Combination of New Solid/Liquid Phase Microextraction Technique Based on Functionalized Multiwalled Carbon Nanotubes with Flame Atomic Absorption Spectroscopy for the Extraction and Determination of Zn(II) in the Environmental Samples

Zarrin Es'haghi[1,*], Ali Sayfi[1], Ali Ahmadpour[2], Ali Akbar Tanha[1] and Ali Samie[1]

[1]*Department of Chemistry, Payame Noor University, 19395-4697 Tehran, I.R. of Iran*

[2]*Department of Chemical Engineering, Faculty of Engineering, Ferdowsi University of Mashhad, Mashhad, Iran, P.O. Box 91775-1111, I.R*

Abstract: A new design of equilibrium hollow fiber solid-liquid phase micro-extraction (HF–SLPME) was developed for the determination of Zn(II) in environmental water samples. Membrane extraction with sorbent interface which we used in this research is a two-phase supported liquid membrane consisting of aqueous (donor phase), organic solvent/nano sorbent membrane (acceptor phase) system operated in direct immersion sampling modes. Where the multiwalled carbon nanotube dispersed in the organic solvent is held in the pores of a porous membrane supported by capillary forces and sonification. All microextraction experiments were supported using an Accurel $Q_{3/2}$ polypropylene hollow fiber membrane (600 μm I.D., 200 μm wall thicknesses, 0.2μm pore size). The experimental setup is very simple and highly affordable. Among most of micro-extraction techniques reported, it is the most effective sample preparation/preconcentration technique. The hollow fiber is disposable, so single use of the fiber reduces risk of cross-contamination and carry-over problems. The proposed method allows the very effective and enriched recuperation of ionic analyte into MWCNTs/organic phase. In order to obtain high enrichment and extraction efficiency of the analyte using this novel technique, the main parameters were optimized. Under the optimized extraction conditions, the method showed good linearity, repeatability, low limits of detection and very excellent enrichment factor (EF = 950).

Keywords: Flame Atomic Absorption Spectroscopy, Hollow Fiber, Multiwalled Carbon Nanotube, Solid/Liquid Phase Microextraction, Zn(II).

1. INTRODUCTION

Conventional liquid–liquid extraction (LLE) has been the main method for enrichment of nitroaromatic compounds from aqueous solutions. Although LLE is widely used it has a number of disadvantages including being Labor intensive, time-consuming and requiring the use of large amounts of high purity solvents. Driven by the need to overcome these drawbacks, new simple and rapid sample preparation techniques have been developed over the last two decades including solid-phase micro-extraction (SPME) [1, 2].

Miniaturized LLE or liquid-phase micro-extraction (LPME), was introduced in 1996, and involved using of a droplet of organic solvent hanging at the end of a microsyringe needle. The organic microdroplet is placed in an aqueous sample, and the analytes present in the aqueous sample are extracted into the organic microdroplet (micro-extract). Subsequently, the organic microdroplet is withdrawn into the syringe, the syringe transferred to a GC, and the microextract injected into the GC for the final Analysis [3-6].

Alternatively, LPME has been performed in a three-phase system in which analytes in their neutral form are extracted from aqueous samples, through a thin layer of an organic solvent on the top of the sample, and into an aqueous microdroplet (micro-extract) placed at the tip of a micro-syringe [7,8]. In the latter, the analytes were transferred to their ionized state (different pH from the sample) to promote trapping within the micro-extract.Subsequently, the aqueous micro-extract was transferred to a HPLC for the final analysis.Based on hanging droplets, two-phase and three-phase LPME were recently reviewed [9]. In both case, high partition coefficients are obtained because they are transferred by diffusion from a relatively large sample volume (1-5 mL) into a micro-extract of typically 5-50 μL. In addition, the consumption of organic solvent is low, and the sample clean-up advantages of LLE are preserved; particularly in the three-phase mode when both extraction and back-extraction are included, excellent clean-up has been observed, even from complicated biological samples. Another way for miniaturizing the LLE process is adding a membrane to phases. Hollow fiber liquid phase micro-extraction (LPME) evolved from this approach.

According to this method, a porous polypropylene hollow fiber impregnated with an organic solvent is used as an acceptor phase [10]. In one of the possible configurations, the fiber is connected at one of its ends to the needle tip of a micro-syringe while the other end is left suspended in the sample solution [11]. This fiber configuration is considered to be an evolution of SDME due to the protective feature of the hollow fiber for the organic phase. Hollow fiber LPME

*Address correspondence to this author at the Department of Chemistry, Payame Noor University, 19395-4697 Tehran, I.R. of Iran;
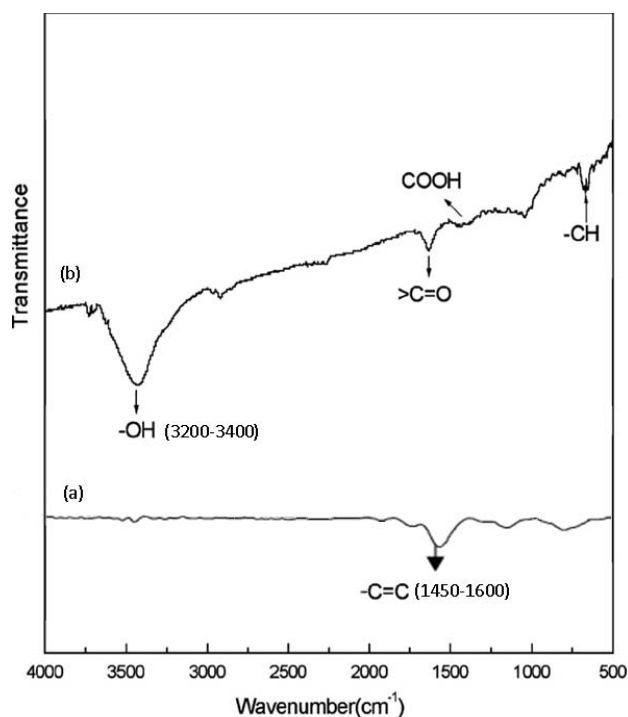Tel: +98-511 8691088; Fax: +98-511 8683001;
E-mail: zarrin_eshaghi@pnu.ac.ir

Fig. (1). FT-IR spectrum of raw and functionalized MWCNTs.

has been successfully applied for the extraction of drugs from a variety of biological fluids or for the preconcentration of pollutants from several environmental matrices [12].

Overall, this recently introduced method proved to be an attractive alternative to other microextraction concepts having the advantages of being simple, inexpensive, sensitive, fast and virtually solvent-free. In addition, the disposable nature of the hollow fiber due to the low cost of analysis per sample eliminated the possibility of carry-over between analyses. Carbon nanotubes (CNTs) [13, 14], has led research to new area in many interdisciplinary investigations as the advantages of CNTs are unique structural, electronic, optoelectronic, semiconductor, mechanical, chemical and physical properties [13-15]. CNTs have the pontential for high impact since they have now become readily available in moderate quantities. Nowadays, in the solid phase extraction studies transition metals at trace level, investigation of the usage of new materials, as solid phase extractor is an important ratio [16-17]. At this point, CNTs have been proposed as a novel solid phase extractor for various inorganic and organic materials at trace levels. CNTs are one of the most commonly used building blocks of nanotechnology and can be visualized as a sheet of graphite that has been rolled into a tube, and divided into multiwalled carbon nanotubes (MWNTs) and singlewalled carbon nanotubes (SWNTs) according to the carbon atom layers in the wall of the nanotubes. Development ofchemical synthesis methods to control the diameter of nanotube, chirality and wall number represent a significant challenge. Presently the three main methods employed for CNTs synthesis are arc-discharge, laser ablation, and chemical vapor deposition (CVD). CNTs walls are not reactive, but their fullerene-like tips are known to be more reactive, so end functionalization of CNTs is used relatively often to generate functional groups (e.g. –COOH, –OH or –CO) [18-21]. CNTs have

been shown to possess great potential as superior adsorbents for removing many kinds of organic and inorganic pollutants such as dioxin volatile organic compounds from air stream or fluoride, 1,2-dichlorobenzene, trihalomethanes, soil organic matters and various divalent metal ions (Cd^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}) from aqueous solution [22].

In this work, multiwalled carbon nanotubes (MWCNTs) were oxidized by various chemical agents and were employed as sorbents to study their characterization. Isotherms and the kinetics of Zn^{2+} sorption in an aqueous solution, which is commonly discharged from many kinds of industrial activities such as chemicals, metals, pulp and paper manufacturing processes, were also conducted to determine the optimal chemical modification of MWCNTs in water and wastewater treatment [23].

2 . EXPERIMENTAL

2.1. Chemicals and Reagents

Methanol, toluene, acetone, hexane, surfactants and 1-Octanol were purchased from Merck (Darmstadt, Germany).

Salts, acids, bases and solvents were of analytical grade were also purchased from Merck too. The hollow fiber polypropylene membrane, Q3/2 Accurel PP (200 µm thick wall, 600 µm inner diameter and 0.2 µm average pore size) was purchased from Membrana (Wuppertal, Germany).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%.

2.2. Instrumentation

The flame atomic absorption spectrometer used in this work was FAAS, Model PU9600 X instrument. The parameters for flame atomic absorption spectrometry used for this investigation was aZn Lamp current, 8 mA; Wavelength, 213.8 nm; Band pass, 0.5 nm;Burner head,standard type; Burner height, 5 mm, Flame, Air–acetylene; Oxidant gas pressure, 1.25 bar; fuel gas flow rate, 2 L/min.

2.3. Modification of MWCNTs

Acid treatment in a sonication bath has been used to yield short MWNTs [24, 25] and introduce acidic groups onto the surface of the MWCNTs (see Fig. **1**).

Multiwalled carbon nanotubes are unique and one-dimensional macromolecules that have outstanding thermal and chemical stability. The large adsorption capacity of CNTs is mainly related to their pore structure, surface area and the existence of a wide spectrum of surface functional groups [26]. Modification of CNTs with specific physicochemical properties can be achieved by chemical reactions. Therefore, in order to meet the growing demand for extractor, modification of CNTs is needed for employing the most efficient CNTs. Earlier observations of multishell nanotubes have showed that oxidation tends to be most vigorous near the tips, providing a mechanism for opening the tubes. In addition, oxidation resulting in thinner tubes [27-30].

However, further investigation of the oxidized tubes reveals a more complicated picture, which is influenced by curvature, pentagon and heptagon position, and probably

Fig. (2). Functionalized MWCNTs dispersed in 1-Octanol.

helicity. The results we report here have been observed consistently in many samples.

MWCNTs usually have cylindrical shapes with the diameter range of 8–10 nm. Due to inter-molecular force, the isolated MWCNTs of different size and direction form an aggregated structure. After functionalization and purification the length of CNTs becomes short and the confined space among isolated CNTs becomes small. Large amount of metal catalysts and amorphous carbon within raw CNTs was removed after purification.

In this study, MWCNTs were treated with two methods. In the first one, raw CNTs were functionalized with acid as following; MWCNTs were dispersed into a flask containing concentrated nitric acid solution refluxed at 140°C for 6 h.

After cooling, the MWCNTs were washed with the deionized water until the pH of the solution approximately reached to 7. Then the solution was filtered and dried at 120 C for 4 h to obtain the acidified MWCNTs.

In the second method raw CNTs (3 g) were heated at 350 °C for 30 min to remove amorphous carbon. After thermal treatment, 0.5g of CNTs was dispersed into a flask containing 20 mL of 70% sodium hypochlorite solution (6 mL of H_2O + 14 mL of NaClO). The solution was then shaken in an ultrasonic cleaning bath (Model XL2020) for 20 min and was heated at 85 C in a water bath for 3 h to remove metal catalysts. After cooling, the CNTs were washed with deionized water until the solution was at a pH of 7. Finally, the solution was filtered through a 0.45 m Nylon fiber filter and purified functionalized -CNTs were obtained [26].

The metal ion sorption capacity of functionalized multi-walled carbon nanotubes (F-MWCNTs) does not have a direct correlation with their specific surface area, pore specific volume and mean pore diameter but strongly depends upon their surface total acidity. The metal ion sorption capacity of CNTs increased as a rise in the amount of surface total acidity (including carboxyls, lactones and phenols) present on the surface site of CNTs. This reflects that the sorption of metal ions onto CNTs is a chemi-sorption

process rather than physisorption process. The oxidized CNTs have more surface total basicities, which are responsible for sorption of anions from aqueous solution, than the raw CNTs. The mechanisms by which the metal ions are sorbed onto CNTs are very complicated and appear attributable to electrostatic attraction, sorption–precipitation and chemical interaction between the metal ions and the surface functional groups of CNTs.

The chemical interaction between the metal ions and the surface functional groups of CNTs is the major sorption mechanism [30-33]. Protons in the carboxylic and phenolic groups of CNTs exchange with the metal ions in the aqueous phase. The solution pH dropped after sorption of metal ion onto CNTs and reached equilibrium, which could be explained by the release of H^+ from the CNT surface into solution. Li *et al.* [34] reported that more electrostatic attraction occurs at a higher solution pH and leads to an increase in sorption of more Zn^{2+} ions onto CNTs.

2.4. HF-SLPME Procedure

Membrane extraction with sorbent interface which we used in this research is a two phases microextraction consisting of aqueous feed and organic solvent/nano sorbent extracting phase. Second phase was supported by a piece of polypropylene hollow fiber and the system operated in direct immersion sampling modes. F-MWCNTs weredispersed in the organic solvent and held in the pores of a porous membrane supported by capillary forces and sonication. The analytes from the aqueous sample diffuse through the pores and inside polypropylene membrane in to MWCNTs dispersing in the organics solvent. The analyte was then trapped in a sorbent (micro) trap besides the organic solvent immobilised in the pores and thus, enriched.

All micro-extraction experiments were performed using an Accurel $Q_{3/2}$ polypropylene hollow fiber membrane (600 µm I.D., 200 µm wall thickness, 0.2 µm pore size). The fiber was cut into small segments with a length of 2.5 cm. 15 µL of a disperse mixture of the F-MWCNTs in 1-Octanol (See Fig. **2**) was gradually injected into the fiber manually using a microsyringe (25 µL). The fiber pores were filled with the mixture and the mixture was homogenized and spread within the pores. The excess amount of mixture was carefully removed from the inside of the fiber. The fiber was then bent into a U-shape and together with a small part of the supporting syringe needle was submerged in the sample solution present in a proper vial (10 mL)according to the donor phase volume. The vial was covered and stirred at 600 rpm for 30 min.

After the extraction,the fiber was transferred into a small glass vial, the fiber and the pores were washed with 2 mL of solution containing 1 mL 0.1 M HCland 1 mL methanol which was collected in the small vial. The Zn(II) concentration was determined in the concentrated phase using atomic absorption spectrophotometer.

The Octanol/F-MWCNTs were immiscible with water and remained within the pores during extraction with no leakage to the aqueous sample. The organic solvent/carbon nanotube formed a thin layer within the wall of the hollow fiber, which typically had a thickness of 200 µm, and the total volume of organic solvent immobilized was typically
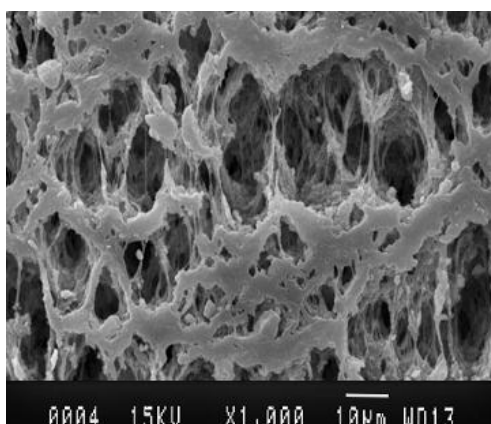
(**a**)
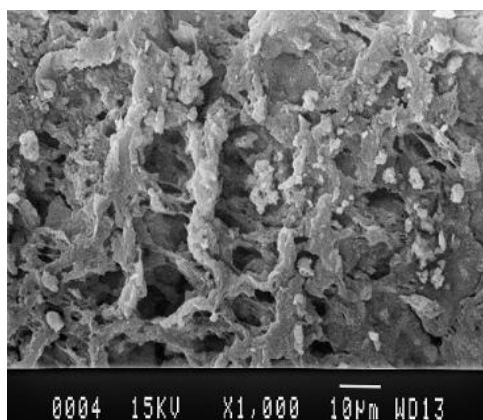
(**b**)

Fig. (3). Scanning electron microscopy (SEM) images of polypropylene pores and structure (**a**) before and (**b**) after filling with functionalized MWCNTs in 1-Octanol.

15–20 mL. For metal ions, with addition of the proper ligand or ion pair, the ions are converted to the de-ionized form to reduce their solubility within the aqueous sample and to the organic phase.

MWCNTs are a good sorbent for metal ions. Thus, analytes are extracted from the aqueous sample, through the organic phase/MWCNTs in the pores of the hollow fiber, and further into an acceptor solution inside the lumen of the hollow fiber. In two-phase LPME, analytes are extracted by passive diffusion from the aqueous sample (donor solution) directly into the organic phase/MWCNTs. This process is described by Eq. (1).

A (Sample) ↔ A (Organic phase/MWCNTs)   (1)

The extraction process depends on the partition coefficient between the organic acceptor solution and the donor solution (Ka/d), defined by Eq. (2).

$$K_{a/d} = C_{eq,a}/C_{eq,d} \qquad\qquad (2)$$

Where $C_{eq, a}$ is the analyte concentration at equilibrium in the acceptor solution and $C_{eq,d}$ is the analyte concentration at equilibrium in the donor solution. The extraction recovery, *R*, and the enrichment, *EF*, in the two-phase LPME system may be calculated by Eqs. (3) and (4)[35, 36].
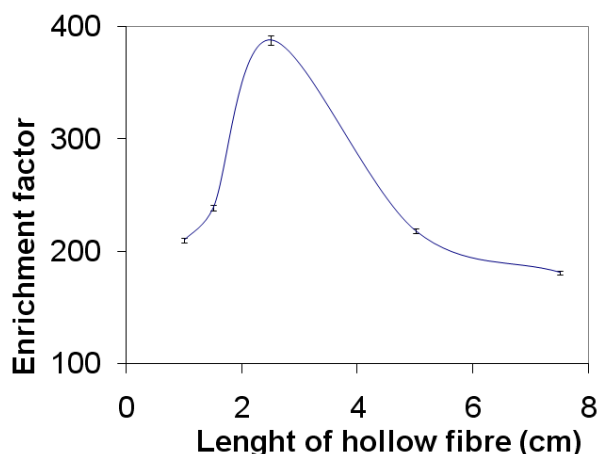
Fig. (4). Fiber length effect on extraction efficiency.

$$R = (100.K_{a/d}.V_a)/(K_{a/d}.V_a + V_d) \qquad (3)$$

$$EF = (V_d.R)/(V_a.100) \qquad (4)$$

where *Va* is the volume of acceptor solution and *Vd* is the volume of donor solution.

All experiments were performed in triplicate and the means of the results were used in calculations. Fig. (**3**) shows the scanning electron microscopy (SEM) images of polypropylene pores and structure before and after filling with functionalized MWCNTs in 1-Octanol.

3. RESULTS AND DISCUSSION

3.1. Experimental Optimization for the HF-SLPME

In order to obtain high enrichment and extraction efficiency of the analyte using novel HF-SLPME technique, the main parameters were optimized.

3.2. Effect of Length of Hollow Fiber

The hollow fiber was cut into small segments with length from 1 to 7.5 cm and suspension of functionalized MWCNTs/Octanol was injected into the lumen of the fiber with microsyringe. Microextractionwas done with the developed method and the results were shown in Fig. (**4**). The extractionefficiency was optimum at hollow fiber lengths of around 2.5cm. Short fiberswould not contain sufficient amount of sorbent andin long ones, the fiber channel would not uniformly filled with acceptor phase. As a result, efficiency impaired in both cases.

3.3. Amount of F-MWCNTs Effect on the Extraction

An amount of 0.15g of F-MWCNTs were dispersed into a flask containing 3, 4, 5.5 and 7 mLof 1-Octanol. The suspensions were than shaken in an ultrasonic cleaning bath for 10 min. 15μL of a dispersed mixture was gradually injected into the fiber manually by using anmicrosyringe. Results were shown in Fig. (**5**).

As was expected, increasing the amount of F-CNTs resulted in an increase at the extraction efficiency because the carboxylic MWCNTs formed a network like a polymer and afforded the additional interactions for the analyte molecules. The treated MWCNTs were terminated with carboxylic acid groups and hydroxyl groups (Fig. **1**). The
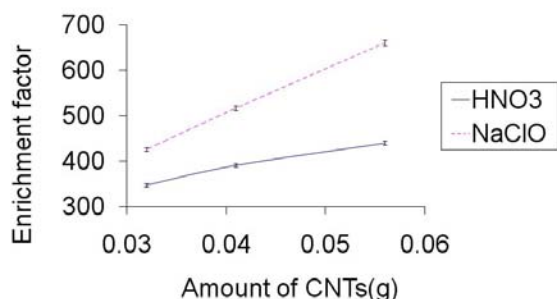
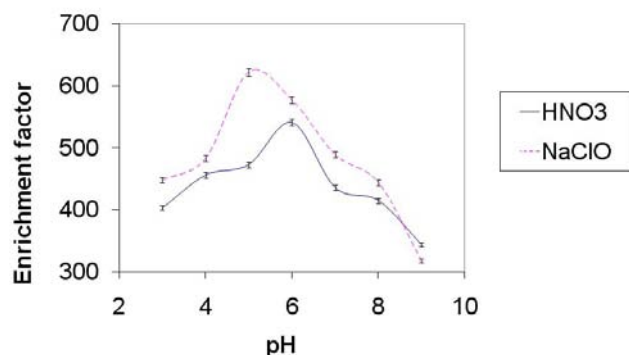**Fig. (5).** Effect of F-MWCNTs amount on extraction efficiency.

Fig. (6). pH effect of sample solution on the extraction with two kinds of F-MWCNTs as sorbent material.

non-treated MWCNTs aggregated in a disorderly fashion, but the functionalized MWCNT, in contrast, was well dispersed because of the presence of the functional groups that repel each other electrostatically. Therefore, the treated MWCNTs were selected as the initial material for the subsequent microextraction procedure.

With increasing the amount of MWCNTs more than 0.056 g of CNTs per 2.5 cm hollow fiber, the injection of massive mixture into the fiber was difficult. Moreover the air bubbles occupied the fiber spaces.Therefore the amount of 0.056 g of CNTs per 2.5 cm hollow fiber was selected.

3.4. Effect of pH

The pH of the solution plays an important role in effecting the adsorption characteristics of Zn(II) onto CNTs. The effects of sample pH in the range of 3-9 were investigated. As shown in Fig. (**6**), best donor phase pH for MWCNTs functionalized with NaClO was 5, and 6 for MWCNTs functionalized with HNO_3respectively. As can be seen, it is known that zinc species can be present in deionized water in the forms of Zn^{2+}, $Zn(OH)^{+1}$, $Zn(OH)^0_2$, $Zn(OH)^-_3$ and $Zn(OH)^{2-}_4$. At pH<8, the predominant zinc species are always Zn^{2+} and the removal of Zn^{2+} is mainly accomplished by adsorption reaction.

Therefore, the low Zn (II) adsorption and extraction efficiency that took place at low pH can be attributed in part to competition between H^+ and Zn^{2+} ions on the CNTs same sites. At pH > 8, The main species are $Zn(OH)^{+1}$, $Zn(OH)^0_2$and $Zn(OH)^-_3$thus the removal of Zn (II) is possibly accomplished by simultaneous precipitation of $Zn(OH)_2(s)$ and adsorption of $Zn(OH)^{+1}$ and $Zn(OH)$ (see Fig. **6**).

3.5. Effect of Volumes of Donor and Acceptor Phases

As the analyte is extracted from relatively large sample volumes into a very small volume of acceptor solution then themicroextractionmethod provide substantial analyte enrichment. The enrichment in LPME is basically determined by the analyte recovery and by the volume of the sample. As was mentioned in equation 4, when the volume of the sample increases, the enrichment factor also increases [12, 36]. Thus decreasing the volume ratio of acceptor and donorphases can lead to an increase in extraction efficiency. In HF–SLPME, extraction is an equilibration process and therefore, the amount of analyte partitioning into the acceptor solution becomes independent of the sample volume when this volume is much higher than the product of the partition constant and the volume of the acceptor solution [36]. Furthermore, a larger sample volume can be disadvantageous due to poorer mass transfers kinetics, resulting in a worse extraction efficiency. Here, we optimized the phase ratio volumes experimentally and fixed on 7 mL.

3.6. Extraction Times

SLPME is not an exhaustive extraction technique. Although maximum sensitivity is attained at equilibrium, complete equilibrium needs not to be attained for accurate and precise analysis. Therefore, the extraction time is one of the important factors that influence the extraction efficiency. Extraction efficiency depends on the time that the analyteis in contact with the organic phase into the pores of hollow fiber and the acceptor solution. It has been reported that longer equilibration times do not have any significant effect on the extraction parameters [37, 38].

Here we found that the extraction efficiency of the HF-SLPME techniqueincreased when the extraction time increased from 15, 60 and 75 min. for F-MWCNTS (functionalized with NaClO), and F-MWCNTS (functionalized with HNO_3) but did not reach equilibrium, respectively. The MWCNTs present a porous layer through which mass transfer can take place by diffusion through the pores.

The porosity of MWCNTs should therefore strongly affect the extraction dynamics. Thus, pores of nanometer dimension found on the surface of MWCNTs might lead to longer equilibrium time for the extraction of the analytes compared with the conventional HF-LPME mode. Therefore, in this work we observed that an equilibration time of 60 and 75 min for F-MWCNTS (functionalized with NaClO), and F-MWCNTS (functionalized with HNO_3) respectively were sufficient to obtain a good extraction. The results were shown in Fig. (**7**).

3.7. Effect of Surfactant on the Extraction

Surfactants can also be added to the solution to better disperse the nanotubes and prevent their re-aggregation. A correct choice of surfactant is fundamental for obtaining a satisfactory pre-concentration and extraction process. In selection of appropriate surfactant, consideration should be given to its interaction with the analyte and matrix, as well as the solubility of the analyte [39]. Anionic surfactants could be a good choice for extraction of cationssuch as Zn(II). Meanwhile ionic surfactantsare water soluble. So we used of sodium lauryl sulfate (SLS) $(C_{12}H_{25}SO_4Na)$ as an
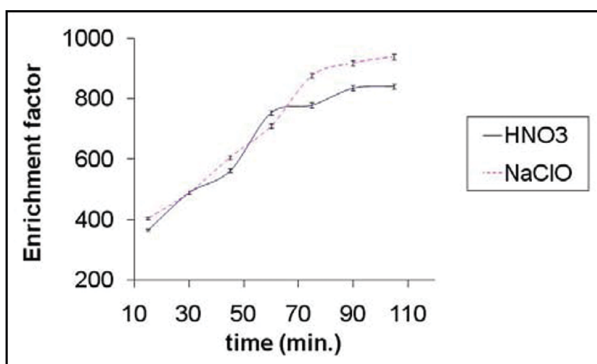
Fig. (7). Effect of time on extraction efficiency.

anionicsurfactant that is used in many cleaning and hygiene products.

The surfactant concentration is also an important parameter for effective extraction.Concentrations of SLS were studied in range 5 to 8 mM, below the criticalmicelle concentration(CMC). When the surfactant concentration in the donor solution goes above the CMC then the extraction efficiency was found to decrease sharply. This is due to a greatertrapping ofZn (II) with micelles. When analytewas added into the micelle solution in which surfactant concentration was over the CMC a fraction of it incorporated into the micelle and this complex could not passes completely through the hollow fiber pores.Furthermore, high concentration of surfactant resultedin relatively high viscosity that caused a reduction of Zn (II) ion transfer into organic phase. Consequently, the data has shown that an optimized concentration of 7 mMwas the best condition for Zn(II) ion extraction.

3.8. Effect of the Stirring Speed

It has been found that increasing the agitation rate of the aqueous sample enhances extraction by aiding diffusion of analyte present in the donor phase through the interfacial layer of the hollow fiber and into the acceptor solution. In SLPME, the hollow fiber protects the acceptor mixture, and consequently high agitation speeds can be applied [12]. Optimization was investigated by performing 30 min extractions on aqueous solutions containing 2 mg/L of target analyte at stir rates of 500, 600, 700, 800 and 900 rpm. As expected increasing the agitation rate (up to 700 rpm) resulted in an increase of the enrichment factor for the target analyte. An agitation rate of more than 700 rpm led to fiber fluctuationsand caused the instability. Furthermore, due to the formation of air bubbles generated on or near the fiber surface, analyte extraction was decreased. On the basis of the above results, 700 rpm was used as the optimum stirring speed.

3.9. Ionic Strength

In order to examine the effect of ionic strength of the sample matrix upon extraction, a series of experiments were carried where the aqueous samples contained different amounts of NaCl. In general, depending on the nature of the contaminants, addition of salt to the sample solution can decrease analytes solubility and consequently increase their hydrophobicity [40]. This is due to the salting-out effect where fewer water molecules are available for dissolving the

analyte molecules, preferably forming hydration spheres around the salt ions [41]. In HF-SLPME, the effect of salt addition in the donor solution prior to extraction has been investigated and the results showed that depending on the target analyte, an increase in the ionic strength of the aqueous solution may enhance, not influence or even limit extraction of analytes [12].

So the effect of increasing 4% salt NaCl was tested to show results. The extraction efficiency is reduced. In fact was shown salting in effect.

This may be due to competitive interaction of Na (I) with active sites on the F-MWCNTs surface which caused decrease in sorption capacity of Zn(II) ions by CNTs. In addition, the presence of salt caused a second effect; the physical properties of the aqueous-organic solvent extraction film were changed. So,salt was not added to the feed solution.

3.10. Adsorption Isotherm Models

The analysis of isotherm is important in developing an adsorption equation. This study employs the Langmuir and Freundlich isotherms to describe the equilibrium adsorption. The Langmuir isotherm assumes monolayer coverage of the adsorption surface and no subsequent interaction among adsorbed molecules. Therefore, the adsorption saturates, and no further adsorption can occur [42]. The Freundlich isotherm is derived to model multilayer adsorption and adsorption on heterogeneous surfaces [43].

Langmuir (LM) equations are as follows:

$$q_e = abC_e/ 1+bC_e \qquad (5)$$

orlinear form of the LM equation is:

$$1/q_e = 1/abC_e + 1/ a \qquad (6)$$

Freundlich (FM) equations are respectively:

$$q_e = K_f C_e^{1/n} \qquad (7)$$

orits linear form:

$$\log q_e = 1/n\, C_e + \log K_f \qquad (8)$$

Where Ce is the equilibrium concentration of Zn(II) (mg/L); a is the maximum sorption capacity (mg/g); b is the Langmuir sorption constant (L/mg); and $K_f$and n are the Freundlich constants. The constants of Langmuir and Freundlich models were obtained from fitting the model to the qe. With the exception of raw MWCNTs, the qe of oxidized MWCNTs are better correlated with Langmuir model. The a and K_f which represent the Zn(II) sorption capacity, are the greatest for the F-MWCNTs(with NaClO), followed by the F-MWCNTs(with HNO$_3$), then the raw MWCNTs. The constant b, which is related to the free energy of sorption, presents the same trend as and K_f, indicating that the oxidized MWCNTs have a higher affinity for Zn(II) than the raw MWCNTs. The magnitude of 1/n quantifies is introduces the favorability of adsorption and the degree of heterogeneity of the CNTs surface. If 1/n is less than unity, suggesting favorable adsorption, than the adsorption capacity increases and new adsorption sites form. Langmuir isotherms of Zn(II) onto raw and oxidized MWCNTshave shown the Zn(II) sorption onto MWCNTs

Table 1. Coefficients of Langmuirand Freundlich Isotherm (25 °C)

Type of CNTs	Langmuir Isotherm			Freundlich Isotherm		
	K_L	q_m	R^2	K_F	n	R^2
Raw CNTs	0.05	21.90	0.964	7.202	1.094	0.985
F-MWCNTs (with NaClO)	0.093	24.20	0.996	2.454	0.945	0.987

Table 2. Analytical Performance Parameters (HF-SLPME)

HF-SLPME Method	F-MWCNTs (HNO3)	F-MWCNTs(NaClO)
Equation	Y=192.04X+131.63	Y=241.27X+225.02
R^2	0.9949	0.9952
LOD(µg/mL) (n=5)	0.0005	0.0004
LOQ(µg/mL) (n=5)	0.0016	0.0013
Linear range (µg/mL)	0.001-6	0.001-8
EF (n=5)	800	950
RSD%	5.67	5.56

Table 3. Industrial Wastewater Analysis

Observed Concentration (µg / mL)	Relative Standard Diviation	Fiber Type
0.25	% 7.2	F-MWCNTs(HNO₃)
0.24	% 6.3	F-MWCNTs(NaClO)

was greatly improved after oxidation by HNO_3 and NaClO solutions, reflecting that oxidation of MWCNTs was required for better performance for sorption of Zn(II) from aqueous solution.

This could be because of the changes in the physicochemical properties of MWCNTs including the increase in carbon content in functional groups and negatively charged carbon surfaces. These modifications made MWCNTs provide not only a more hydrophilic surface but also a more negatively charged surface (See Table **1**).

4. ANALYTICAL PERFORMANCE

The performance parameters of the HF-SLPME technique, such as calibration curve equations, correlation coefficient, liner dynamic range, limits of detection and quantification, relative standard deviations (RSD%) were studied. The results are listed in Table **2**.

The linearity was checked for concentration range from 0.0005 to 10 ppm with triplicate measurements for each concentration. A good linearity was observed with squared regression coefficient of (R^2)>0.99.

5. ENVIRONMENTAL WATER SAMPLE ANALYSIS

The real water samples to demonstrate the potential of this method as a viable extraction technique for environmental samples were analyzed. The concentration of Zn(II) from an industrial wastewater , after extraction with

the HF-SLPME was determined. Samples were taken from a factory in Mashhad, Iran. Results are summarized in Table **3**.

CONCLUSIONS

A novel, fast and simple procedure based on the non-exhaustive MWCNTs assisted HF-SLPME equilibrium sampling combined with FAAS has been developed to extract Zn(II) from the aqueous samples. The experimental setup is very simple and highly affordable. Among all microextraction techniques reported, this technique is one of the most effective sample preparation/pre-concentration techniques. The hollow fiber is disposable, so single use of microextraction device reduces the risk of cross-contamination and carry-over problems. The proposed method allows the very effective and enriched recuperation of ionic analyte into MWCNTs/organic phase. This procedure can be successfully used for the analysis of organic and inorganic analytes in the aqueous samples. Moreover, the method was applied to the analysis of environmental water samples giving good qualitative and quantitative results. Other advantages of this method are good repeatability, low limits of detection and %RSD.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflicts of interest.

ACKNOWLEDGMENTS

REFERENCES

[1] Arthur, L.; Pawliszyn, J. Solid phase microextraction with thermal desorption using fused silica optical fibers Catherine. *Anal. Chem.*, **1990**, *62*, 2145–2148.
[2] Lord, H.; Pawliszyn, J. Evolution of solid-phase microextraction-technology. *J.Chromatogr. A.*, **2000**, *885*, 153-193.
[3] Jeannot, M.A.; Cantwell, F.F. Solvent Microextraction into a Single Drop, *Anal. Chem.,* **1996**, *68*, 2236-2240.
[4] Jeannot, M.A.; Cantwell, F.F. Mass Transfer Characteristics of Solvent Extraction into a Single Drop at the Tip of a Syringe Needle. *Anal. Chem.,* **1997**, 69, 235–239.
[5] He, Y.; Lee, H.K. Liquid-Phase Microextraction in a Single Drop of Organic Solvent by Using a Conventional Microsyringe. *Anal. Chem.,* **1997**, *69*,4634-4640.
[6] Zhao, L.; Lee, H.K. Application of static liquid-phase microextraction to the analysis of organochlorine pesticides in water. *J. Chromatogr. A.,* **2001**, *919*, 381-388.
[7] Ma, M.; Cantwell, F.F. Solvent Microextraction with Simultaneous Back-Extraction for Sample Cleanup and Preconcentration. *Anal. Chem.*, **1998**, *70*, 3912–3919.
[8] Ma, M.; Cantwell, F.F. Solvent Microextraction with Simultaneous Back-Extraction for Sample Cleanup and Preconcentration: Quantitative Extraction. *Anal. Chem.*, **1999,** *71*, 388–393.

[9]　Psillakis, E.; Kalogerakis, N. Developments in single-drop microextraction, TrAC Trends. *Anal. Chem.*, **2002**, *21*, 54-64.

[10]　Pedersen-Bjergaard, S.; Rasmussen, K.E. Liquid−Liquid−Liquid Microextraction for Sample Preparation of Biological Fluids Prior to Capillary Electrophoresis. *Anal. Chem.*, **1999**, *71*, 2650–2656.

[11]　Zhu, L.; Zhu, L.; Lee, H.K. Liquid–liquid–liquid microextraction of nitrophenols with a hollow fiber membrane prior to capillary liquid chromatography. *J.Chromatogr. A.*, **2001**, *924*, 407-414.

[12]　Psillakis,E.; Kalogerakis, N. Developments in liquid-phase microextraction, TrAC Trends. *Anal. Chem.*, **2003**, *22*, 565-574.

[13]　Iijima, S. Helical microtubules of graphitic carbon. *Nat.*, **1991**, *354*, 56-58.

[14]　Iijima,S.; Ichihashi, T. Single-shell carbon nanotubes of 1-nm diameter. *Nat.*, **1993**, *363*, 603-605.

[15]　Tagmatarchis,N.; Zattoni, A.;Reschiglian, P.; Prato, M. Separation and purification of functionalised water-soluble multi-walled carbon nanotubes by flow field-flow fractionation. *Carbon.*, **2005**, *43*,1984-1989.

[16]　Du, D.; Wang, M.; Zhang, J.; Cai, J.; Tu, H.; Zhang, A. Application of multiwalled carbon nanotubes for solid-phase extraction of organophosphate pesticide. *Electrochem. Comm.*, **2008**, *10*, 85-89.

[17]　Tuzen, M.; Saygi, K.O.; Soylak, M. Solid phase extraction of heavy metal ions in environmental samples on multiwalled carbon nanotubes. *J. Haz. Mat.*, **2008**, *152*, 632-639.

[18]　Cassell, A.M.; Raymakers, J.A.; Kong, J.; Dai, H. Large-scale CVD synthesis of single-walled carbon nanotubes. *J. Phys. Chem. B.*, **1999**, *103*, 6484–6492.

[19]　Odom, T.W.; Huang, J.L.; Kim, P.; Lieber, C.M. Atomic structure and electronic properties of single-walled carbon nanotubes. *Nat.*, **1998**, *391*, 62-64.

[20]　Osorio, A.G.; Silveira, I.C.L.; Bueno, V.L.; Bergmann, C.P. H2SO4/HNO$_3$/HCl-Functionalizationnanotubes in aqueous media, App. Surf. Sci. **2008**, *255*, 2485–2489.

[21]　Zhou, Z.; Wang, S.; Lu, L.; Zhang, Y.; Zhang, Y. Functionalization of multi-wall carbon nanotubes with silane and its reinforcement on polypropylene composites, *Comp. Sci. Technol.*, **2008**, *68*, 1727–1733.

[22]　Rao, G.P.; Lu,C.; Su, F. Sorption of divalent metal ions from aqueous solution by carbon nanotubes: A rev. *Sep. Purif. Technol.*, **2007**, *58*, 224-231.

[23]　Liu, J.; Rinzler, A.G.; Dai, H.; Hafner, J.H.; Bradley, R.K.; Boul, P.J.; Lu, A.; Iverson, T.; Shelimov, K.; Huffman, C.B.; Rodriguez-Macias, F.; Colbert, D.T.; Smalley, R.E. Fullerene pipes. *Sci.*, **1998**, *280*, 1253-1256.

[24]　Saito, T.; Matsushige, K.; Tanaka, K. Chemical treatment and modification of multi-walled carbon nanotubes. *Physica. B.*, **2002**, *323*, 280-283.

[25]　Esumi, K.; Ishigami, M.; Nakajima, A.; Sawada, K.; Honda, H. Chemical Treatment of Carbon Nanotubes. *Carbon.*, **1996**, *34*, 279–281.

[26]　Lu, C.; Chiu, H. Adsorption of zinc(II) from water with purified carbon nanotubes. *Chem. Eng. Sci.*, **2006**, *61*, 1138–1145.

[27]　Stafiej, A.; Pyrzynska, K. Adsorption of heavy metal ions with carbon nanotubes. *Sep. Purif. Technol.*, **2007**, *58*, 49-52.

[28]　Lu, C.; Chung, Y.L.; Chang, K.F. Adsorption of trihalomethanes from water with carbon nanotubes, *Water Res.*, **2005**, *39*, 1183-1189.

[29]　Lu, C.; Chiu, H. Chemical modification of multiwalled carbon nanotubes for sorption of Zn^{2+} from aqueous solution. *Chem. Eng. J.*, **2008**, *139*, 462-468.

[30]　Lu,C.; Liu, C. Removal of nickel(II) from aqueous solution by carbon nanotubes. *J. Chem. Technol. Biotechnol.*, **2006**, *81*, 1932–1940.

[31]　Li, Y.H.; Wang, S.; Luan, Z.; Ding, J.; Xu, C.; Wu, D. Adsorption of cadmium(II) from aqueous solution by surface oxidized carbon nanotubes. *Carbon*, **2003**, *41*, 1057–1062.

[32]　Li, Y.H.; Wang, S.; Wei, J.; Zhang, X.; Xu, C.; Luan, Z.; Wu, D.; Wei, B. Lead adsorption on carbon nanotubes. *Chem. Phys. Lett.*, **2002**, *357*, 263–266.

[33]　Akhtar, N.; Iqbal, J.; Iqbal, M. Removal and recovery of nickel(II) from aqueous solution by loofa sponge-immobilized biomass of Chlorella sorokiniana: characterization studies. *J. Haz. Mat.*, **2004**, *108*, 85–94.

[34]　Li, Y.H.; Ding, J.; Luan, Z.; Di, Z.; Zhu, Y.; Xu, C.; Wu, D.; Wei, B. Competitive adsorption of Pb^{2+}, Cu^{2+} and Cd^{2+} ions from aqueous solutions by multiwalled carbon nanotubes. *Carbon.*, **2003**, *41*, 2787-2792.

[35]　Ho, T.S.; Pedersen-Bjergaard, S.; Rasmussen, K. E. Recovery enrichment and selectivity in liquid-phase microextraction: Comparison with conventional liquid–liquid extraction. *J. Chromatogr. A.*, **2002**, *963*, 3-17.

[36]　Basheer, C.; Alnedhary, A.A.; Rao, B.S.; Balasubramanian,R.; Lee, H.K. Ionic liquid supported three-phase liquid–liquid–liquid microextraction as a sample preparation technique for aliphatic and aromatic hydrocarbons prior to gas chromatography-mass spectrometry. *J. Chromatogr. A.*, **2008**, *1210*, 19-24.

[37]　Pálmarsdóttir, S.; Thordarson, E.; Edholm, L.E.; Jönsson, J.A.; Mathiasson, L. Miniaturized supported liquid membrane device for selective on-line enrichment of basic drugs in plasma combined with capillary zone electrophoresis. *Anal. Chem.*, **1997**, *69*, 1732–1737.

[38]　Hoffmann, M.R.; Hua, I.; Höchemer, R. Application of ultrasonic irradiation for the degradation of chemical contaminants in water. *Ultrason. Sonochem.*, **1996**, *3*, S163-S172.

[39]　Rubio, S.; Pérez-Bendito, D. Supramolecular assemblies for extracting organic compounds, TrAC Trends. *Anal. Chem.*, **2003**, *22*, 470-485.

[40]　Shen, G.; Lee, H. K. Hollow fiber-protected liquid-phase microextraction of Triazine herbicides, *Anal. Chem.*, **2002**, *74*, 648–654.

[41]　Boyd-Boland, A.A.; Pawliszyn, J. Solid-phase microextraction of nitrogen-containing herbicides, *J. Chromatogr. A.* **1995**, *704*, 163-172.

[42]　Langmuir, I. The constitution and fundamental properties of solids and liquids. *J. Am. Chem. Soc.*, **1916**, *38*, 2221-2295.

[43]　Freundlich, H. M. F. Over the adsorption in solution. *J. Phys. Chem.*, **1906**, *57*, 385- 470.