized water until the pH of the solution reached 7.00. Then the solution was filtered and dried at 60 °C for 4 h to obtain the carboxylate MWCNTs (COOH-MWCNTs). FT-IR spectra of raw and acid-functionalized MWCNTs are shown in Fig. 2(a) and (b), respectively. The high symmetry presented on raw CNTs makes very weak infrared signals due to the weak difference in charge state between carbon atoms. The peak related to C=C bonding at approximately 1651 cm^{-1} is seen very week in the spectrum of raw CNTs, because of very low formation of electric dipoles. This typical peak, however, can clearly be noticed on functionalized CNTs (F-MWCNTs). Acid functionalization breaks the symmetry of nanotubes, which enhances the generation of induced electric dipoles. The peak appearance of functionalized MWCNTs in the ~3500 cm^{-1} region specifies the stretching OH from carboxylic groups. Acid treatment also results in the appearance of a peak approximately at ~1470 cm^{-1}, which corresponds to the C—O stretching representative the introduction of carboxylic groups due to surface oxidation.

Pre-concentration and extraction of metal ions

A 0.04 g of functionalized MWCNTs was dispersed in 1 mL 1-octanol/ethanol (1:1 v/v) mixture. Then the synthesized gel was dispersed inside this mixture. The extraction and pre-concentration procedure for target analytes in standards and water samples were as follows: first of all the hollow fiber was cut into segments with 1.5 cm length. The fiber segment was cleaned with acetone to remove impurities and directly dried in air. Then the fiber was immersed inside the 1-octanol for a few seconds to fill the membrane pores of the hollow fiber wall. After that, 3.0 µL of the acceptor phase (sol–gel/MWCNTs) was injected into the lumen of the hollow fiber with a microsyringe. The surface of fiber was washed with water to remove surplus organic solvent. Then the segments sealed at both ends by 2.5 mm tip of tack as stoppers (Fig. 3).

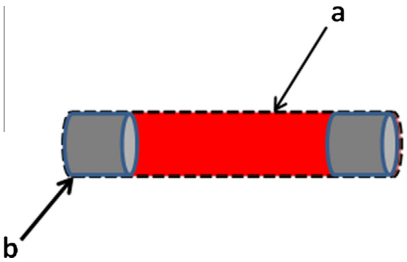

Fig. 3 Simple scheme of pseudo-stir bar HF-SLPME device: (a) filled hollow fiber membrane by sol–gel and CNT mixture and (b) magnetic stoppers (iron pins; 2.5 mm × 0.6 mm).

This fiber was placed into the 5 mL of sample solution present in a proper vial (25 mL volume). The vial was placed on a magnetic stirrer for 1 h at the appropriate agitation speed, 400 rpm. In this section the analytes from the sample solution diffuses through the porous polypropylene membrane into the acceptor solution. With this methodology, analytes of interest can be extracted from aqueous sample, into a thin layer of organic solvent (N-octanol) sustained in the pores of a porous hollow fiber, and further into the sol–gel acceptor located inside the lumen of the hollow fiber.

When the extraction process finished, the hollow fiber was taken out from the vial and transferred into a glass vial containing 3.0 mL of HNO_3(1 M):MeOH (70:30 v/v) mixture and the analytes were desorbed from fiber by stirring for 30 min at the appropriate agitation speed, 150 rpm. Then the 1.0 mL of this solution was diluted with supporting electrolyte up to 11.0 mL and transferred into the measurement cell for DPASV analysis.

Results and discussion

Effect of pH

The pH is an important analytical parameter for microextraction. The difference in acidity between the donor phase and sorbent can promote the extraction of analytes from the donor phase to the acceptor phase [12]. The final experimental results are given in Fig. 4. The results indicated that when the pH values of the working solution were conducted at a pH in the range of about 4.0 to about 7.0, the pre-concentration factors of Pb^{2+} and Cd^{2+} were at highest value. Therefore pH 5.0 was selected for further steps. The peak current fluctuations observed in pH values lower than 5 were because the partial protonation of the ionizable species [13,14]. At low pH, the carboxylic groups on the sorbent were mainly in neutral form.

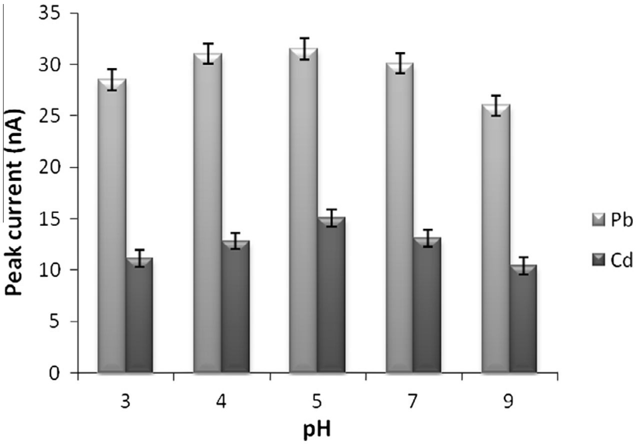

Fig. 4 Effect of feed solution pH on the extraction. Conditions: analytes concentration, 50 ng mL^{-1}; donor phase volume, 5.0 mL; acceptor phase volume 3.0 µL; stirring speed, 150 rpm; extraction time, 60 min; room temperature.

Thus, the influence of MWCNTs and metal ions on each other significantly decreases [10]. The peak current fluctuations above the pH 5 might be justified by the formation of insoluble metal hydroxides in the solution.

Effect of organic solvent type used for sol dispersion

The type of organic solvent is an essential consideration for an efficient extraction of target analyte from aqueous solution to pores of the hollow fiber. This organic solvent should be able to make homogeneous composite from synthesized sol. In addition, the organic solvent should have a low solubility in water and low volatility to prevent the solvent loss during the extraction, especially when faster stirring rates and long extraction time are used [15]. Several dispersion solvents were investigated. According to the results, 1-octanol was found to provide the highest extraction efficiency.

Effect of ligand as stripping agent

The objective of this study is to investigate ligand effect as stripping agent in microextraction of cadmium and lead in relation to various experimental variables. The microextraction process includes a desorption step in which metal ions that adsorbed by fiber, finally transported to the acceptor by ligand as a stripping agent. Stripping agent was found to be the key factor in determining an effective system for the recovery of metal ions. In addition, application of reagents capable to complex metal ions is an alternative method for stripping the metal ions from fiber into the receiving phase. This agent that is added to desorption solvent, almost increase desorption of analytes from adsorbent fiber. This work is done by complex formation between metal ions and different ligands as stripping agent. Results in Fig. 5 show this agent effect. Different ligands, i.e. L_1, L_2, L_3 and L_4 were assayed as stripping agent to evaluate the influence of different complexing agents to strip metal ions in final acceptor phase. The use of ligands as stripping agent (L_1, L_2, L_3 and L_4) provides faster cadmium and lead extraction and back-extraction kinetics than L_0 (L_0 = no ligand). It was found that L_1 for Pb extraction and L_2 for Cd extraction are the most efficient stripping agents in this investigation. But for simultaneous determination of each both metal ions in real samples L_2 were used as best striping agent in final optimized measurements. In comparison with three other ligands, L_2 have different donor groups like N, O and I that could be good sites for complex formation with Pb and Cd ions (See Fig. 5).

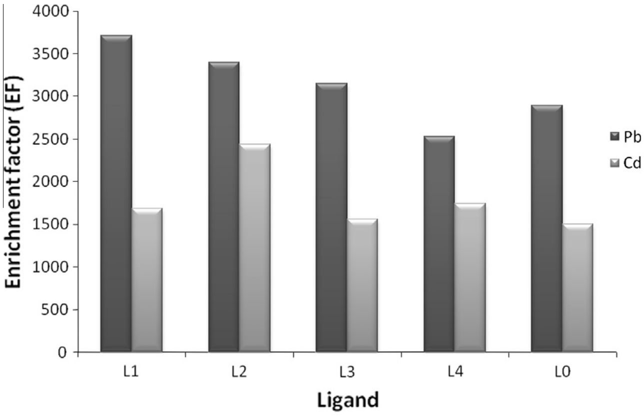

Fig. 5 Effect of stripping agent: Conditions: analytes concentration, 50 ng mL^{-1}; molar concentration ratio of ligand to analyte, 10; pH, 5.0; donor phase volume, 5.0 mL; acceptor phase volume 3.0 μL; extraction time, 60 min; stirring speed, 200 rpm; room temperature.

To ensure that the ligand is sufficient for all the analytes, ligand concentration was set at ten times the concentration of the analyte.

Effect of functionalized MWCNTs concentration

Carbon nanotubes (CNT) have some highly desirable sorbent characteristics which make them attractive for a variety of analytical applications. Great adsorption capacity and fast resorbability make CNT excellent for micro-scale sorbent for liquid phase analysis. CNTs exhibit an extraordinary adequacy of mechanical, structural and electronic properties that have made them potentially beneficial in nanotube-reinforced materials, as the sorbents

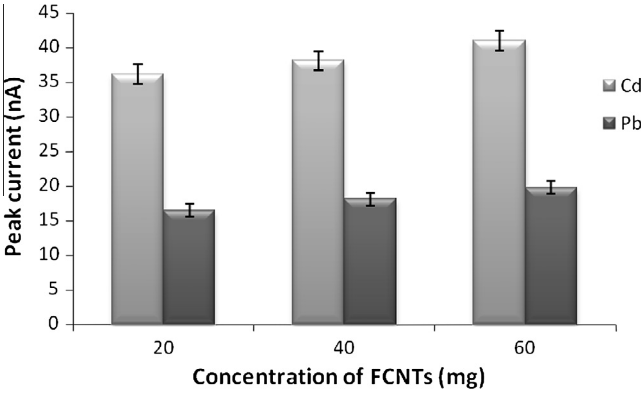

Fig. 6 Effect of functionalized MWCNTs concentration. Conditions: analytes concentration, 50 ng mL^{-1}; molar concentration ratio of ligand (L2) to analyte, 10; pH, 5.0; donor phase volume, 5.0 mL; acceptor phase volume 3.0 μL; extraction time, 60 min; stirring speed, 200 rpm; room temperature.

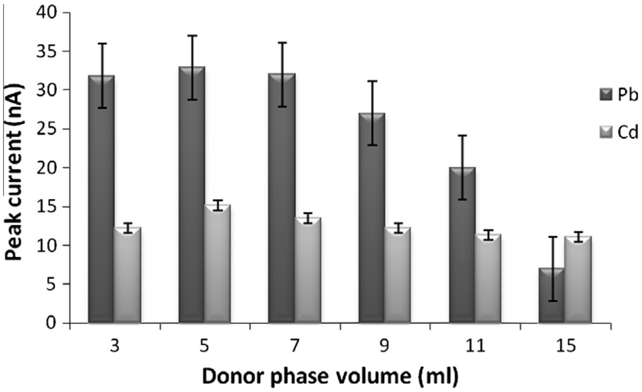

Fig. 7 Effect of donor phase volume on the extraction. Conditions: analytes concentration, 50 ng mL^{-1}; molar concentration ratio of ligand (L2) to analyte, 10; pH, 5.0; acceptor phase volume 3.0 μL; stirring speed, 150 rpm; extraction time, 60 min; room temperature.

Table 1 Performance of the method.[a]

Analytes	Pre-concentration factor	RSD% ($n = 5$)	Linear range (ng mL^{-1})	Regression coefficient (r)	Limit of detection (ng mL^{-1}) ($n = 5$)	Limit of quantification (ng mL^{-1}) ($n = 5$)
Pb^{2+}	3710	2.10	0.05–500	0.993	0.015	0.05
Cd^{2+}	2440	4.82	0.05–500	0.996	0.012	0.04

[a] Method conditions: hollow fiber membrane, MWCNTs in sol–gel (60 mg mL^{-1}); donor phase volume, 5.0 mL with pH 5.0; stripping agent, L_1 for Pb^{2+} and L_2 for Cd^{2+}; acceptor phase volume 3.0 µL; extraction time, 60.0 min; stirring speed, 200 rpm at room temperature. DPASV was used with three electrode arrangement; hanging mercury drop electrode (HMDE) as a working electrode, Ag/AgCl (saturated KCl) as a reference electrode and Carbon electrode as an auxiliary/counter electrode.

for SPME [16]. They have been proven to possess great potential for extracting heavy metal ions such as Cu^{2+} [17], Cd^{2+} [18], and Pb^{2+} [19]. The influence of MWCNTs amount on the extraction capacity has been examined to adding functionalized MWCNTs at 20, 40 and 60 mg mL^{-1} in sol. The results are shown in Fig. 6, display that the FCNTs concentration has positive effect on the extracted amount of the $Pb^{2+}$and Cd^{2+}. The optimal concentration of FCNTs was obtained at 60 mg mL^{-1}. At higher than 60 mg mL^{-1} FCNT concentrations, injection the mixture into the hollow fiber with a microsyringe was difficult to do.

Effect of the donor phase volume

The volume of donor phase is a critical and important factor in the solid phase microextraction of the metal ions to obtain high pre-concentration factor [20–27]. Donor phase volumes were optimized by changing the volume of the donor phase between 3 and 15 mL while the volume of acceptor phase was kept constant at 3.0 µL. As the volume of the sample enhanced, the pre-concentration factor also enhances [28,29]. However, a larger sample volume can be disadvantageous due to poorer mass transfers kinetics that result in a poor extraction efficiency. This would ultimate to a decrease in the microextraction output [30,31]. The results are displayed in Fig. 7. According to the results, the optimum volume for donor phase was 5.00 mL.

Table 2 Determination of Pb^{2+} and Cd^{2+} in river water samples.

Sample	Pb^{2+}		Cd^{2+}	
	Conc. (ng mL^{-1})	RSD% ($n = 5$)	Conc. (ng mL^{-1})	RSD% ($n = 5$)
S_1	0.480	3.54	0.132	3.26
S_2	0.473	2.48	0.125	2.21
S_3	0.522	3.19	0.124	2.26
S_4	0.495	3.14	0.145	2.08
S_5	0.517	2.40	0.112	2.63
S_6	0.522	2.23	0.127	2.24
S_7	0.521	2.64	0.104	2.92
S_8	0.499	2.98	0.123	2.59
S_9	0.504	2.34	0.132	3.08
S_{10}	0.533	2.26	0.114	2.65

Effect of extraction time

The effect of extraction time on the process was investigated by monitoring the peak current with exposure time over 15, 30, 45, 60 and 90 min with a sample volume of 5 mL at a room temperature. The amount of analyte that could be extracted depends on the partition coefficient of the analyte among the aqueous sample and organic solvent in the pores of the fiber wall and thereinafter, among the organic solvent and sorbent, on the lumen of the fiber, as acceptor phase. Complete equilibrium needs not to be attained for accurate and precise analysis [32]. The results display that the absorption signal generally increased with extraction time. After 60 min, with additional extraction time, the signal became constant afterward.

Effect of the stirring rate on extraction process

The stirring of the hollow fiber can decrease the thickness of the diffusion film and reduce the time needed to reach equilibrium [33,34]. In these experiments 150, 200, 250 and 300 rpm stirring rates for extraction were investigated. The higher stirring speed than 200 led to mechanical stress of the fiber [35]. The stirring speed of 200 was chosen as the optimum stirring rate for extraction.

Effect of desorption solvent

Significant parameters affect sorption process such as the desorption solvent. The desorption or elution solvent must be free from co-elutings with the analytes. For polar compounds and mixtures of polar and non-polar compounds there is no ideal universal desorption solvent. According to these conditions and based on our previous experience for desorption of Pb (II) and Cd (II) cations from the nano-sorbent, desorption solvents investigated included neat acetonitrile and methanol, different concentrations of both organic solvents (100% and 70%) with and without modifiers such as HCl and HNO_3. The best overall method appears to be 70%

Table 3 Recovery tests for Pb^{2+} and Cd^{2+} extraction with HF-SLPME coupled with DPASV under optimized conditions.

Sample	Spiked (ng mL^{-1})		Found (ng mL^{-1})		Recovery (%)	
	Pb (II)	Cd (II)	Pb (II)	Cd (II)	Pb (II)	Cd (II)
Tap water	0	0	0	0	–	–
	0.05	0.05	0.051	0.048	102	98

MeOH with 30.0% HNO_3. After seeing which of the above resulted in best sensitivity, further experiments were carried out with HNO_3 (1 N): MeOH (30:70 v/v).

Salt effect

For evaluation of the effect of ionic strength on promotion of extraction efficiency, different experiments were performed by adding varying NaCl amount from 0% to 5% (w/v). Other experimental conditions were kept constant. The results showed that salt addition has no significant effect on the pre-concentration factor. Therefore, the extraction efficiency is nearly constant by increasing the amount of sodium chloride, and the extraction experiments were carried out without adding salt.

Quantitative evaluation and real samples

The analytical data under the optimized proposed method are summarized in Table 1. For the detection limits, many formulas exist for calculating these values. One of the most widely used methods is known as 3-Sigma (3σ). The basic methodology is as follows. Seven or eight replicates of a blank are analyzed by the analytical method, the responses are converted into concentration units, and the standard deviation is calculated. This statistic is multiplied by 3, and the result is the detection limit. Similarly, the limit of quantification is 10-Sigma (10σ).

Relative standard deviations (RSD%) were determined and all the parameters are listed. The working linear range for the optimized procedure was between 0.05 and 500 ng mL^{-1} for Cd (II) and Pb (II).

The pre-concentration factor that is ratio of concentration between acceptor phase and initial donor phase aqueous solution was obtained under the optimized conditions for Cd (II) and Pb (II) and was 2440 and 3710 in 5 mL of a water sample, respectively. For determination of experimental pre-concentration factor, peak currents after extraction of analyte should be divided to peak currents before extraction at the same concentration and conditions. To accomplish this, after extraction of analyte on to the fiber including 3 μL of sol solution, analyte was eluted by the desorption solvent. Then the 1 mL of this solution was diluted with supporting electrolyte up to 11.0 mL. Thus peak current after extraction divided to peak current before extraction multiple by dilution factor. The donor phase volume was 5.0 mL and the volume of sol solution (acceptor phase volume) was 3 μL. The proposed method has been applied to Darongar (Dargaz, Iran) river water samples. As shown in Table 2 the average amounts of Pb (II) and Cd (II) in 10 samples were found to be 0.507 and 0.124 ng mL^{-1} respectively.

The calibration graphs for each both metals are linear in the range of concentrations from 0.05 ng mL^{-1} to 500 ng mL^{-1}. The detection limits are 0.012 ng mL^{-1} and 0.015 ng mL^{-1}, for cadmium and lead respectively. The relative standard deviations for five replicate measurements of 50 ng mL^{-1} cadmium and lead are 4.82%, and 2.10%, respectively. The relative recoveries in various water samples at a spiking level of 0.05 ng mL^{-1} ranges were 98% and 102% for cadmium and lead respectively (Table 3). These results illustrated that the matrix effect was relatively low. This method was perfectly effective for heavy metals (see Fig. 8 and Table 2).

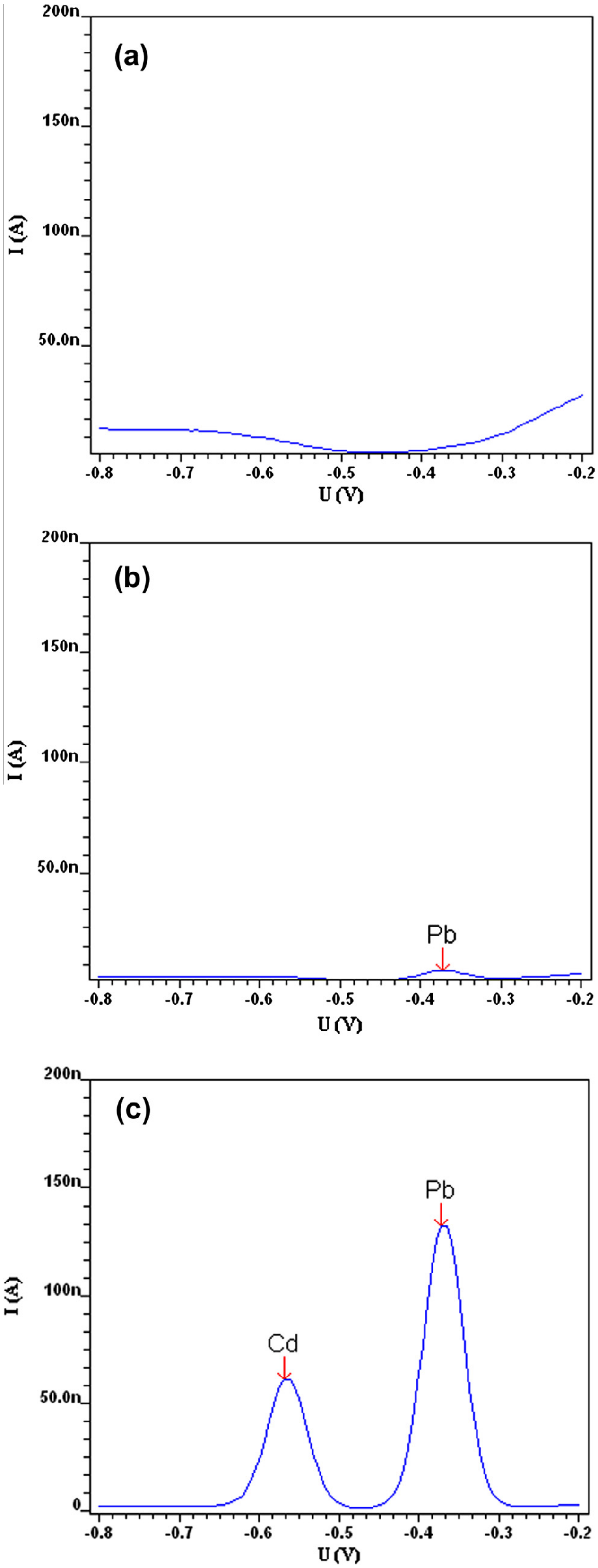

Fig. 8 Differential pulse voltammograms of Cd (II) and Pb (II) obtained from (a) the blank voltammogram, (b) River water sample and (c) the same sample after microextraction under optimal conditions.

Table 4 Comparison of similar micro extraction procedures for determination of Pb^{2+} and Cd^{2+} in water samples.

Analyte	Extraction method	Detection technique	Pre-concentration factor	Extraction time (min)	Sample volume (mL)	Linear range (ng mL^{-1})	Ref.
Pb	DLLME	FAAS	450	0	25	1–70	[36]
Pb	SI-DLLME	FAAS	265	2	12	2.3–260	[37]
Pb	SDME	ETAAS	16	20	1	0–40	[38]
Pb	CF-SDME	ETAAS	45	15	7.5	0–60	[39]
Pb	IL-SDME	ETV-ICP-MS	60	10	1.5	0.05–40	[40]
Pb	IL-SDME	ETAAS	76	7	1.75	0.025–0.8	[41]
Cd	IL-USA-DLLME	ETAAS	67	2	10	0.02–0.15	[42]
Cd	LPME	ETAAS	390	15	2	0.01–1	[43]
Cd	LPME-SFO	FI-FAAS	640	15	160	0.08–30	[44]
Cd	SDME	ETAAS	65	10	5	0.01–1	[45]
Pb + Cd	SDME	ETC-ICP-MS	190,140	15	0.2	0.01–50	[46]
Pb + Cd	HF-LPME	ICP-MS	7329	15	2.5	0.02–30	[47]
Pb + Cd	CPE	FI-FAAS	18	5	15	25–2000, 2.5–500	[48]
Pb + Cd	DLLME	ETAAS	115	0	5	0.03–1, 0.01–0.3	[49]
Pb + Cd	LPME-SFO	ETAAS	380,420	10	25	0.025–0.4, 0.001–0.015	[50]
Pb + Cd	HF-SPME	DPASV	3710, 2440	60	5	0.05–500	This work

Conclusions

This procedure has been applied to the determination of Pb (II) and Cd (II) in river water and could be used for other aqueous samples. The polypropylene porous membrane shows high stability and adequate to be used in a method based on FCNTs reinforced sol–gel combined with ASV for the extraction and determination of lead (II) and cadmium (II) in a single stage, with extraction and back-extraction occurring at the same time. The method was compared with the other previous works (Table 4). In comparison with the other conventional sample preparation methods, the developed method has the merits of good separation efficiency and elevated pre-concentration, considerable precision and high sensitivity.

Conflict of interest

The authors have declared no conflict of interest.

Compliance with Ethics Requirements

This article does not contain any studies with human or animal subjects.

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