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Fe_3O_4@graphene nanocomposite reinforced hollow fiber-solid phase microextraction for preconcentration and determination of organophosphate pesticide in Environmental samples

Diyanoosh Mardanbeigi[a] and Mahmoud Ebrahimi[a]*

[a]Department of Chemistry, Mashhad Branch, Islamic Azad University, Mashhad, Iran

ABSTRACT

Hollow fiber-solid phase micro-extraction (HF-SPME) technique containing derived Fe3O4/ graphene nanocomposite as a novel high efficiency sorbent, coupled with gas chromatography was used to extraction and determination of three organophosphate pesticides; diazinon, fenitrothion and aqueous samples. First, magnetite nanoparticles (Fe_3O_4-NPs) were synthesized by chemicalco-precipitation of Fe(II) and Fe(III) ions (where the ratio of Fe(III) to Fe(II) is 2:1, surface of Fe_3O_4-NPs were modified with graphene (GO/MNPs). In this method, organophosphate pesticides were extracted by the synthesized nanocomposite and analytes by gas chromatography. Experimental parameters related to microextraction such as type of extraction time, organic solvent and agitation rate have been investigated and optimized. The extraction method has been validated for several types of real samples, and no matrix effect was observed. The technique requires minimal sample handling and solvent consumption. Using optimum conditions, low detection limits (0.00011–0.00016 $\mu g L^{-1}$) and good linearity (R^2 > 0.96) were obtained. Repeatability ranged from 3.11 to 4.91%. Finally the obtained results indicated that the method can be successfully applied for microextraction and determination of pesticides in environmental samples.

Keywords: HF-SPME**,** organophosphate pesticide, Fe3O4

INTRODUCTION

Organophosphate compounds (OPs), which are most widely used as pesticides in agriculture for pest control and as nerve agents at military and home, are highly toxic chemicals [1–3]. They can be traced in a wide range of surface Water and soil. Due to the low concentrations, OPPs in water samples are not directly analytes with conventional methods such as gas chromatography (GC) orhigh-performance liquid chromatography (HPLC). Solid phase extraction (SPE) [3,6], supercritical fluid extraction (SFE) [7] have been used for analytes of these insecticides. SPME is a simple, fast and solvent-free technique [8] and due to many advantages has been applied to the determination of OPPs [8–10] in aqueous samples.

Solid-phase microextraction (SPME), a solvent-free extraction procedure, possesses several advantages into conventional liquid–liquid extraction (LLE) due to its simplicity [11–14]. Solid-phase micro-extraction (SPME) that has almost all the attributes of an ideal method to sample preparation such as solvent-less extraction, selective, rapidness, and high recover-ies without the possibility of degradation of the analytes , involves the use of a fused silica fiber coated with a liquid polymer or a solid adsorbent, which extracts different kinds of analytes including both volatile and non-volatile from gaseous or liquid sample [15,16].

Wang et al. have reported nanostructured a-Fe_2O_3–graphene composite prepared by a solution based hydrothermal route [17]. Shen et al. [18] synthesized hematite nanoparticles and graphene composite through a high temperature

reaction of ferric triacetylacetonate with graphene oxide in 1-methyl-2-pyrrolidone. According to the best of our knowledge, report on the synthesis of hematite– graphene oxide nanocomposite by a simple and economical method like the conventional sol–gel method is still absent in the literature.

In this paper, an approach to synthesize two-layer core–shell nanoparticles is used because between the Fe_3O_4 core and outerlayer, GO is introduced to avoid the interaction between the two layers and inhibit acid dissolution of the core. Because of their large surface area, mesoporous structure and extraordinary length, the as-prepared Fe_3O_4/GO nanocomposite exhibited high capacity and selectivity in the enrichment of OPs. In this research, GO has been used as a middle. We have benefited from organic solvent that can be used to generate aporous nanocomposite with a high surface area and prevent from agglomeration MNPs [19] for extraction the following three OPs: diazinon, malathion and fenitrotion. For ease of use, and reduce the time of extraction process, we have used of hollow fiber liquid solid phase microextraction (HF-LSPME) technique. In HF-LSPME, the arganic solvent containing synthesized nanocomposite was injected into lumen a segments of polypropylene hollow fiber. The novel method of nanocomposite – reinforced HF-LSPME has overcome some of the existing drawbacks on conven-tional SPME fibers such as their high cost, sample carry-over effects, poor reusability and fiber damage.

Among the available adsorbents, magnetic nanoparticles(MNPs) particularly magnetite (Fe_3O_4), have got rapid and significant progress for extraction [20,21]. This is because of high surface area to volume ratio which enhances the extraction efficiency and low toxicity [22]. Therefore, the MNPs adsorbents, adequate, results by using less amounts of then nanoparticles adsorbents, and high activities made by the size quantization effect [23]. However, by reducing the size of the metal oxide from microm-eter to nanometer, the surface energy increases which leads to the poor stability. As a result, MNPs tend to agglomeration dueto Van der Waals forces or other interactions [24]. Thus, in this research the magnetite nanoparticles are covered with a graphene oxide network. On the other hand, graphene deposited on the surface of mag-netic nanoparticles avoids the aggregation induced by the magnetic dipolar attraction between nanomagnetics, thus enhance the better dispersion of magnetic nanoparticles in organic solvent [23].

MATERIALS AND METHODS

Apparatus

The Varian 3800CP gas chromatography (Palo Alto, CA, USA) equipped with a flame ionization detector was employed for determination of the analytes. Separation was carried out on a ZB-35, 30 m×0.25 mm capillary column with a 0.15 µm stationary film thickness, 65% dimethyl–35% diphenyl polysiloxane copolymer column (Phenomenex, USA). The GC split valve was opened (split ratio: 1/10) and nitrogen was used as a carrier gas at the constant flow rate of 1.6 mL/min. The oven temperature was programmed as follows: initial 60 ◦C, from 60 ◦C (held for 3 min) to 100 ◦C at the rate of 20 ◦C/min, from 100 ◦C (held 0 min) to 175 ◦C at the rate 15 ◦C/min, from 175 ◦C (held 2 min) to 210 ◦C at the rate 3 ◦C/min, from 210 ◦C (held 2 min) to 280 ◦C at the rate 10 ◦C/min and held at 285 ◦C for 6min. The column oven was initially held at 50 ◦C for 4 min, programmed to 100 ◦C at a rate of 10 ◦C/min and then to 260◦C at 20◦C/min. The injections were carried out using a 10µL Hamilton microsyringe (Bonaduz, Switzerland) and 10 mL extraction vial. Stirring of the solutions was carried out by a Heidolph MR3001 magnetic stirrer (Schwabach, Germany) and a 8×1.5 mm magnetic stirring bar**.**

Chemicals and materials

Target pesticides: diazinon, fenitrothion and malathion were purchased from Riedel-de Haen (Seelze-Hannover, Germany). Stock solutions of pesticides (1000 µg/mL) were prepared by dissolving calculated amounts of them in methanol. Fresh working solutions were prepared daily by diluting the stock solution in distilled water. All experiments were carried out at room temperature, 22±0.5 ◦C. Graphite powder (325mesh, 99.995%) was obtained from Alfa Aesar (MA,USA). P_2O_5 , $K_2S_2O_8$, H_2O_2, $KMnO_4$, HCl and H_2SO_4 were purchased from Sinopharm Chemistry Reagent Co. Ltd,China (Shsanghai,China). Acetonitrile, methanol, acetone, toluene, and 1-octanol were purchased from Merck (Schuchardt, Germany). analytes, solvents, salts, acids, and bases were of analytical grade. 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).

Synthesis and characterization of iron oxide functionalized graphene oxide

GO was synthesized by the oxidation of exfoliated graphite using modified Hummer's method from graphite powder using $NaNO_3$, H_2SO_4, and $KMnO_4$ in an ice bath as reported in literature [24]. A stock solution of GO single layers

(0.30 mg mL^{-1}) was obtained after sedimentation steps to eliminate unexfoliated materials. GO thin films were obtained by filtration through anodized aluminum oxide membrane with a nominal pore size of 0.02 µm. Graphene oxide (0.5. g) was dispersed into 40.0 mL of deionized water for one hour. Then, 0.44 g of $FeCl_3$,$6H_2O$ and 0.12 g of $FeCl_2$,$4H_2O$ were added to the solution. The mixture was heated up to 80 °C under nitrogen atmosphere and vigorous stirtiring (1000 rpm). Subsequently, 2.0 mL of ammonia solution (25 wt%) was rapidly added to the mixture which resulted in instant formation of black precipitate. The reaction was left to stand for 5 min and then the precipitate was collected using a magnet, washed with double distilled water, dried in vacuum at 60 °C and stored for later use.

The GO/MNPs after drying were thoroughly dispersed in 1-octanol by ultrasonication at room temperature for 0.5 h. GO/MNPs nanocomposite in 1-octanol reinforced hollow fiber-solid phase microextraction for preconcentration and determination of organophosphate pesticide in environmental samples.

HF-SLPME procedure

Extraction procedure Fig. 1 shows a simplified schematic of the application of HF-SPME to extract and determination Organophosphate compounds, in real sample. Extraction was made as follows: fibers were cut into little pieces with alength of 2.0 cm each and ultrasonically washed in acetone for 2 min to eliminate impurities. Afterward, the segments directly dried in air. 7.0 µl of the dispersed mixture of the nanocomposite at organic solvent was slowly injected into the lumen of hollow fiber utilize a syringe. The bottom and top of the segments were closed by heat. This fiber was immersed in 5.0 ml of the sample solution containing the analytes in a glass vial, and was agitated at 400 rpm of agitation speed for 40 min. At the end of the extraction, the hollow fiber was taken away from the vial, cleaned with water and conveyed into a vial with screw cap containing 300 µl of methanol, for desorption via the sonication for 15 min. Then 1 µl of the des-orbed solution was injected for GC analytes . All experiments were arranged in triplicate, and the means of the results were reported. The extraction with sorbent used in this research is a two-phase supported of an aqueous organic solvent/nano sorbent system operated in direct immersion sampling mode. The GO/MNPs dispersed in the organic solvent are introduced in the lumen hollow fiber. The analytes from the aqueous sample diffuses through the porous polypropylene membrane into the GO/MNPs, which were dispersed in the organic solvent and stuffed the hollow fiber lumen. the analytes tes are transferred to the small volume of acceptor phase that was flowing on the inside of the hollow fiber lumen and are thus enriched. 7µL of GO/MNPs in1-octanol was drawn into a microsyringe. The GO/MNPs in1-octanol in the syringe was injected to the lumen of hollow fiber. The hollow fiber was then placed in the aqueous solution. The vial was stamped and the stirrer turned on. At the end of the extraction for a preordained period of time at room temperature the hollow fiber was taken out from vial and transferred into a glass vial containing the organic solvent (300 µL methanol) and the analytes were desorbed from fiber with ultrasonic agitation and centrifuged for 5 min at 2000 rpm. 1.00µL of the desorption solvent was withdrawn into the GC microsyringe and then injected into the GC-FID for further analytes . Due to the low cost, and to prevent the carryover effect, each hollow fiber piece only once was used in the experiments .

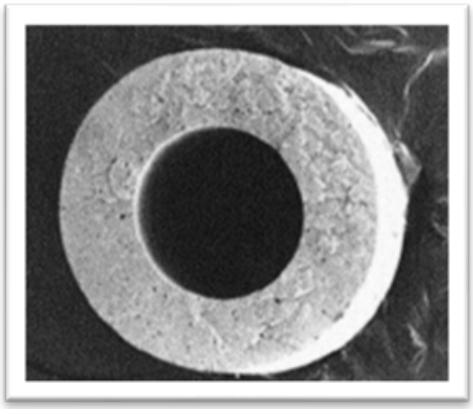

Fig. 1 SEM of polypropylene hollow fiber structure.

Sample analysis

Wastewater and river water treatment

Wastewater and river water samples were filtered through a filter paper before analysis

Experimental optimization for the HF-SLPME mmm

The FT-IR spectra were recorded for graphene oxide and iron Oxide functionalized grapheme oxide (Fig. 2). As demonstrated, the characteristic absorption bands at 1250 and 1100 cm $^{-1}$ corresponding to C–O stretching of epoxy and alkoxy, respectively, at 1730 cm $^{-1}$ corresponding to C-O stretching of carboxyl group and at 1630 cm $^{-1}$ corresponding to aromatic C=C of un-oxidized graphitic domains are similar in both spectra. The absorption band around 578 cm $^{-1}$ in Fig. 2 is corresponding to Fe–O which is the characteristic of Fe_3O_4 and confirms the successful synthesis of graphene oxide and its functionalization with ironoxide nanoparticles.

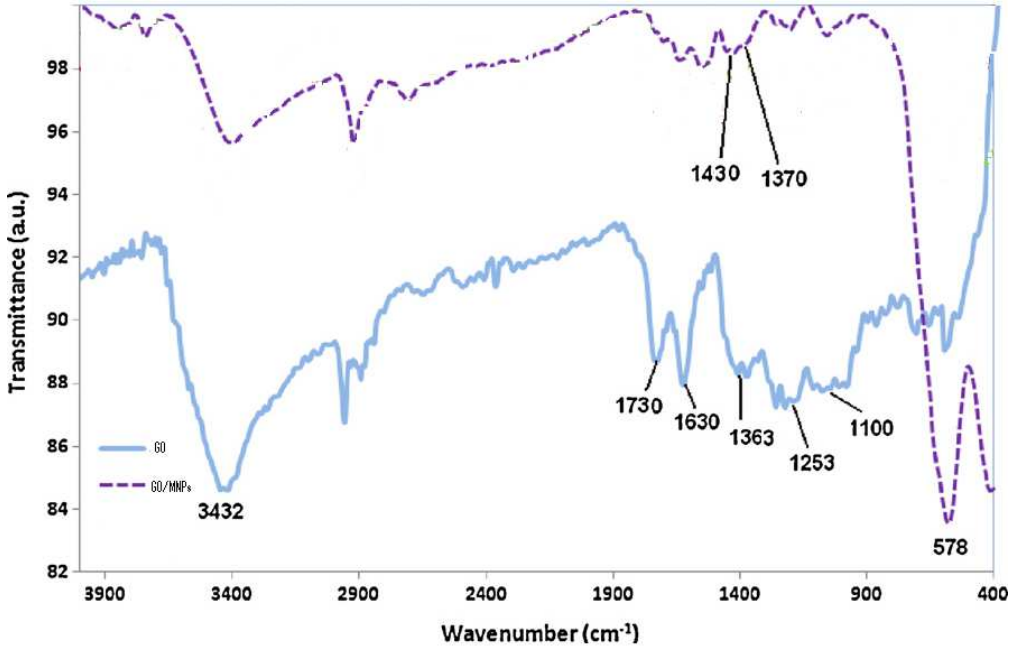

Fig. 2 FT–IR spectra of the GO and GO/MNPs

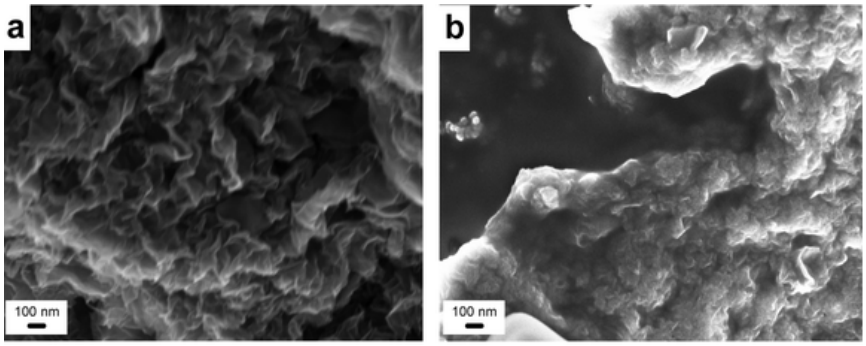

Fig. 3 TEM image (a) GO (b) GO/MNPs

Fig. 3 shows TEM images of GO and GO/MNPs.

The affect of the time on the extraction efficiency

The affection of the time extraction is an equilibrium process and extraction time affects on the equilibrium conditions. Over the extraction solute molecules have enough chance extraction device and for accumulation in it.

Therefore, extraction time is a significant factor that influences on the extraction efficiency. Extraction was performed from 2 to 40 min to determine the effect of extraction time on the method efficiency. The results that were shown in Fig. 4 . All the analyses exhibited that average peak of analyses the highest increase in the peak areas in the period of 25 min. Afterwards the mean peak areas were decreased with increasing of extraction time. So, a period of 25 min was used for the subsequent experiments.

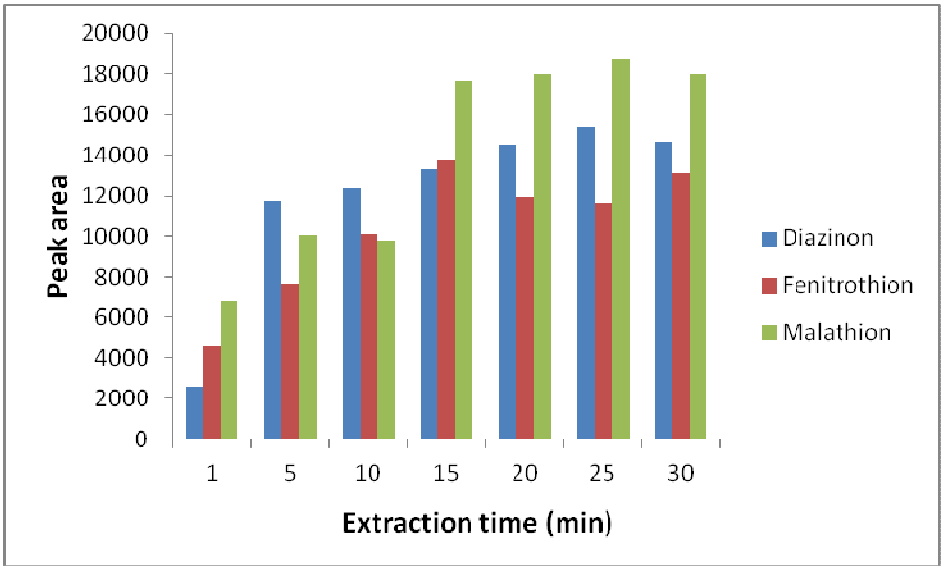

Fig 4. The effect of extraction time on the extraction efficiency of organophosphorus compounds

Effect of type desorption solvent volume

Accordingly, several desorption solvents such as acetonitrile, 1-octanol, cyclohexane and methanol were investigated. Based on the obtained results, methanol was found to get the best extraction efficiency. It is worthy of notice that an aqueous solution spiked with the pesticides compounds (at the concentration level of 10 µg/mL) was used in the extraction studies.

Desorption solvent volume is important on the desorption role of extraction device as well as the overall time required by extraction to reach equilibrium. Four different desorption volumes (0.1–1.0 mL) for spiked target analyses (10 µg/L) were studied. Highest extraction efficiency was observed when 0.3 mL desorption solvent volume was used. Decrease in peak area response was noted when larger desorption solvent volume applied in the extraction. Repeatability was decreased in the desorption solvent volume less than 0.3 mL. Thus 0.3 mL was used as the optimal volume desorption solvent**.**

Effect of the donor phase volume

The piece of the hollow fiber segment (really, volume of the acceptor phase) was arranged at 2.0 cm and the reduced length was compatible with small sample volumes, which are favorably relevant in some analyses in environmental applications. In addition, the enrichment of the analytic increases with rising the volume ratio of sample solution to acceptor solution [25]. The pre-concentration factor in HF-SLPME basically depends upon the phase volume of the sample and the acceptor. As the volume of the sample increases, the pre-concentration factor also increases [25].
In HF-SPME, extraction is an equilibration procedure, therefore the amount of analyte partitioning into the acceptor phase becomes without connection to the sample volume when this volume is much higher than the product of the partition constant and the volume of the acceptor phase. The effect of donor phase volume on the extraction efficiency of OPs compounds when using hollow fiber SLPME with methanol as the desorption solvent. Other extraction conditions: OPs concentration 10 µg/L, stirring rate 300 rpm, desorption time 5 min, extraction time 10 min.

The other hand, a larger sample volume can even be disadvantageous due to poorer mass-transfer kinetics, resulting in undesirable extraction efficiency [25]. In the this work, the phase ratio of acceptor and donor solutions was

improved efficiency by changing the volume of the donor phase between 2 and 15 mL while the volume of acceptor phase was kept constant at 5 µL. As seen in Fig. 5, however, the extraction results acquired for the analytes were most favorable to suggest a phase ratio of 1000 (7mL donor phase volume). Also, with an increase in the aqueous phase volume, acceptor phase acceptor may too be a concern. This would takes one to a decrease in the microextraction efficiency. Therefore, we selected a volume of 7 mL as the best performance donor phase volume.

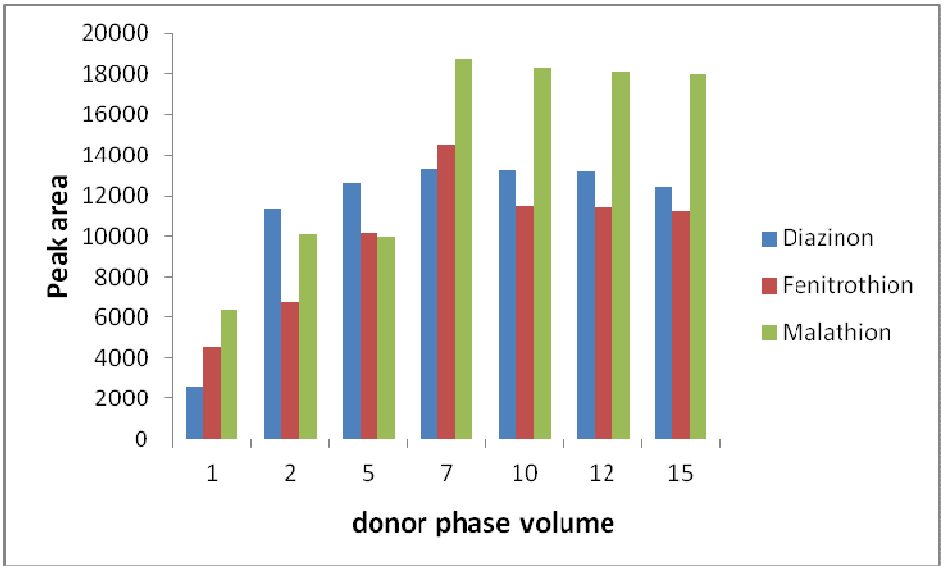

Fig. 5. The effect of donor phase volume on the extraction efficiency of OPs compounds when using HF-SLPME with methanol as the desorption solvent.

Effect of the desorption time

To reach the highest responsiveness, the desorption time was also appraised to ensure. Experiments showed that for all the studied four OPs compounds, desorption was almost complete after 5 min. Repeatability decreased in the desorption time less than 5 min . On the other hand, Above this time the amount of extracted analyte remained unchanged. Thus 5 min was used as the best desorption time.

Effect of the stirring rate

In order to hasten the mass transfer velocity from donor through organic membrane into acceptor in the extraction, magnetic stirring is usually used speedup means. The instrument's response was recorded for several stirring rates ranging from 0 to 1000 rpm for an extraction time of 25 min of 7mL aqueous samples with each target analytes concentration of 10 µg/mL. The results confirmed that perturbation of the sample enhances extraction. However, higher stirring rates (>600 rpm) decreased the preconcentration factors.

Effect of the amount of GO/MNPs on the extraction

The effect of the amount of GO/MNPs on the microextraction capacity has been studied and 0.25 mg/mLwas the optimal amount of the GO/MNPs (the range was between 0 and 0.5 mg/mL) in this work. The results confirmed that increasing of the amount of GO/MNPs refused repeatability. Since with increasing the amount of GO/MNPs, the injection of massive reinforced composite into the fiber was difficult. Furthermore the air bubbles occupied the fiber spaces. Thus 15 mg of GO/MNPs was used as the optimum amount.

Effect of pH sample solution

The pH value of aqueous feed-phase plays an essential role in the extraction process. Considering the feed solution pH is also one of the important factors that it progresses the transfer of OPs from the feed to the adsorbent. Therefore, after survey of the pH effect in the pH range 5–11, by adding the appropriate hydrocholoric acid or sodium hydroxide solution to the aqueous donor phase.

The results confirmed that the analytes extraction performance reached a better level at pH 6 (see Fig. 5). Afterwards the peak areas were decreased with increasing of pH. It is due to the happening of degradation under high alkaline condition. Based on thorough consideration, pH 6 was selected for further experiments.

One of the most important factors in process of surface absorption of malathion, fenitrothion and diazinon on magnetic nanoparticles and finally, increase in efficiency of extraction is pH level. pH of solution plays an important role in mechanism of surface absorption of the desired compound on surface of magnetic nanoparticle and form and load of the desired sample. Surface lead of magnetic nanoparticles is condition of pH<7 is positive. On the other hand, compounds of diazinon and malathion were decomposed in strong acid and alkaline pH ratios. In this study, pH levels of 5, 6, 7, 8 and 9 have been investigated and it was observed that in pH=7, the maximum level of sub-peak can be obtained. Therefore, pH=7 has been considered here as optimized pH level. In this pH, level of nanoparticle is positive, molecular form of analytes is stable and the condition is provided for surface absorption that has high extraction efficiency.

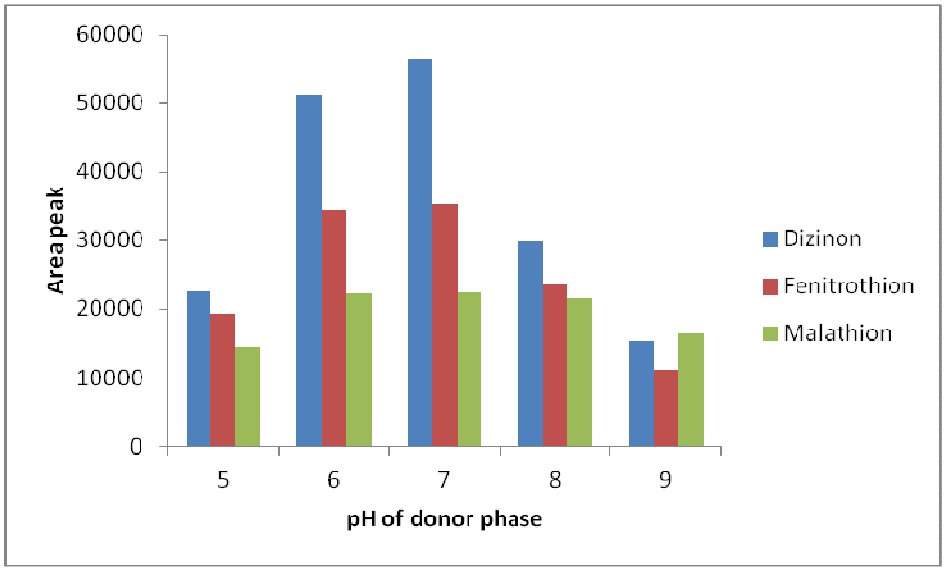

Fig 6. The effect of pH of aqueous feed on the extraction

Figures of merit

To appraise the practical suitability and applicability of the HF-SPLME technique,
the figures of merit of this method comprise pre-concentration factor, the corresponding regression equation, correlation coefficient (r^2), limit of detection (LOD) and and linear dynamic range (LDR) were investigated under the best conditions. Calibration curves in wastewater were plotted against the concentration levels of the OPs compounds. For each level, four replicate extractions were performed. The results are tabulated in Table 1. In addition, the theoretical pre-concentration factor (PF) is given by the following equation:

$$PF = \frac{A_{RP,final}}{A_{PS,initial}} \times \frac{V_{aq}}{V_{In}}$$

where $A_{RP,final}$ and $A_{SP,initial}$ are the final and initial peak areas after and before microextraction of the OPs compounds in organic solvent, respectively that were obtained based on direct injection of the OPs solutions in methanol into the GC for analysis. V_{aq} and V_{In} are volume aqueous sample and internal volume of hollow fiber. the matured method has the merits of considerable analysis improved pre-concentration and speed, good separation efficiency, high sensitivity and notable precision.

Table 1. Figures of merit of the proposed method in the determination of the pesticide compounds in aqueous matrices.

Analyte	LDR [a](ng/mL)	R [b]	LOD[c] (3σ) (ng/mL)	PF[d]	RSD% (n=5)	RR%[e]	Regression equation[f]
Diazinon	10-13000	0.989	16	345	3.54	89	Y=8781.1X+14679
Fenitrothion	10-19000	0.9923	11	1567	3.11	94	Y=51390X+49876
Malathion	10-20000	0.9798	11	487	4.91	85	Y=365.80+967.65

a Liner dynamic range; b Correlation coefficient; c Limit of detection; d Pre-concentration factor; e Relative Recovery after spiked amount of analytes

f Y and x are peak area and concentration of the analytes (ng/L), respectively

Real samples

Applicability of the extraction method to extract the OPs compounds from aqueous samples were inspect ed. The analytical results of aqueous matrices are given in Table 2. The obtained results showed the RSD% about 10.9–12.8% for pesticides compounds. To evaluate the efficiency of the proposed method in real samples, it was in aprosperous manner applied to assay target analytes in an wastewater and river water, Mashhad, Iran as real samples. The all target pesticides were not found in the wastewater and river water samples, so relative recovery was determined as the ratio of the concentrations found in wastewater and river water samples spiked with the same amount of OPs compounds under the optimized conditions. The average relative recovery of the analytes from the weastwater and river water samples were higher than 89% . The results are tabulated in Tables 2. This exhibits that matrix effect does not have any significant effect on the extraction efficiency of the proposed method. HF-SLPME is a non-exhaustive extraction procedure and the relative recovery (determined as the ratio of the concentrations in real and blank samples, spiked with the same amount of OPs), instead of the absolute recovery (used in majority of extraction procedures), was employed.

The proposed method has several advantages such as good precision and accuracy, low cost,simplicity, quite short extraction time, and minimum organic solvent consumption. The hollow fiber SLPME device is disposable, so the single use of the hollow fiber reduces the risk of cross-contamination and carry-over problems. This procedurecan be successfully used for the analysis of OPs compoundsin aqueous samples. In addition, the experimental setup is highly affordable and very simple. Among the all reported microextraction techniques, this technique is an effective sample pre-concentration technique.

Table.2. Detected concentrations (ng/mL) of OPs compounds in weaswater and river water samples.

	River water	20µgL^{-1}spiked weaswater Founded±SDa		river water	20µgL^{-1}spiked river water Founded±SDa	
Analtye	**Conc.[a]**	**RSD% [b]**	**RR%[c]**	**Conc.[a]**	**RSD% [b]**	**RR%**
Diazinon	nd[d]	11.3 ± 0.14	93	nd[d]	12.8 ± 0.31	94
Fenitrothion	nd	12.9 ± 0.11	93.4	nd	10.9± 0.11	89
Malathion	nd	10.8 ± 0.12	100.3	nd	11.9 ± 0.11	93.5

a Founded concentration (ng/mL). ; b Relative standard deviation (n=5).; c Relative Recovery after spiked amount of analytes.; d Spiked amount of analytes

CONCLUSION

Conditions for the extraction and analysis of trace amounts OPs compounds in different aqueous samples such as extraction and desorption time, stirring speed and volume of the donor phase, and extraction time were investigated. The hollow fiber SLPME device is disposable, so the single use of the hollow fiber reduces the risk of cross-contamination and carry-over problems. This procedure can be successfully used for the analysis of othere analytes in biological and aqueous samples.

In addition, the experimental setup is very simple and highly affordable. Among the all reported microextraction techniques, this technique is an effective sample preparation/pre-concentration technique. We suggested on the use of LC–MS detection for further studies, for achieve the selective and specific detection technique as for application to monitor samples.

REFERENCES

[1] G.D. Liu, Y.H. Lin, *Anal. Chem.* 78 (**2006**) 835.
[2] D. Du, J. Wang, J.N. Smith, C. Timchalk, Y.H. Lin, *Anal. Chem.* 81 (**2009**) 9314.
[3] V.B. Kandimalla, H.X. Ju, *Chem. Eur. J.* 12 (**2006**) 1074.

[3] L.G. Sultafos. *J. Toxicol. Environ. Health*. 43, 271–289.
[4] T.E. Fielding, W.A. Telliard, Methods for the determination of non conventional pesticides in municipal and industrial wastewater, United States Environmental Protection Agency, Washington, **1992**.
[5] D. Barcelo, *J. Chromatogr*. A 643 (**1993**) 117.
[6] C. Molina, M. Honing, D. Barcelo, *Anal. Chem*. 66 (**1994**) 4444.
[7] I.J. Barnabas, J.R. Dean, S.P. Owen, *Analyst* 119 (**1994**) 2381.
[8] C.L. Arthur, J. Pawliszyn, *Anal. Chem*. 62 (**1990**) 2145.
[9] Z. Yao, G. Jiang, J. Liu, W. Cheng, *Talanta* 55 (**2001**) 807–.
[10] D.A. Lambropoulou, T.A. Albanis, *J. Chromatogr*. A 922 (**2002**) 243.
[11] J. Pawliszyn, Solid-Phase Microextraction: Theory and Practice, Wiley–VCH, New York, **1997**.
[12] N. Fidalgo-Used, G. Centineo, E. Blanco-González, A. Sanz-Medel, *J. Chromatogr*. A 1017 (**2003**) 35.
[13] L. Cai, J. Xing, L. Dong, C. Wu, *J. Chromatogr*. A 1015 (**2003**) 11.
[14] S. Hamm, E. Lesellier, J. Bleton, A. Tchapla, *J. Chromatogr*. A 1018 (**2003**) 73.
[15] H. Kataoka, K. Saito, *J. Pharm. Biomed. Anal*. 54 (**2011**) 926.
[16] A. Spietelun, M. Pilarczyk, A. Kloskowski, J. Namie´snik, *Chem. Soc. Rev*. 39(**2010**) 4524.
[17] D. Wang, Y. Li, Q. Wang, T. Wang, *J. Solid State Electrochem*. 16 (**2012**) 2095.
[18] J. Shen, Y. Hu, M. Shi, N. Li, H. Ma, M. Ye, *J. Phys. Chem*. C 114 (**2010**) 1498.
[19] J.E. Vanbenschoten, B.E. Reed, M.R. Matsumoto, P.J. McGarvey, *J. Water Environ.Res*. 66 (**1994**) 168.
[20] J.A. Coston, C.C. Fuller, J.A. Davis, *Geochim. Cosmochim. Acta* 59 (**1995**)3535.
[21] H. Zhang, G.Q. Zhu, *Appl. Surf. Sci*. 258 (**2012**) 4952.
[22] A. Henglein, *J. Chem. Rev*. 89 (**1989**) 1861.
[23] T. Pradeep, Anshup, *J. Thin Solid Films* 517 (**2009**) 6441.
[24] Z. He, T. Hong, J. Chen, S. Song, *J. Sep. Purif. Technol*. 96 (**2012**) 50.
[25] Z. Es'haghi, *Anal. Chim. Acta* 641 (**2009**) 83.