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Novel unbreakable solid-phase microextraction fibers on stainless steel wire and application for the determination of oxadiargyl in environmental and agricultural samples in combination with gas chromatography–mass spectrometry

Ali Es-haghi [a,*], Masoud Baghernejad [b], Habib Bagheri [b]

[a] Department of Physico Chemistry, Razi Vaccine & Serum Research Institute, P.O. Box 31975/148, Karaj, Iran
[b] Environmental and Bio-Analytical Laboratories, Department of Chemistry, Sharif University of Technology, P.O. Box 11365-9516, Tehran, Iran

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ABSTRACT

Sol–gel based solid-phase microextraction fibers supported by a stainless steel wire were fabricated and employed for GC–MS determination of oxadiargyl in real samples. The fibers were based on four compounds with different polarity: polar and non-polar (end-capped) poly(dimethylsiloxane) (PDMS), polyethylene glycol (PEG), and poly(ethylene-propyleneglycol)-monobutyl ether (UCON). For this purpose, the surface of the stainless steel was initially modified by (3-mercaptopropyl) trimethoxysilane. The results of the modification procedure were evaluated by cyclic voltammetry and energy dispersive X-ray (EDX) spectroscopy. After the modification, four different sol–gel based SPME fibers with different values of polarity, polar and non-polar PDMS, PEG, and UCON have been prepared and investigated. They are supposed to be employed to determinate oxadiargyl in agricultural and environmental samples prior to gas chromatography–mass spectrometry analysis. Most important parameters that affect the extraction efficiency were also optimized. Under optimized conditions, the proposed method was found to be linear for the concentrations ranging from 100 ngL^{-1} to 2 mgL^{-1} with $R^2=0.997$. Limit of detection (LOD) of 40 ngL^{-1} and relative standard deviation of less than 10% were obtained. Relative recovery in environmental and agricultural samples was in the range of 73–96%.

1. Introduction

Solid-phase microextraction (SPME) is a simple sampling and sample preparation method that combines extraction, pre-concentration and sample introduction in one step, does not require the use of solvents, and permits desorption directly into the injector of the chromatographic systems [1–4].

In SPME, extraction is conducted by a thin film of coated materials on a solid support. Several fiber coatings with different values of polarity are commercially available [5–10]. However, they exhibit drawbacks such as fragility, which necessitates taking extra care during usage. Moreover, the fibers do not have a resistance to high temperature and tend to swell in organic solvents [11]. In recent years, a new generation of super elastic SPME fiber assemblies have been commercialized. However, the latter are expensive. To overcome the fragility of fused silica, commonly used as the support for polymeric coatings in SPME applications, other materials, mainly metallic wires such as platinum [12–15], anodized aluminum [16], gold [17,18], copper [19], titanium [11,20], and nickel–titanium alloys [21–26], have been proposed to substitute the silica rod.

Application of stainless steel wires as substrate for SPME fiber coating has been reported elsewhere [27–34]. In these applications, the fiber coatings have been assembled using different techniques such as physical deposition, electrochemical deposition, adhesive methods, and sol–gel technology. Besides these technologies, sol–gel based methods have gained increasing attraction due to their simplicity, flexibility for coating composition and operational stability of the coating [35]. In a sol–gel process, the surface area of the solid support should endorse the growth of the polymeric chain. In the above mentioned reported works, stainless steel has been directly used as a support, though it is known that the surface density of hydroxyl groups is not sufficiently high to ensure a uniformly bonded coating to be obtained [36].

Rice cultivation is an economically important agricultural activity in many areas around the world. To control weed growth,

* Corresponding author. Tel.: +98 26 34570038; fax: +98 26 34552194.
E-mail address: a.eshaghi@rvsri.ac.ir (A. Es-haghi).

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many kinds of herbicides are directly applied on the flooded soil. Therefore, tracing these chemicals and studying their chemical interactions in soil and aqueous solutions is necessary for sustaining the environment and human health. The transfer of herbicides from agricultural systems to rivers and groundwater is of major concern for aquatic organisms and human health. Moreover, the herbicide residues may represent environmental risk and influence rotational crops [37]. Oxadiargyl, 5-tert-butyl-3-[2,4-dichloro-5-(prop-2-ynyloxy)phenyl]-1,3,4-oxadiazol-2(3H)-one, is a herbicide which is effective on grasses, broad-leaved weeds and annual sedges. It has been used primarily for weed control in rice and cane fields [38]. It degrades under anaerobic conditions and is dissipated rapidly into the sediment phase from water [39]. There are only a few works related to determination of oxadiargyl concentration in plant and aqueous samples [40,41] which were not sufficiently sensitive for the monitoring of oxadiargyl fate, especially along the last part of the monitoring plan [42].

The aim of this work is to develop SPME fibers on stainless steel wire as a mechanically stable and cheap alternative to existing methods of fiber preparation. The surface of the stainless steel was initially modified by (3-mercaptopropyl)trimethoxysilane (MPTS) and its surface was evaluated by energy dispersive X-ray (EDX) spectroscopy and cyclic voltammetry (CV). After modification, four different sol–gel fibers: polar and non-polar polydimethylsiloxane (PDMS), polyethylene glycol (PEG), and poly(ethylene propylene glycol) monobutyl ether (UCON) were applied to investigate their suitability for the determination of herbicide oxadiargyl in paddy water, lettuce, rice, and soil samples prior to gas chromatography–mass spectrometry analysis.

2. Experimental

2.1. Materials and chemicals

Oxadiargyl (99.0%) was purchased from Bayer (Monheim am Rhein, Germany). Methoxytrimethylsilane, hydroxyl terminated polydimethylsiloxane, poly(ethylene propylene–glycol) monobutyl ether (UCONHTF 14) and ethanol were purchased from Fluka (St. Gallen, Switzerland). Tetramethylorthosilicate (tetramethoxysilane), poly(methylhydrosiloxane) (PMHS), trifluroaceticacid (TFA), polyethyleneglycol 400 (PEG 400), methylene chloride, methanol, sodium hydroxide, hydrochloride acid, ammonia, acetone and n-hexane were purchased from Merck (Darmstadt, Germany). Ultra pure water was used for preparation of blank and real samples (SG Wasseraufbereitung, Germany).

A stock solution of oxadiargyl (1000 mgL^{-1}) was prepared in methanol, and stored at 4 °C. A series of standard solutions of oxadiargyl (10–10,000 $\mu g\ L^{-1}$) was prepared weekly and stored in a refrigerator. The working standard solutions were prepared at various concentrations by diluting the stock solution as required in water and stored at 4 °C. (3-mercaptopropyl)trimethoxysilane (95%) was purchased from Sigma-Aldrich (Steinheim, Germany).

2.2. Instrumentation

SPME syringe was purchased from Supelco (Bellefnote, PA, USA). The SPME fiber assembly was prepared in our laboratory [43] and the proper fiber was assembled on it using a thermal resistant glue. A Yellowline TTS2 vortex mixer (Lennox, Ireland) and a Hettich universal 32R centrifuge (Hettich, Germany) were used to prepare sol solutions and separate precipitate from them. A Sonica 3300EP ultrasonic bath (SOLTEC, Milan, Italy) was used to prepare sol–gel and purify the materials.

An Agilent 6890N gas chromatograph (GC) equipped with a split/splitless injector, an Agilent 5975C mass selective detector (MSD), and an Auto Sampler COMBI PAL (CTC analytics, Switzerland) were used. The mass spectrometer (MS) was operated in the electron ionization (EI) mode (70 eV). Helium (99.999%) was employed as a carrier gas and its flow rate was adjusted to1 ml min^{-1}. The chromatographic separation was performed on a GC column HP5-MS (30 m × 250 μm ID and film thickness 0.25 μm) (J&W Scientific, USA). The initial temperature of the column was set at 60 °C and held for 3 min, then increased by 40 ° $Cmin^{-1}$ to 180° C and maintained for 4 min, finally increased by 30 °C min^{-1} to 280 °C and held for 2 min. The injector temperature was set at 275 °C and desorption process was carried out in the splitless mode for 5 min. The temperature of GC–MS interface, ion source and quadrupole was set to 280, 230, and 150 C, respectively. The MS was operated in selected ion monitoring (SIM) mode at *m*/*z* of 213 and 178. The scanning electron microscopy (SEM) images and EDX spectrum were obtained by a TESCAN VEGA II XMU (Brno, Czech Republic). Cyclic voltammetry (CV) was performed using an Autolab model PGSTAT 20 potentiostat/galvanostat (Metrohm, The Netherlands).

2.3. Preparation of the MPTS self-assembled monolayers on stainless steel

Stainless steel wires were cleaned by sonication consecutively in ethanol, acetone and again in ethanol for 10 min in each, to remove any contaminants. The surface of the stainless steel wires were modified using MPTS. The film of the latter was formed on the surface of the stainless steel by dipping into a solution of 10^{-3} M of MPTS in ethanol for 3 h. After the formation of film, the surface was rinsed with ethanol, subsequently dried in a stream of argon and stored under argon atmosphere before characterization [44].

2.4. Cyclic voltammetry characterization

Cyclic voltammograms (CV) were acquired on bare as well as coated substrates. A three-electrode electrochemical cell with platinum wire and saturated calomel electrode (0.24 V vs. standard hydrogen electrode) as the counter and reference electrodes were used. CV measurements pursued to determine the efficiency of the chemisorption were carried out in 0.1 M NaOH electrolyte at a sweep rate of 10 mV s^{-1} in the potential window ranging from −0.6 to +0.4 V. This potential range includes an anodic oxidation reaction, producing more chromium and iron oxidative products.

2.5. Energy dispersive X-ray (EDX) spectroscopy characterization

EDX spectra obtained for bare and modified stainless steel were compared to each other by elemental analysis of basic elements' (Fe, C, Cr, Ni, O, S, and Si) weight percentages.

2.6. Chemical modification of trimethoxy tail groups of the monolayer

Hydrolysis of the MPTS was carried out by immersion of the surfaces modified wires in 0.1 M HCl for 1 h. The MPTS-modified surfaces were then dipped for 10 min in water and dried in desiccator.

2.7. Preparation of SPME fibers

Four kinds of SPME fibers were employed: (1) polar and (2) non-polar poly(dimethylsiloxane) (PDMS), (3) UCON, and (4) polyethyleneglycol(PEG). They were prepared as reported previously [36] except that PEG 400 was used instead of PEG 4000. The surface characteristics of the sol–gel coated fibers were

investigated by the scanning electron microscopy (SEM) technique.

2.8. Preparation of real samples

Before analysis of the real samples, i.e. soil, rice, and lettuce, they were homogenized and 2 g of which were weighted in a centrifuge tube. After spiking with known amounts of oxadiargyl, samples were left for 24 h at room temperature. Then, 10 ml of water was added to the samples, and they were vigorously shaken for 10 min, centrifuged and the supernatant was separated for subsequent SPME. Paddy water samples were spiked with a known amount of oxadiargyl and analyzed under optimized conditions for relative recovery studies.

2.9. SPME procedures

A home-made sol–gel fiber was mounted in a SPME fiber holder. The extraction was conducted in a 10 ml glass vial. The samples were prepared by introducing 8 ml of 400 $\mu g l^{-1}$ solution of oxadiargyl into empty vials. The vials were sealed with aluminum cap and silicone septum. The SPME fiber was immersed into the solution by piercing the septum with a needle of the fiber assembly and then depressing the plunger while the solution was stirred at 600 rpm. After reaching equilibrium, the SPME probe was withdrawn from the vial and inserted into the GC injection port for thermal desorption. Thermal desorption was carried out in the GC injection port at 275°C, while the split valve was kept closed and after 5 min was opened.

3. Results and discussion

3.1. Characterization of the MPTS self-assembled monolayers

As it was mentioned, stainless steel wire has been used as the SPME fiber substrate to overcome the shortcomings of conventional fragile fused silica rods. Stainless steel surface is neutral against most of the organic compounds. Although stainless steel has been used as the SPME fiber solid support [28–33], our preliminary studies showed that the direct coating of stainless steel has short lifetime and the substrate surface has only been covered partially by coating materials. Furthermore, the applicability of MPTS as a metal surface modifier for preparing SPME fibers has been reported in previous studies [45]. In this study, the surface of stainless steel was first modified by MPTS as the interface between solid support and the sol–gel coating material and then extraction phases were prepared by sol–gel process.

The surface modification by MPTS was investigated by CV and EDX spectroscopy. Fig. 1 shows CVs of bare and modified stainless steel wire. Two anodic peaks (peaks I and II) were observed when bare stainless steel was used as a working electrode. Peak I originates from the ethanol oxidation and peak II represents the formation of Fe_2O_3, Cr_2O_3, and Fe_2CrO_3 from FeO and CrO. Both oxidation peaks decreased in the second scan because of the irreversible formation of oxidized forms of Fe and Cr. Moreover, for MPTS-covered stainless steel wire (CV C), formations of Fe_2O_3, Cr_2O_3, and Fe_2CrO_3 were inhibited completely. These results show that the oxide species such as FeO and CrO can react with MPTS to form a monolayer and the surface of the stainless steel is protected against further oxidation in the course of the anodic scanning.

The EDX spectra of the bare and surface modified stainless steel wires are shown in Fig. 2A and B, respectively. Weight percentages of Si, C, and S on the surface of the stainless steel wire were obtained using EDX analysis and the results showed a significant increase in the weight percentage of the mentioned elements

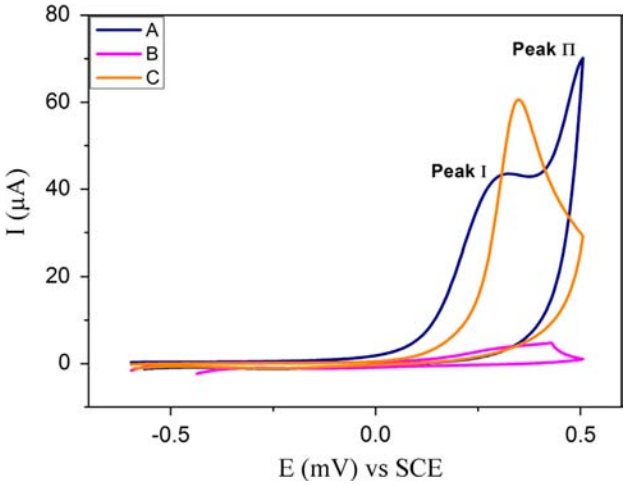

Fig. 1. Cyclic voltamograms of the A) bare stainless steel wire B) second cycle of the bare stainless steel wire, and C) surface modified stainless steel wire.

upon modification. Since the modified surface has been copiously rinsed with absolute ethanol and water, this weight percentage increment is due to the presence of chemisorbed MPTS on the stainless steel wire.

After surface modification, the trimethoxy tail groups of the MPTS layer were hydrolyzed to the sol–gel active hydroxyl group which is utilized for subsequent coating. Finally, four different kinds of sol–gel based fibers were prepared and the surface morphology of the fibers was investigated using SEM. The obtained images of the sol–gel fibers (Fig. 3) show highly porous surfaces, which results in high loading capacity and extraction efficiency.

3.2. Optimization of SPME procedure for the analysis of oxadiargyl

3.2.1. Selection of the fiber

The affinity of the coatings to the oxadiargyl was investigated using four kinds of sol–gel fiber coatings: (1) polar and (2) non-polar PDMS, (3) UCON and (4) PEG. As it can be seen in Fig. 4, PEG coated fiber could extract and retain the target analyte more than the other three. The relative high polarity of PEG coated fiber enables it to extract and retain relatively polar compounds such as oxadiargyl more than the other types of fibers. Therefore, PEG has been chosen for the extraction procedure.

3.2.2. Extraction time

In an equilibrium extraction mode of SPME, the maximal amount of analyte can be extracted by the fiber. Although the extraction time is longer under equilibrium conditions, the extraction procedure is much more reproducible than the non-equilibrium extraction. In this study, the extraction time varied in the range of 1–0 min. As Fig. 5 shows, equilibrium extraction was achieved after 10 min and this time was chosen as the extraction time for subsequent evaluation.

3.2.3. Effect of pH

The charge density of the fiber and nature of the analyte are the main factors affecting the analyte extraction. Both these variables change with pH of the solution. In this study, pH effect was studied in the range of 1.0–11.0. As it is illustrated in Fig. 6, the extent of analyte adsorption increases with the pH increase from 1.0 to 7.0. The extraction efficiency decreases with increasing increment of pH from 7.0 to 11.0. Since the PEG fiber surface can be charged at higher and lower pH values than 7.0, the extraction efficiency decreases because of relatively less polarity of oxadiargyl.

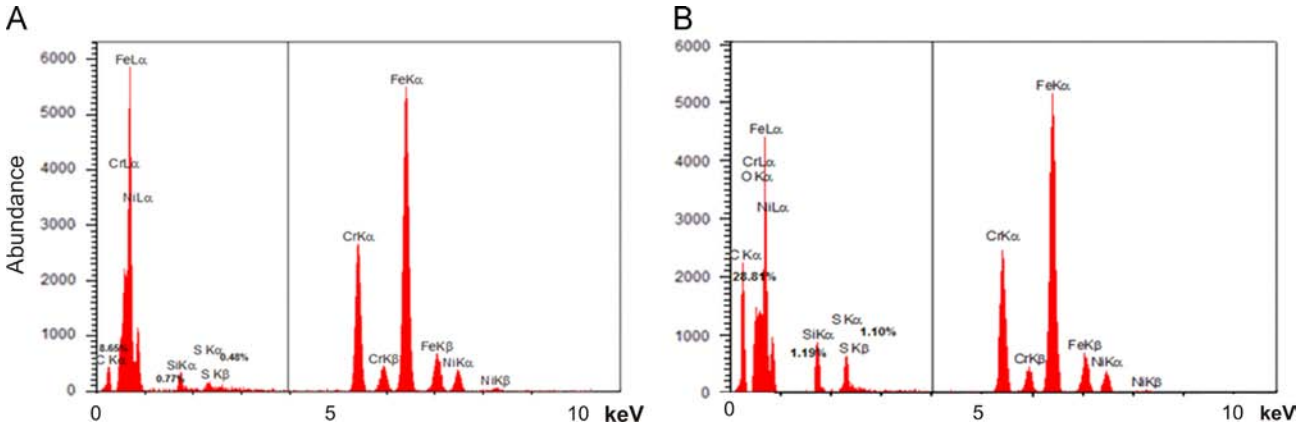

Fig. 2. EDX spectrum and weight percentage of carbon, silica, and sulfur on A) bare and B) surface modified stainless steel wire.

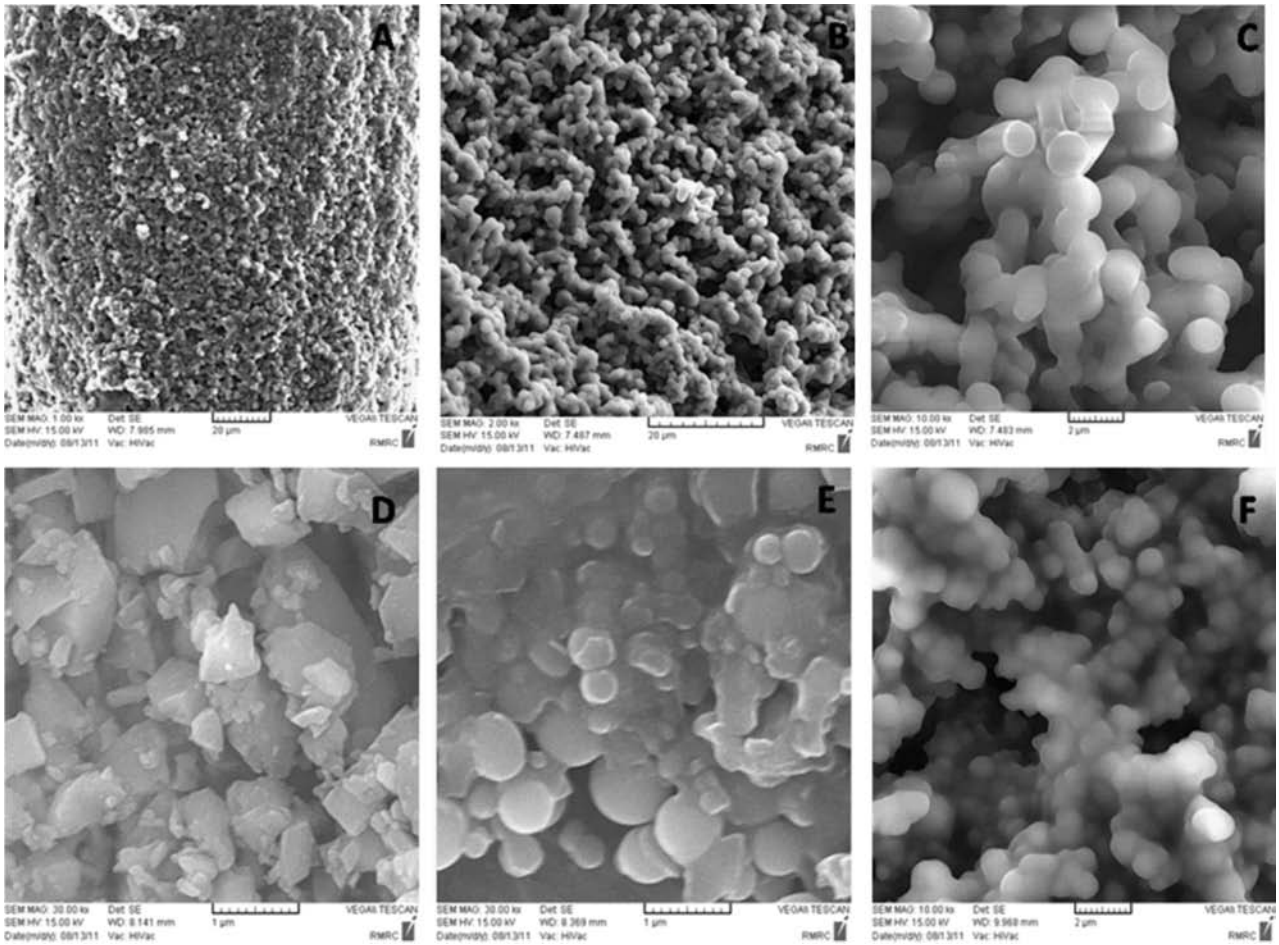

Fig. 3. SEM images of PEG (A–C), polar PDMS (D), non-polar PDMS (E), and UCON (F) coated SPME fibers.

Therefore, pH 7.0 has been chosen as the optimum pH for further studies.

3.2.4. *Effect of ionic strength*

The effect of ionic strength on the extraction efficiency has also been evaluated. In the present study, NaCl was used and its concentration varied in the range of 0.0–30% (w/v). Usually, an increase of the ionic strength of aqueous solutions decreases the solubility of organic compounds which results in a higher tendency toward the fibercoating and consequently higher extraction efficiency. The result showed (data not shown) that 30% salt content indeed gives the highest extraction efficiency.

3.2.5. *Effect of extraction temperature*

Effect of temperature on the extraction efficiency of oxadiargyl was investigated in the temperature range of 10–50 °C. As it is shown in Fig. 7, extraction efficiency obviously shows a maximum at 30 °C. According to SPME theory, in the first part of this profile, the distribution constant of analyte between fiber and solution increases with temperature increase and therefore a higher extraction efficiency is obtained. With further increase of

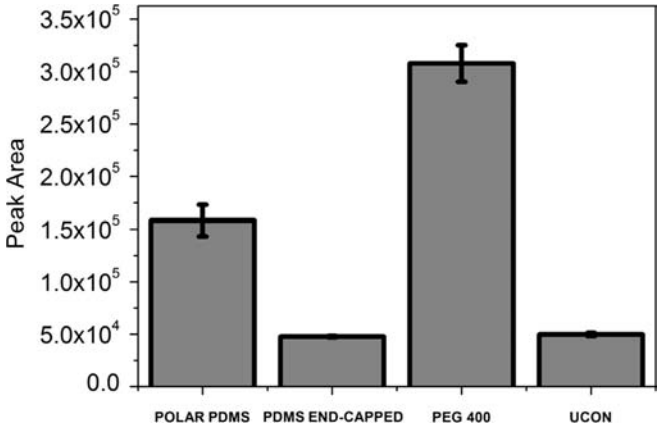

Fig. 4. Different kinds of fibers' responses to the analyte.

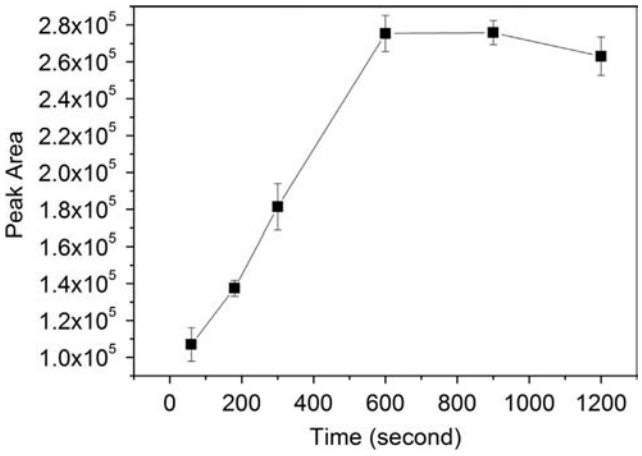

Fig. 5. Extraction time profile of oxadiargyl.

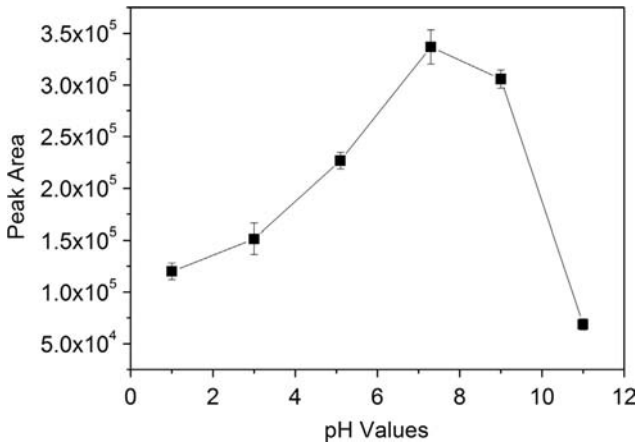

Fig. 6. Effect of sample pH on extraction efficiency.

temperature in the second part of the profile, the distribution constant decreases. Therefore, extraction temperature of 30 °C was chosen.

3.2.6. Desorption conditions

In SPME experiments, the highest possible desorption temperature without damaging the fiber coating should be applied to the fiber in order to avoid the carry over of the analyte during the extraction process. Thermal desorption was investigated by varying the temperature of injection chamber in the range of 230–275 °C.

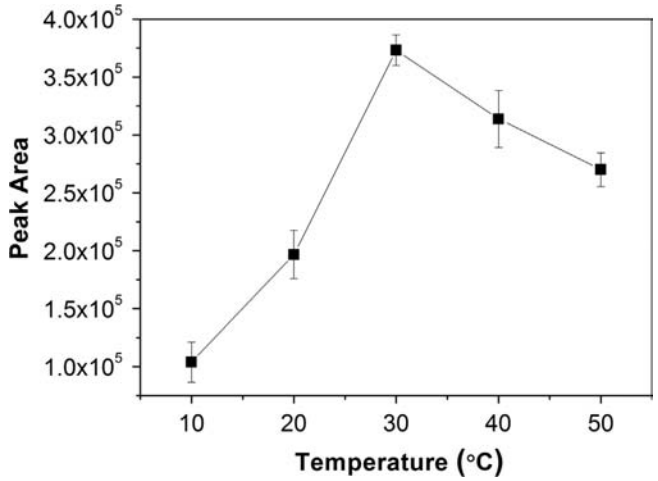

Fig. 7. Effect of sample temperature on extraction efficiency.

The maximum of analyte signal was obtained at the temperature higher than 265 °C. Also, desorption time amounts to 0.1–7 min. After each desorption process, carry over effect was inspected. Finally, the temperature of 265 °C for 5 min was chosen while no carry over was observed.

3.3. Analytical evaluation

The analytical parameters including linear range, correlation coefficient of calibration, single fiber repeatability, fiber-to-fiber reproducibility and limit of detection (LOD) and quantization (LOQ) of oxadiargyl were investigated under the optimized extraction conditions (desorption temperature 265 °C, desorption time 5 min, extraction temperature 30 °C, extraction time 10 min, NaCl content 30%, pH 7.0). A wide linear range of 100 ng L^{-1}–2 × 10^{-6} μg L^{-1} and low LOD and LOQ of 20 and 100 ng L^{-1}, respectively, have been observed for the proposed method which demonstrates improvement of the method compared to previous studies [40,41]. The repeatability of the method was studied by performing three consecutive extractions from aqueous solutions at three concentration levels. The RSDs were all below 10%.

The fiber-to-fiber reproducibility was investigated using three fibers prepared by the same process and RSDs ranged from 5 to 10%. In addition, the fiber durability was investigated by extracting the analyte from aqueous standard solution in between the analytical evaluation studies. Data showed that the variation in chromatographic response to the extracted analyte was less than 4% after about 100 extractions. Such a long durability allows the application of the fiber for a long time without a significant decrease in extraction efficiency.

3.4. Real samples

The applicability of the optimized method to real samples was evaluated. Considering the extensive application of oxadiargyl in paddy fields, their possible transfer to the surface and groundwater as well as carryover on rotational crops, the optimized method was applied to the spiked paddy water, soil and rice samples. In addition, determination was conducted on lettuce as rotational crops. The results showed that the proposed analytical technique can be applied to the real samples with relative recoveries of 96%, 70%, 73%, and 79% for paddy water, lettuce, soil, and rice, respectively. In addition, the sensitivity of the proposed method helps the monitoring of oxadiargyl at low concentration levels [45]. This is of great importance especially during the last part of the monitoring plan where the concentration is very low.

Such data can be used to evaluate environmental risks of this herbicide and to manage its applications. In addition, given the variety of herbicides and the change in their chemical compositions, the results can shed light on the behavior of similar herbicides in the soil and water systems.

4. Conclusion

In this work, novel sol–gel based fibers on stainless steel substrates were prepared. Commonly used friable fused silica rod was replaced by the stainless steel wire which could provide high strength, and prolong the fiber life cycle. In addition to the common characteristics of sol–gel fibers, such as excellent thermal resistance, marvelous stability was obtained.

Additionally, development of a truly simple, rapid, inexpensive, solvent free, and robust extraction method based on the use of these fibers for determination of oxadiargyl in agricultural and environmental samples was the predominant goal of this study. Influential parameters on the extraction efficiency, such as fiber coating type, extraction and desorption conditions were investigated and optimized. The novel fiber exhibited lower LOD and LOQ values and a satisfying repeatability. The developed method is an efficient extraction method in comparison with other methods for determination of oxadiargy.

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