Iranian Journal of Analytical Chemistry

Volume 5, Issue 1, March 2018 (25-32)

مجله ایرانی شیمی تجزیه

دوره ۵، شماره ۱، فروردین ماه ۱۳۹۷ (۳۲-۲۵)

میکرو استخراج و تغلیظ همزمان سرب (II)، روی(II) و نقره (I) توسط کامپوزیت نانولوله کربنی سل-ژل تثبیت شده در غشاهای فیبر متخلخل

زرین اسحاقی*، عفت اسماعیلی شهری

بخش شیمی، دانشگاه پیام نور، صندوق پستی ۳۶۹۷-۱۹۳۹۵ ، تهران، ایران

تاریخ دریافت: ۲ اسفند ۱۳۹۶ **تاریخ پذیرش: ۲۳ فروردین ۱۳۹۷**

Simultaneous Microextraction and Concentration of Lead (II), Zinc (II) and Silver (I) in Carbon Nanotube Sol−Gel Composite Immobilized Hollow Fiber Membranes

Zarrin Es'hagi*, Effat Esmaeili-Shahri

Department of Chemistry, Payame Noor University, 19395-3697, Tehran, Iran

Received: 21 February 2018 **Accepted:** 12 April 2018

چکیده

روش میکرواستخراج فاز جامد با فیبر متخلخل حاوی نانوکامپوزیت سل-ژل مسلح به نانولوله‌های کربنی ادغام شده با اسپکتروفتومتری فرابنفش – مرئی برای پیش‌تغلیظ و اندازه‌گیری سرب، روی و نقره در نمونه‌های آبی بکار رفته است. در این روش یک جاذب با کارایی بالا حاوی مخلوط نانولوله‌های کربنی و یک ژل با تخلخل میکرو به داخل قطعه‌ای از فیبر پلی پروپیلنی متخلخل تزریق‌شده تا ژله‌ای شدن بصورت درجا انجام شود. ارزیابی روش انجام شده و نتایج رضایت بخش بدست آمده است. این نتایج مدیون سطح تماس بزرگ و تخلخل نانو جاذب بوده است. تحت شرایط بهینه منحنی‌های کالیبراسیون خطی برای یون‌های سرب، روی و نقره به ترتیب در محدوده ۰/۲ – ۷/۰ ، ۰/۳ – ۷/۰ و ۲/۰ – ۵۰ میکروگرم بر میلی‌لیتر رسم گردیده‌اند . حد تشخیص‌های یونهای مذکور ۰/۰۳۲، ۰/۰۵۷ و ۰/۳۲۵ میکروگرم بر میلی لیتر بوده است. انحراف استاندارد های نسبی بدست آمده کمتر از ۸/۰ ٪ بوده است.

واژه‌های کلیدی

میکرواستخراج فاز جامد با فیبر متخلخل؛ اسپکتروفتومتری فرابنفش – مرئی؛ نانولوله‌های کربنی؛ سرب (II)؛ روی(II)؛ نقره (I).

Abstract

Hollow fiber-solid phase microextraction (HF-SPME) technique containing multiwalled carbon nanotubes (MWCNTs) reinforced sol-gel nanocomposite coupled with UV–Vis spectrophotometry was applied for preconcentration and determination of lead, zinc and silver in water samples. In this technique, a high efficiency sorbent containing mixture of MWCNTs and a microporous gel was injected into a piece of a polypropylene hollow fiber for in situ gelation. The method validation was included and satisfying results were obtained. It owes large surface area and porosity of the nano-adsorbent. Under the optimal conditions, linear calibration curves were established for the concentration of Pb2+, Zn2+ and Ag+ in the range of 0.2–7.0, 0.3–7.0 and 2.0–50 µg/mL respectively. The limits of detection were 0.032, 0.057 and 0.325 µg/mL for Pb2+, Zn2+ and Ag+. The relative standard deviations (RSDs) were found to be less than 8.0 %.

Keywords

Hollow fiber-solid phase microextraction; Spectrophotometry UV-Vis; Multiwalled Carbon Nanotube, Lead (II), Zinc (II), Silver (I).

1. INTRODUCTION

Water is the source of life. All living creatures on the Earth surface includes human, animals and plants need water. But water resources are in critical conditions of getting finished around the world, unfortunately. This problem is more severe, particularly in arid regions on the Earth surface, including Iran [1]. Due to the amount of water resources and per capita consumption, Iran is in the group of countries facing physical scarcity of water. On the other hand, considering the amount of rainfall during the year, approximately 90% of the Iran is arid or semiarid. In order to provide the possibility of using limited water sources in arid regions, Iranians invented the first reliable supply of water, called Qanat or Kariz. In fact, Qanat is a way that has been dug in the ground water and allows the water from foothills areas, rivers and wetlands was brought to points of the Earth surface. The Qanat system consists of a canal in the

---

*Corresponding Author: eshaghi@pnu.ac.ir

depth of the earth to communicate to series of wells (bars) that getting sources from mother well (first well) in order to convey water to the surface and water management for agriculture and other applications. These wells have been drilled vertically in a sloping surface distances from 20 to 200 meters between the wet zone and dry zone of the Qanat. Extraction system of Qanat so that the water without help, costs and no electricity or heat flow and using only gravity is removed from aquifers in highlands to the lower surface [2]. Some of the longest and oldest Qanats of the world for example, Qasabeh Shahr, Aliabad and Deh-Juimand are located in Gonabad. Gonabad is a city in the capital of Gonabad County, in Razavi Khorasan Province, Iran. The main Qanat of Gonabad is Qasabeh Shahr. Its main well depth is more than 340 meters and their lengths are 45 kilometers. This Qanat after many centuries still provides drinking and agricultural water for the people of this region [3]. With regard to the Qanat is an essential component of lives of the people of the city and the success of its economy moving forward, it is very important that the Qanats is not contaminated for example by metallic species. Toxic heavy metal pollution of water resources is a major environmental problem due to their non-biodegradable, persistence nature and tends to accumulate in living organisms, further reducing the quality of life and may eventually cause death. Various instrumental methods such as inductively coupled plasma atomic emission spectroscopy (ICP-AES) [4], atomic absorption spectroscopy (AAS) [5], electrochemical methods [6] and Spectrophotometry [7] have been used for determination of heavy metals. Absorption spectroscopy in UV-Vis region could be employed for its simplicity, speed, versatility, accuracy and cost [8]. The successful application spectrophotometric methods are based on the color-forming reaction so that suitable spectrophotometric reagents react with nonabsorbing species such as metal ions to yield products that absorb in the UV-Vis region. Diphenylthiocarbazone (Dithizone, abbreviated here as DTZ, Fig. 1) has been shown to serve as one of these effective reagents for the extraction-determination of metal ions because it can act as a mono-dentate or bi-dentate ligand [9].

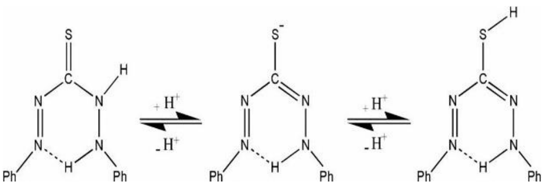

Fig. 1. Structural formula of DTZ molecule and its anions.

In bi-dentate manner, DTZ produces bis-chelate complexes through sulfur and nitrogen atoms with the general formula M $(DTZ)_2$, where M is metal ions [10].

The determination of traces of heavy metal ions in environmental samples is limited by variety of factors, particularly the low concentrations of metal ions, which are near or below the limit of detection of the instrument and matrix effects of real samples. In order to achieve accurate and trustworthy results, a preconcentration step is frequently necessary when the metal ions are determined directly by Spectrophotometry [11]. Among the different methods for the preconcentration of heavy metal ions, the most common sample preparation technique is solid-phase microextraction (SPME). SPME which is based on fiber coated with a small volume of extracting phase has proven to be the most attractive one due to its specificity such as rapid, general, high sensitivity, solvent free process, and economical method. Extraction phase in SPME can be a liquid polymer with high molecular weight or a solid adsorbent, usually a high surface area from porous material [12]. The use of nano-structured materials as functional coating for SPME has received considerable interest in recent years. The nano-coating involves a higher surface area-to-volume ratio that can increase active sites for interaction with analytes and therefore, provides greater extraction capacity [13].

Carbon nanotubes (CNTs) are an allotrope of carbon that has two main types of single-wall carbon nanotubes (SWCNTs) and multiwall carbon nanotubes (MWCNTs). The use of CNTs as sorbent is based on their unique properties suitable for SPME, such as strong adsorption ability for interactions with organic molecules, via van der waals forces and hydrophobic interactions. In addition, their mechanical strength, chemical and thermal stability should also be considered [14]. But, CNTs can form aggregates due to the large intermolecular van der Waals attraction [15]. Therefore, sol–gel technology is used to disperse CNTs in molecular levels. The novel method of carbon nanotube-reinforced hollow fiber solid-phase microextraction (CNTs-HF-SPME) is a modified SPME technique. On the other hand, SPME fibers have important drawbacks, such as relatively high cost, metallic contamination on the fibers especially in trace metal analysis, sample carry-over, the stripping of coatings and short lifetime [16]. Eshaghi et al prepared new SPME device of using of polypropylene hollow fiber as a way of stabilizing sorbents [17]. Due to its low cost, low organic-solvent consumption and microporous structure, polypropylene hollow fibers are a good alternative for common SPME fibers. The porous wall has high potential for mass transfer in the extraction procedure with membrane selectivity, because they act as a channel through which the analytes molecules in the donor phase and the sorbent inside the fiber were in contact with each other [18]. So, we decided to modify hollow-fiber solid phase micro-extraction (HF-SPME) with MWCNTs as sorbents and to apply in SPME promote the CNTs-HF-SPME technique by inserting CNTs into the nanocomposite sol-gel sorbent, to preconcentrate Pb^{2+}, Zn^{2+} and Ag^{+} from water samples.

2. EXPERIMENTAL

2.1. Reagents

Stock solutions of metal ions were prepared by dissolving Pb $(NO_3)_2$, Zn $(NO_3)_2{\cdot}7\ H_2O$ and $AgNO_3$ all purchased from Merck (Darmstadt, Germany) in double distilled water. Other chemicals were of analytical reagent grade and were obtained from Merck (Darmstadt, Germany) too. The stock solution of DTZ was prepared in carbon tetrachloride with a concentration of 100.0 µg/mL. Accurel Q 3/2 polypropylene hollow fiber (200 µm wall thickness, 600 µm inner diameter, and 0.20 µm pore size) was obtained from Membrana (Wuppertal, Germany). MWCNTs (98% purity) were purchased from the Petroleum Industry (Tehran, Iran).

2.2. Instrumentation

FTIR spectra were recorded on a Shimadzu 8400S Fourier transform instrument from Shimadzu, Japan. The microstructure of samples was investigated by scanning electron microscopy (SEM) (Tescan-Vega, Czech Republic). PG instrument-UV-T80^{+} double beam UV-visible spectrophotometer using 10 mm path Quartz cells were utilized for absorbance measurements. The absorption spectra of the complexes and DTZ in carbon tetrachloride have been showed in Fig. 2 and Fig. 3.

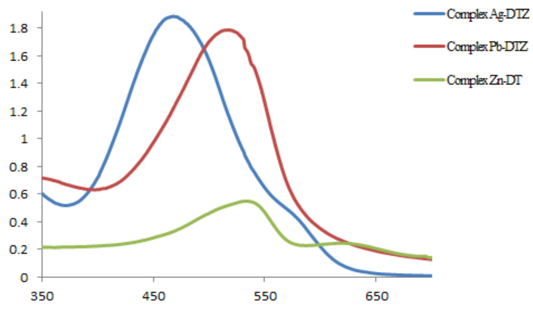

Fig. 2. The absorbance spectra of the complexs Pb-DTZ, Zn-DTZ and Ag-DTZ in carbon tetrachloride during extraction. Conditions: analytes concentration, 2 µg/L; pH, 3.5 for Ag and 8.5 for Pb and Zn; acceptor phase volume 6.0 µL; stirring speed, 700 rpm.

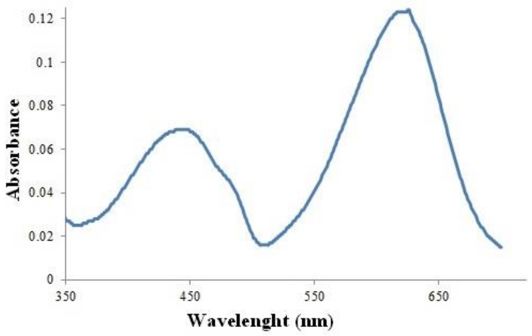

Fig. 3. . The absorbance spectra of the DTZ in carbon tetrachloride.

As can be seen, the maximum absorptions complexes of Zn-DTZ, Pb-DTZ, and Ag-DTZ are 531 nm, 518 nm and 468 nm, respectively. Fig. 3 depicts that the maximum absorption DTZ as a chelating agent is 431 nm and 620 nm. So, DTZ reagent does not interfere in the determination of analytes.

2.3. Carbon nanotube treatment

Before using MWCNTs for step of sol–gel preparation, oxidization of MWCNTs is necessary. This process not only can create a larger number of functional groups onto the surface of MWCNTs, which enhance the ion-exchange capability of carbon, but also in order to better disperse MWCNTs in the organic solvent. Oxidization of MWCNTs was performing as follows: 1.0 gr untreated MWCNTs was suspended in 150 mL of concentrated nitric acid and was refluxed for 5 h. The mixture was cooled and washed with distilled water until the pH value drop off to 7.0. Afterward, the functionalized MWCNTs were dried at 70°C.

2.4. Preparation of the sol–gel Nano composite

The preparation of the sol-gel solution was according to our previous works [19] as follows: 640 µL TEOS, 500 µL methanol and 130 µL Tris Hydroxyl Methyl Amino Methane (5%) solution as base catalyst were added into a vial and the mixture stirred and heated at 50°C for hydrolysis operation. Next, 20 µL of concentrated ammonium hydroxide and 60 mg of MWCNTs-COOH were added and the mixture was centrifuged at 2000 rpm for 5 min. The gel at the bottom of tube was washed with water and ethanol and dispersed in 1 mL 1-octanol/ethanol (1:1 v/v) mixture.

2.5. Hollow fiber-solid phase microextraction (HF-SPME)

Fig. 4 shows a simplified schematic of the application of HF-SPME to extract analytes. Extraction was made as follows: hollow fibers were cut manually into 2 cm pieces and washed with acetone to remove impurities so directly dried in air. A 6.0 µL of acceptor phase containing the gel of MWCNTs-COOH was injected into the lumen of the hollow fiber. The both open ends of the fiber were closed to prevent leakage. The prepared fiber was placed in a glass vial and subjected to 5 mL of aqueous analyte solution (pH optimized). The vial was covered and the solution was stirred at 700 rpm for 40 min. During the appropriate time extraction, the analytes diffuses from the solution to the sorbent through the porous hollow fiber. Then, fiber was taken out from the vial and transferred into another vial. After adding mole ratio from DTZ reagent and reaction time required forming complex, the complex formed is extracted into the organic phase with 2 mL of carbon tetrachloride, and lastly the measurements of absorbance are done by UV-Vis spectrophotometry in maximum absorptions. The blank solutions were also run using the whole mentioned components except analytes for all analyses.

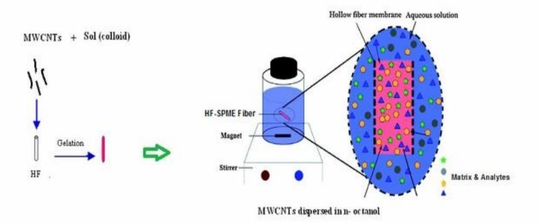

Fig. 4. Schematic representation of HF-SPME.

3. RESULTS AND DISCUSSION

3.1. Structural Characterization of sorbent

The FTIR spectra of MWCNTs-COOH are illustrated in Fig. 5. In this spectrum, the broad peak at 3442 cm^{-1} refers to the O-H stretch of the hydroxyl group. The peak at 1626 cm^{-1} can be attributed to the stretching vibrations of C=O group,in addition, the peaks at 1124 cm^{-1} and 1162 cm^{-1} are assigned to the C-O stretching vibration indicating that carboxylic groups are introduced on the surfaces of the MWCNTs after the treatment with HNO_3. The peak related to C=C bonding is at nearly 1584cm^{-1} and the peaks around 2800–3000 cm^{-1} may also arise from the C–H stretch modes [20]. SEM images of untreated MWCNTs and MWCNT-COOH are displayed in Fig. 6. It is observed that the raw materials consisted of MWCNTs and impurities such as catalyst particles and amorphous carbon. In compared with the untreated MWCNTs, acid treatment in MWCNT-COOH causes the length of the MWCNTs decreased and the structure of the tubes became less well defined.

Factors affecting the extraction efficiency such as, the amount of nanocomposite, sample agitation, Desorption conditions, donor phase volume, the extraction time, pH and the ionic strength of the solution were studied and optimized.

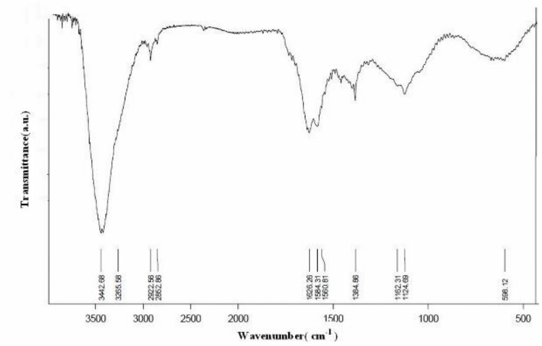

Fig. 5. FTIR spectra of MWCNTs-COOH.

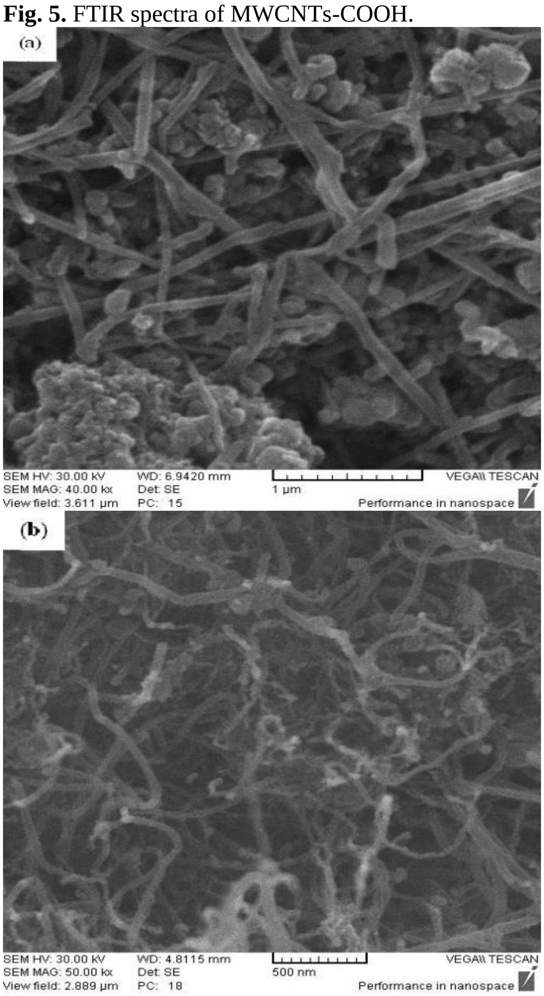

Fig. 6. SEM images of surface morphology of CNTs. (a) untreated MWNTs; (b) MWCNT- COOH.

3.2. Optimization of hollow fibre-solid phase microextraction (HF-SPME) parameters

3.2.1. Effect of the amount of functionalized MWCNTs.

In order to determine the influences of the amount of MWCNTs on the extraction capacity, amounts 20, 40, 50 and 60 mg/mL MWCNTs-COOH added to sol-gel solutions. The results showed that the optimal concentration of MWCNTs was obtained at 60 mg. Although MWCNTs concentration have positive effect on the extracted amount of the cations but the results demonstrated that increasing of the amount of MWCNTs higher than 60 mg/mL of gel decreased repeatability since the injection of massive reinforced composite into the fiber was done hardly. So 60 mg/mL was selected as optimized condition.

3.2.2. *Effect of salt*

More commonly, the presence of salt increases the ionic strength of the solution and can improve the recovery extraction. The effect of adding $NaNO_3$ to aqueous sample was investigated in concentrations 1% and 5% w/v. The results displayed the absorbance decreased with increasing salt concentration in the aqueous sample. So no salt was added to the sample solution in further extractions. An explanation for this may be related to changes in the physical properties of the Nernst diffusion, which results in reducing the diffusion of the analytes from the sample towards the acceptor phase [21].

3.2.3. *Effect of the sample agitation*

Different stirring rates (300–800 rpm) were evaluated. As can be expected, the agitation of the sample could greatly improve the extraction efficiency, because extraction kinetics can be accelerated by stirring of the samples. It was found that the extraction efficiency was increased with the increase of stirring rate up to 700 rpm and then decrease with the further increase of stirring rate, since the higher stirring speed led to formation of air bubbles and decreased the preconcentration factors. Based on these facts, the stirring rate of 700 rpm was used for all the subsequent experiments.

3.2.4. *Selection of pH*

Adjustment of the pH of the sample can improve the sensitivity of the method for basic and acidic analytes, because the sample pH is an important factor which has influence on the extraction recovery of analytes. Fig. 7 presents the effect of the donor phase pH on the analytes absorbance. The pH was studied in the range 3.5-8.5 by adding the appropriate sulfuric acid or sodium hydroxide solution to aquatic sample. It is obvious that when the pH of the donor phase was 3.5, the absorbance of Ag^+ was higher under other conditions, while the optimum pH was 8.5 for Pb^{2+} and Zn^{2+}. However the strong base pH might be decreased extraction efficiency by the formation of insoluble metal hydroxides in the solution.

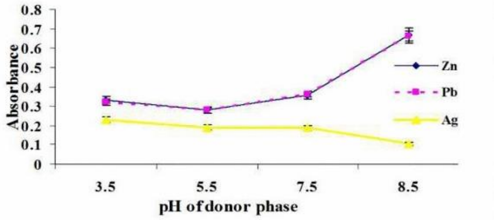

Fig. 7. Effect of feed solution pH on the extraction. Conditions: analytes concentration, 2 µg/L; donor phase volume, 5.0 mL; acceptor phase volume 6.0 µL; stirring speed, 700 rpm; extraction time,40 min.

3.2.5. *Effect of the donor phase volume*

The effect of donor phase volume on the extraction efficiency of metal ions was also studied. The phase ratio of donor and acceptor solutions was optimized by used difference donor phase at the interval of 2 mL. In the present study, the volume of acceptor phase was constant at 6.0 µL because the length of the hollow fiber fragment was constant. It could be observed that enrichment factors enlarged steadily with increasing donor phase volume from 3 mL to 5 mL. The maximum of enrichment factor was obtained at 5 ml. But larger sample volume than 5.0 mL give weak analyte absorbance. This phenomenon might be due to the saturation of the MWCNTs capacity for a large sample volume [22]. So, optimum donor phase volume was selected as 5.0 mL.

3.2.6. *Extraction time*

The partitioning of analyte into 1-octanol is one of the slow steps in the mass transfer [23]. Therefore, extraction time is a decisive factor for improving the extraction efficiency. The range of extraction times examined was between 20 and 60 min. Fig. 8 shows the effect of extraction time on the method efficiency. The results, demonstrated that the absorbance increased with extraction time. After 40 min, with additional extraction time, the absorbance began to decrease due to the reduction of mass transfer as driving force. Eventually, 40 min was selected as the extraction time for the further analyses.

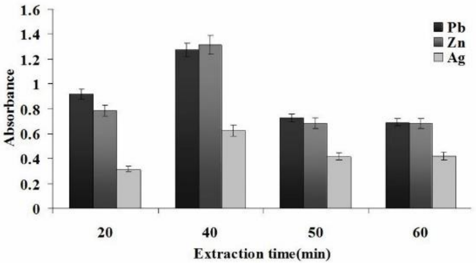

Fig. 8. Effect of extraction time on the extraction. Conditions: analytes concentration, 2µg/L; pH, 3.5 for Ag and 8.5 for Pb and Zn; acceptor phase volume 6.0 µL; stirring speed, 700 rpm.

3.2.7. Desorption conditions

A crucial step in HF-SPME is choosing the suitable extracting solvent. Desorption solvent should have high solubility for the target analytes. In addition to, the following factors should be considered such as selectivity, extraction efficiency, and the level of evaporation and toxicity. On the basis of these considerations, carbon tetrachloride, chloroform and acetonitrile were investigated. These solvents were selected because they could dissolve DTZ as well as. Carbon tetrachloride and chloroform solvents form stable complexes with ions morever acetonitrile desorbes ions from the solution in less time but make the complex less stable than those carbon tetrachloride and chloroform. The results showed that the extraction efficiency were higher in the presence of carbon tetrachloride in comparison with the other solvents.

The volume of the organic phase was important on the desorption capacity of HF-SPME device. The range of organic solvent volume was between 2.0 and 4.0 mL. The highest extraction efficiency was observed when 2.0 mL carbon tetrachloride was used. Lower volumes of organic solvent tend to loss during agitation because of its high volatility, and higher volumes cause lower enrichment factor. To reach the highest sensitivity, desorption time was also evaluated in the range of 10–30 min to ensure all compound was completely desorbed from sorbent. Experiments showed that for all analytes, the absorbance increases with the increase of desorption time up to15 min and no significant increase in extraction efficiency can be observed when a longer desorption time was employed. Thus, this time were chosen for succeeding analysis.

3.3. Analytical performance

Under the optimized conditions, enrichment factors, repeatability (RSD), linearity, limit of detection and limit of quantification were investigated. The results are given in Table 1. The calibration graph was linear in the range 0.2–50 µg/mL with. Results had a good correlation coefficient between 0.9910 and 0.9939 and the linear regression equations for Pb^{2+}, Zn^{2+}and Ag^{+} was: $y = 0.5138 x + 0.0475$, $y = 0.518 x + 0.0475$ and $y = 0.0349 x + 0.286$, where y represents the absorbance value of the ions, and x denotes the concentration of the ions. The enrichment factors were between 3443 and 3624. Detection limits were evaluated as three times the standard deviation of the blank for three replicate and were calculated to be in the range of 0.032–0.352 µg/mL. Limit of quantification (LOQ) was estimated as the ten times the standard deviation of the blank and were determined to be in the range of 0.107–1.170 µg/mL. Three different extractions from three independent samples were carried out to test the repeatability of the method. The repeatability of the method (RSD %) were less than 8% (Table 1).

Table 1. Performance of the method.

Analytes	Enrichment factor	RSD%(n=3)	Linear range (µg/mL)	LOD[a] (µg/mL)	LOQ[b] (µg/mL)
Pb^{2+}	3624	4.12	0.2-7.00	0.032	0.107
Zn^{2+}	3570	5.68	0.3-7.00	0.057	0.189
Ag^{+}	3443	7.23	2.0-50.0	0.352	1.170

[a] Limit of detection.

[b] Limit of quantification.

3.4. Real samples

To assertion the applicability of the HF-SPME based on MWCNTs-COOH reinforced sol–gel method, Qasabeh shahr Qanat water sample was analyzed using this technique. The analytical results of water matrix are given in Table 2. Founded amount of the cations without spiking of analyte was 0.70 and 0.65 µg/mL Pb^{2+} and Zn^{2+}. These findings show that, unfortunately, how underground water supplies are contaminated by industrial wastes. To demonstrate the potential of this method as a viable extraction technique for industrial wastewater samples the standard solutions of cations was spiked into wastewater samples of Gonabad industrial zone. The relative recovery of from wastewater was determined as the ratio of the concentration in the wastewater and distilled water samples spiked at the same concentration level. An average relative recovery of was obtained for real samples at the mentioned concentration level (n = 5).

Table 2. Concentrations of metal ions in the water samples.

Analyte	Concentration (µg/mL)	Spiked amount (µg/mL)	Relative recovery%
Pb^{2+}	0.70	0.200	77.0
Zn^{2+}	0.65	1.00	78.4
Ag^{+}	Not detect	1.20	61.0

4. CONCLUSION

A new method of HF-SPME based on MWCNTs-COOH reinforced sol–gel combined with UV-Vis spectroscopy for the extraction and determination of Pb^{2+}, Zn^{2+} and Ag^{+} has been developed. The procedure offers a useful multi-element pre-concentration technique in water samples with acceptable accuracy and precision. In comparison with the established methods for determination of heavy metals, many advantages can be achieved with this novel method such as simplicity, rapidness, high sensitivity, remarkable enrichment performance and low cost and less consumption of toxic organic solvent. The disposable nature of the hollow fiber totally obviates the possibility of sample carry over and ensures high reproducibility.

DISCLOSURE STATEMENT

ACKNOWLEDGMENTS

The authors wish to thanks Payame Noor University for financial support of this research.

REFERENCES

[1] M. Faramarzi, K.C. Abbaspour, R. Schulin and H. Yang, Modelling blue and green water resources availability in Iran, *Hydrol. Process* 23 (2009) 486-501.

[2] F. Boustani, Sustainable water utilization in arid region of Iran by Qanats, Proceeding of world Academy of science, engineering and technology, *Int. J. Soc. Mang. Econ. Bus. Eng.* 2 (2008) 213-216.

[3] K.S. McLachlan, *The neglected garden: The politics and ecology of agriculture in Iran,*: I.B.TAURIS and Co & Ltd, London (1988).

[4] S.R. Oliva, B. Valdés, M.D. Mingorance, Evaluation of some pollutant levels in bitter orange trees: Implications for human health, *Food Chem. Toxicol* 46 (2008) 65-72.

[5] T.G. Kazi, N. Jalbani, J.A. Baig, G.A. Kandhro, H.I. Afridi, M.B. Arain, M.K. Jamali and A.Q. Shah, Assessment of toxic metals in raw and processed milk samples using electrothermal atomic absorption spectrophotometer, *Food Chem. Toxicol* 47 (2009) 2163-2169.

[6] J.E. Belgaied, Release of heavy metals from Tunisian traditional earthenware, *Food Chem. Toxicol* 41 (2003) 95-98.

[7] V.N. Bulut, D. Arslan, D. Ozdes, M. Soylak and M. Tufekci, Preconcentration, separation and spectrophotometric determination of aluminium (III) in water samples and dialysis concentrates at trace levels with 8-hydroxyquinoline–cobalt (II) coprecipitation system, *J. Hazard. Mater* 182 (2010) 331-336.

[8] C.B. Ojeda and F.S. Rojas, Determination of rhodium: since the origins until today: spectrophotometric methods, *Talanta* 67 (2005) 1-19.

[9] X. Zhai and S. Efrima, Silver colloids and macroemulsions of metal interfacial colloidal films: interaction with dithizone, *J. Phys. Chem.* 100 (1996) 10235-10242.

[10] B. Romberg and H. Müller, Photometric screening-test for heavy metals under flow injection conditions using extractive determination with dithizone *Anal. Chim. Acta* 353 (1997) 165-172.

[11] M. Ghaedi, F. Ahmadi and A. Shokrollahi, Simultaneous preconcentration and determination of copper, nickel, cobalt and lead ions content by flame atomic absorption spectrometry, *J. Hazard. Mater* 142 (2007) 272-278.

[12] C.L. Arthur and J. Pawliszyn, Solid phase microextraction with thermal desorption using fused silica optical fibers, *Anal. Chem.* 62 (1990) 2145-2148.

[13] A. Mehdinia and M. Fazlollah Mousavi, Enhancing extraction rate in solid-phase microextraction by using nano-structured polyaniline coating, *J. Sep. Sci* 31 (2008) 3565-3572.

[14] E. Mohammadifar, F. Shemirani and B. Majidi, A new sorbent of modified MWCNT for solid phase extraction and determination of trace amount of palladium in environmental samples, *J. Anal. Chem.* 70 (2015) 136-142.

[15] Y. Yang, J. Chen and Y.P. Shi, Determination of diethylstilbestrol in milk using carbon nanotube-reinforced hollow fiber solid-phase microextraction combined with high-performance liquid chromatography, *Talanta* 97 (2012) 222-228.

[16] R. Jiang, F. Zhu, T. Luan, Y. Tong, H. Liu, G . Ouyang and J. Pawliszyn, Carbon nanotube-coated solid-phase microextraction metal fiber based on sol–gel technique, *J. Chromatogr. A* 1216 (2009) 4641-4647.

[17] Z. Es’haghi, M.A. Golsefidi, A. Saify, A.A. Tanha, Z. Rezaeifar and Z. Alian-Nezhadi, Carbon nanotube reinforced hollow fiber solid/liquid phase microextraction: a novel extraction technique for the measurement of caffeic acid in Echinacea purpurea herbal extracts combined with high-performance liquid chromatography, *J. Chromatogr. A* 1217 (2010) 2768-2775.

[18] M. Ebrahimi, Z. Es‘haghi, F. Samadi and M. S. Hosseini, Ionic liquid mediated sol–gel sorbents for hollow fiber solid-phase

microextraction of pesticide residues in water and hair samples *J. Chromatogr. A* 1218 (2011) 8313-8321.

[19] Z .Es'haghi and E. Esmaeili-Shahri, Sol–gel-derived magnetic SiO_2/TiO_2 nanocomposite reinforced hollow fiber-solid phase microextraction for enrichment of non-steroidal anti-inflammatory drugs from human hair prior to high performance liquid chromatography, *J. Chromatogr. B* 973 (2014) 142-151.

[20] M.S. Tehrani, P.A. Azar, P.E. Namin and S.M. Dehaghi, Removal of lead ions from wastewater using functionalized multiwalled carbon nanotubes with tris (2-aminoethyl) amine, *J. Environ. Prot* 4 (2013) 529 – 536.

[21] Z .Es'haghi, M. Ebrahimi and M.S. Hosseini, Optimization of a novel method for determination of benzene, toluene, ethylbenzene, and xylenes in hair and waste water samples by carbon nanotubes reinforced sol–gel based hollow fiber solid phase microextraction and gas chromatography using factorial experimental design, *J. Chromatogr. A* 1218 (2011) 3400-3406.

[22] H.H. See, M.M. Sanagi, W.A.W. Ibrahim and A. Naim, Determination of triazine herbicides using membrane-protected carbon nanotubes solid phase membrane tip extraction prior to micro-liquid chromatography, *J. Chromatogr. A* 1217 (2010) 1767-1772.

[23] A.L. Theis, A.J. Waldack, S.M. Hansen and M.A. Jeannot, Headspace solvent microextraction, *Anal. Chem.* 73 (2001) 5651-5654.