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Simultaneous Determination of Permethrin and Deltamethrin in Water Samples by Magnetic Solid-phase Extraction coupled with Dispersive Liquid–Liquid Microextraction combined with Gas Chromatography

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ABSTRACT

In this study, new and efficient method, magnetic solid phase extraction coupled with dispersive liquid–liquid microextracton (MSPE-DLLME) combined with gas chromatography-flame ionization detector (GC-FID) was developed for the preconcentration and determination of permethrin and deltamethrin in water samples. Several factors influencing the extraction efficiency including amount of sorbent, sorption time, type of extraction solvent and its volume, type of disperser solvent and its volume and elution time were investigated and optimized. Using optimum extraction conditions, dynamic linear range of 0.5–100 μg L^{-1} for both, limits of quantification (LOQs) of 0.6 μg L^{-1} for both and limits of detection (LODs) of 0.01 μg L^{-1} for both were obtained. Finally, the method was successfully applied for the extraction and determination of permethrin and deltamethrin in water samples in the range of micrograms per litre with RSDs < 4 %.

KEYWORDS

Magnetic solid-phase extraction, dispersive liquid–liquid microextraction, permethrin, deltamethrin, gas chromatography, water samples

1. Introduction

Insecticides on the basis of pyrethrine were first introduced in the 1950s. Pyrethrines are a class of natural substances which originates from the blossom of the chrysanthemum. Pyrethrines were, and still are, used as natural insecticides against vermin in households. Nevertheless, the production of pyrethrine is expensive and the resources are limited. For these reasons synthetic pyrethroids were developed based on the basic structure of natural pyrethrines.[1]

Synthetic pyrethroids are utilized in households and greenhouses, as well as to control fleas and scabies. Moreover, these compounds are used for wood and textile protection.[2–4] It has been firmly established that synthetic pyrethroids act as powerful neurotoxic agents.[5] The molecular basis for the neurotoxicity of pyrethroids have been attributed to their actions on voltage-dependent sodium channels[5,6] and on receptor-regulated channels, like the nicotinic[7,8] and GABA-gated chloride channels.[9,10] Effects on Ca^{2+},Mg^{2+}-ATPases have also been reported.[11–13]

Determination of pesticides in different sample matrices is usually performed after pretreatment steps using either gas chromatography (GC)-mass spectrometry (MS),[14] GC-electron capture and ion trap mass spectrometric detectors,[15] GC-nitrogen-phosphorus detector,[16] GC-flame photometric detector,[17] GC-flame ionization detector,[18] or high performance liquid chromatography (HPLC) with different detectors (e.g. MS/MS spectrometry,[19] diode array detector).[20] The use of ultra-performance liquid chromatography in detection of pesticides has also been reported.[21]

Different preconcentration methods such as solid-phase extraction (SPE),[22] solid-phase microextraction (SPME),[20] liquid-phase microextraction (LPME),[17] single drop microextraction (SDME),[23] headspace solid-phase microextraction (HSPME),[14] dispersive liquid–liquid microextraction (DLLME),[24] homogeneous liquid–liquid microextraction (HLLME),[25] ultrasonic assisted headspace single drop microextraction (USA-HSDME),[16] vortex-assisted liquid–liquid microextraction (VALLME),[26] ultrasound-assisted solvent extraction followed by dispersive liquid–liquid microextraction,[27] supercritical fluid extraction combined with dispersive liquid–liquid microextraction,[18] microwave-assisted extraction-solid-phase extraction,[28] or SPE in combination with DLLME[29] have been used for the preparation of water samples containing pesticides.

Solid phase extraction (SPE) has become a well-established sample preparation method to extract and preconcentrate desired components.[30–33] Application of magnetic nanoparticles in SPE (MSPE) simplifies sample pretreatment and overcomes some limitations of conventional SPE.[34] The sorbent does not need to be packed into cartridges (as in traditional SPE), and the separation steps can be carried out easily by applying an external magnetic field. Nanoparticles (NPs) possess large surface area, high adsorption capacity, and rapid adsorption rate; so, low amounts of sorbent and short equilibrium time are required to extract analytes from large volumes of samples.[35–37]

Magnetic nanoparticles (MNPs) are materials composed of

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magnetic elements, including iron, cobalt and nickel. MNPs also have certain characteristic properties such as super paramagnetism, high coercivity, high magnetic susceptibility and low curie temperature.[38] Iron oxide MNPs may exist in different forms, such as magnetite, maghemite, hematite, and goethite or their combinations, depending on the Fe(22)/Fe(222) ratio, which influences size, composition, morphology, and magnetic properties of the particles.[39–41] With the latest developments in nanotechnology,[42] MNPs can be applied for magnetophoretic separation of a wide range of materials[41] as they provide several advantages over other available separation methods. The advantages include, recyclability for multiple usage, high-throughput process, low operational cost, high efficiency, flexible implementation, and scalability.[43] These features make MNPs very attractive in many fields such as biotechnology/biomedicine,[44] environmental remediation,[45] data storage,[46] and other emerging fields. However, unavoidable problems may occur, associated with particles in this nanosize range, such as their intrinsic instability/tendency to form aggregates and their interaction with the (often high ionic strength) media. The inherent magnetic forces contribute to the attractive forces among NPs which may lead to aggregation.[47,48] Stabilization of MNPs may be achieved by coating the particles, either by chemical bonding or physical adsorption, with different capping agents. Among the different types of coatings used as sorbents for the extraction of organic analytes, composites of conductive polymers are of interest. This is due to their multifunctional properties including hydrophobicity, acid–base character π–π interaction, polar functional groups, ion exchange property, hydrogen bonding and electroactivity.[49–53]

Dispersive liquid–liquid microextraction (DLLME) was introduced by Rezaee and co-workers in 2006.[54] In this method, an appropriate mixture of extraction and disperser solvents are used. The method has attracted much attention due to its advantages such as short extraction time, low consumption of organic solvent, and simplicity.[55–57]

In this study, polypyrrole as a conductive polymer was coated on the surface of Fe_3O_4 nanoparticles. The samples were first extracted by magnetic solid phase extraction (MSPE), then the eluents were recovered, and subjected to dispersive liquid–liquid microextracton (DLLME) for further purification and enrichment of permethrin and deltamethrin compounds. The effect of principle factors such as sorbent amount, extraction time, extraction solvent, extraction solvent volume, disperser solvent, disperser solvent volume, and desorption time were studied.

2. Experimental

2.1. Chemical and Reagents

Permethrin (>98 %) and deltamethrin (99.7 %) were provided by Sigma-Aldrich (UK). Carbon tetrachloride (>99.5 %), 1,1,2-trichloroethane (>98 %), chloroform (>99.8 %), and chlorobenzene (>99 %), as extraction solvents and acetone (>99.8 %), acetonitrile (>99.9 %), ethanol (>99.5 %), and methanol (>99.9 %), as disperser solvents were obtained from Merck (Darmstadt, Germany). Double-distilled water was used for preparation of aqueous solutions. An amount of 0.001 g of permethrin and deltamethrin were dissolved in 10.0 mL of methanol to obtain standard stock solution with a concentration of 100 mg L^{-1}. A fresh 10 mg L^{-1} standard solution containing permethrin and deltamethrin was prepared in methanol every week and stored at 4 °C. Ferric chloride (>98 %), ferrous chloride (99.5 %), sodium hydroxide (>99 %), reagent grade NaCl (>99.5 %) and pyrrole (>97 %) were purchased from Merck.

2.2. Instrumentation

The chromatographic analysis was performed on an Agilent GC-7890 system equipped with a split/splitless injector system and flame ionization detector for separation and determination of permethrin and deltamethrin. Highly pure helium gas (99.999 %, Air Products, UK) was passed through a molecular sieve and oxygen trap (Crs, USA) and was employed as a carrier gas with a flow rate of 1.5 mL min^{-1}. The injection port was held at 290 °C and operated in the splitless mode for 1 min then split valve was opened and split ratio of 1:5 was applied. Separation was carried out on a DB5, 25 m × 0.32 mm i.d. and 0.25 μm film thickness from SGE (Victoria, Australia) capillary column. The oven temperature was kept at 230 °C for 5 min and then increased to 285 °C at the rate of 10 °C min^{-1}, and was held for 10 min. The FID oven temperature was maintained at 300 °C. Hydrogen was generated by hydrogen generator (OPGU-2200S, Shimadzu) for FID at a flow rate of 40 mL min^{-1}. The flow of air (99.999 %, Air Products) for FID was 400 mL min^{-1}. The model 2010 D Centurion Scientific centrifuge (Westsussex, UK) was used for separation of sediment phase from sample solution.

2.3. Preparation of Magnetic Nanoparticles of Fe_3O_4

The chemical co-precipitation method was used in the preparation of the Fe_3O_4 NPs [48]. First, a stock solution was prepared by mixing 10.4 g of $FeCl_3{\cdot}6H_2O$, 4.0 g of $FeCl_2{\cdot}4H_2O$, and 1.7 mL of HCl (12 mol L^{-1}) in 50 mL of deionized water in a beaker. The solution was then degassed using nitrogen gas for 20 min before use. Simultaneously, 500 mL of 1.5 mol L^{-1} NaOH solution was degassed (for 15 min) and heated to 80 °C in a reactor. The solution of iron salts was then added dropwise using a dropping funnel for 30 min under nitrogen gas protection with vigorous stirring (1000 rpm) using a glassware stirrer. During the entire process, the solution temperature was maintained at 80 °C and nitrogen gas was used to prevent the intrusion of oxygen. After the reaction, the Fe_3O_4 NPs precipitate obtained was separated from the reaction medium using a magnetic field, and then washed four times with 500 mL of deionized water. Finally, the NPs obtained were resuspended in 500 mL of degassed deionized water.

2.4. Preparation of the PPy/Fe_3O_4 Nanocomposites

The PPy/Fe_3O_4 nanocomposites were synthesized by *in situ* polymerization of the pyrrole (Py) monomer in the presence of suspended Fe_3O_4 nanoparticles, using $FeCl_3$ as oxidant at ambient temperature. In a typical polymerization technique, 0.2 g of Fe_3O_4 nanoparticles were added to 25 mL deionized water in a conical flask and ultrasonicated for 10 min for better dispersion of Fe_3O_4 into water. A quantity of 3 g of $FeCl_3$, oxidant was added to the deionized water containing the Fe_3O_4 nanoparticles and was shaken for 10 min. To this mixture 0.8 mL of pyrrole was added to the mixture using a syringe. Then the reaction mixture was kept under constant shaking for 3 h at ambient temperature. Finally, to stop the reaction, acetone was added to the reaction mixture. The black powder obtained was filtered and washed with distilled water until the filtrate became colourless and finally washed with acetone. Then the composites were dried at 100 °C for 8 h.

2.5. MSPE-DLLME Procedure

Ten millilitres of the aqueous sample solution were transferred to a beaker and spiked at a given concentration of the target analytes. Fe_3O_4@PPy NPs (20 mg) was added into a beaker containing 10 mL aqueous solution spiked at the level of 100 μg L^{-1} of the analytes, and mechanically stirred for 10 min

(Fig. 1a). The magnetic adsorbent was isolated from a solution using a magnet (Fig. 1b). Thereafter, the magnetic adsorbent was mixed with 800 μL methanol using a vortex mixer for 0.5 min (Fig. 1c) and separated using magnet (Fig. 1d), and thereafter the eluent was transferred into a vial for DLLME step. For the extraction process (DLLME), 40 μL of 1,1,2-trichloroethane was added to the eluent, and then the mixture was rapidly injected into a conical test tube containing 5 mL double-distilled water. After agitation for 0.5 min using a vortex mixer, a cloudy solution resulting from the dispersion of fine droplets of 1,1,2-trichloroethane in the aqueous solution was formed in the test tube (Fig. 1f). Then the solution was centrifuged for 5 min at 2000 rpm (Fig. 1g) to force the dispersed fine particles of 1,1,2-trichloroethane to sediment at the bottom of the test tube (Fig. 1h). Thereafter, 2 μL of the organic (1,1,2-trichloroehane) phase was injected into GC-FID for analysis.

3. Results and Discussion

3.1. Characterization of Fe_3O_4@ PPy Nanoparticles

The obtained NPs were stable under these conditions for up to about one month and were characterized using a transition electron microscope (TEM). The obtained product is shown in Fig. 2. The shape, size and morphology of the synthesized Fe_3O_4@PPy NPs were determined by TEM and SEM. Furthermore, the coated PPy was characterized by FT-IR. The shape and size of the nanoparticles were observed by TEM (Fig. 3). The TEM images of Fe_3O_4@PPy particles show that an obvious coating of PPy is immobilized on the surface of Fe_3O_4 NPs. The coated PPy layer is clearly seen due to the different electron densities of magnetic nanoparticles core (with dark colour) and PPy coating (with light colour) in TEM micrograph. The synthesized Fe_3O_4@PPy NPs showed a spherical shape with an average diameter of about 5–10 nm, however, the nanoparticles tended to aggregate.

In addition, the size and morphology of the resultant Fe_3O_4@PPy NPs were determined by SEM (Fig. 4). The Fe_3O_4@PPy NPs have a nearly spherical shape with a smooth and uniform surface morphology. Due to agglomeration of the particles and the lower resolution of SEM in comparison to TEM, size of the particles in SEM image is larger than that in TEM image.

The coated PPy was characterized by FT-IR in a range of 4000 and 400 cm^{-1}. FT-IR spectra for bare and PPy-coated Fe_3O_4 NPs are illustrated in (Fig. 5). The characteristic absorption peaks of Fe_3O_4 NPs, appeared in two spectrums (a and b), corresponding to the stretching vibrations of hydrogen-bonded surface water molecules and hydroxyl groups at 3400 cm^{-1} and the Fe—O transverse vibration at 580 cm^{-1} were observed. Coating of PPy onto Fe_3O_4 NPs was confirmed by the appearance of characteristic PPy bands in spectrum (b). The weak bands at 2800 and 2900 cm^{-1} were assigned to the stretching vibrations of C—H bonds. The absorption peak at 1050 and 1314 cm^{-1} were attributed to the bending vibration of C—H bond in the pyrrole ring and C—N stretching vibration. The absorption bands at 1549 and 1460 cm^{-1} belong to C—C asymmetric and symmetric stretching vibrations of the pyrrole ring, respectively. The absorption bands at 2358 and 909 cm^{-1} belong to C—H vibrations and the absorption bands at 3737 and 3820 cm^{-1} belong to N—H vibrations. These results indicate that PPy has been successfully coated on the surface of Fe_3O_4 NPs.

3.2. Effect of Sorbent Amount

To study the effect of sorbent quantity on the extraction efficiency of permethrin and deltamethrin, different amounts of sorbent in the range of 10–25 mg were added to the solution (Fig. 6). Finally, an amount of 20 mg of sorbent was found as the optimum value.

3.3. Effect of Extraction Time

The extraction recovery strongly depends on the mass transfer of the analytes from sample solution to the extraction media. To study the effect of this parameter, the extraction was performed in the range of 5–30 min. The extraction time profile for permethrin and deltamethrin showed that the equilibrium was reached quite rapidly. The developed method offers a short extraction time which could be due to the dispersion of sorbent throughout the sample solution during the extraction and the absence of internal diffusion resistance. Overall, a duration time

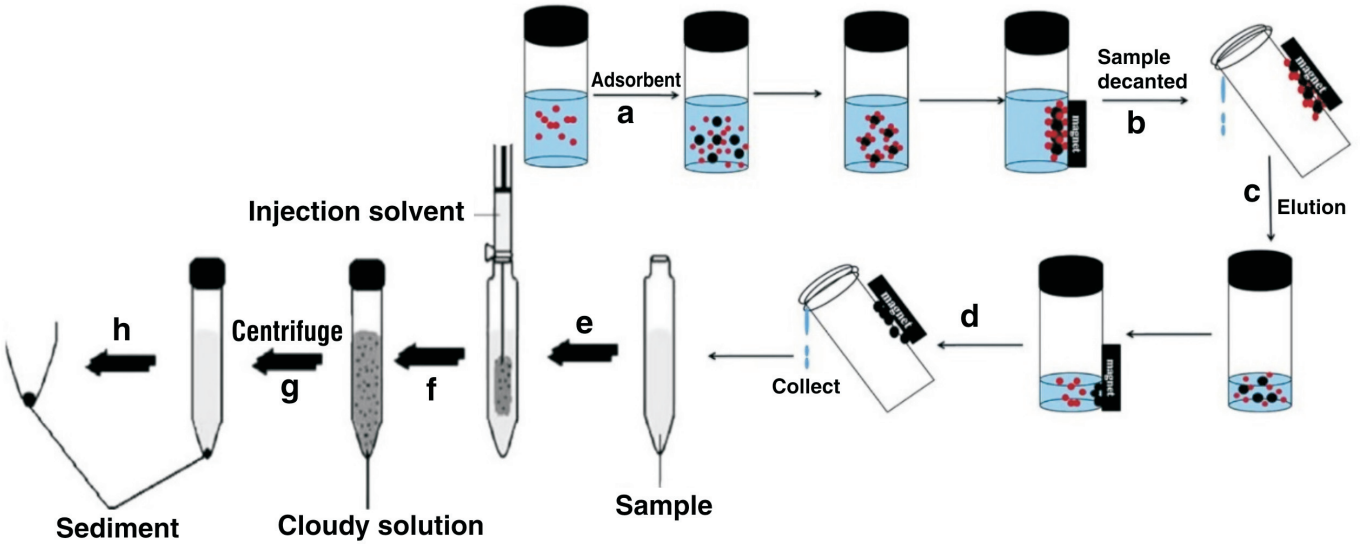

Figure 1 NPs was added to the solution and mechanically stirred (**a**), the magnetic adsorbents were isolated from the solution with the magnet (**b**), analytes adsorbed were eluted with methanol (**c**), the eluent was separated from the NPs with the magnet (**d**), 1,1,2-trichloroethane was added to the eluting solvent of MSPE (**e**), a cloudy solution resulting from the dispersion of fine droplets of 1,1,2-trichloroethane in the aqueous solution (**f**), the solution was centrifuged (**g**), the organic phase settled in the bottom of the conical test tube (**h**).

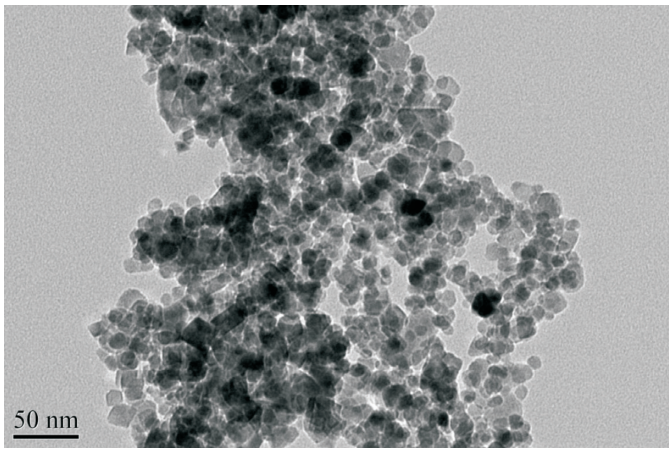

Figure 2 TEM image of prepared Fe_3O_4.

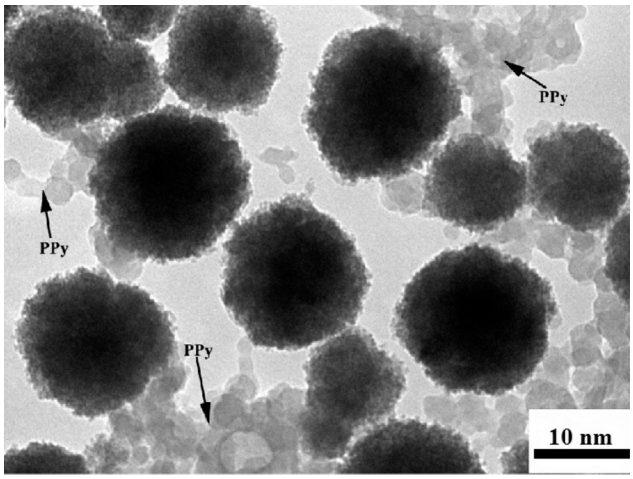

Figure 3 TEM images of Fe_3O_4@PPy.

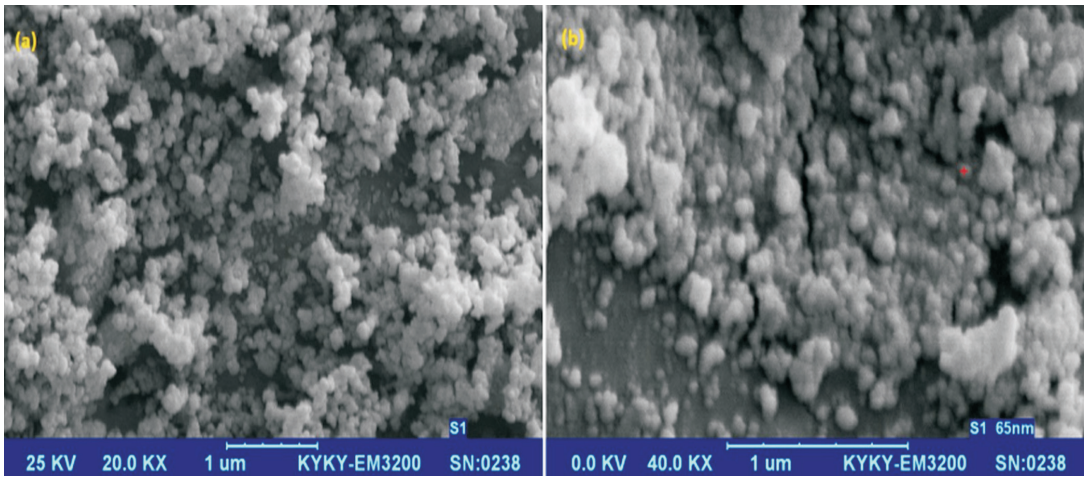

Figure 4 SEM images of Fe3O4@PPy NPs, (**a**) ×20 000 (**b**) ×40 000.

of 20 min was found to be the optimum value for the extraction time (Fig. 7).

3.4. Effect of Elution Solvent Type and its Volume

In MSPE-DLLME procedure, the elution solvent used for the SPE step also plays a role as a disperser solvent during the DLLME stage. For this purpose, acetone, acetonitrile, ethanol and methanol, were selected and tested as elution solvents. The Fe_3O_4@PPy was eluted using 800 μL of each solvent. The results (Fig. 8) indicated that the extraction efficiency, when using methanol, was more effective than the other potential elution solvents. Therefore, methanol was selected as the elution solvent in further experiments.

To obtain the optimized volume of elution solvent, various experiments were carried out using different volumes of methanol (700–1000 μL). According to the results shown in Fig. 9, methanol volumes lower than 800 μL decreases the extraction efficiency, indicating lower volumes cannot elute the analytes

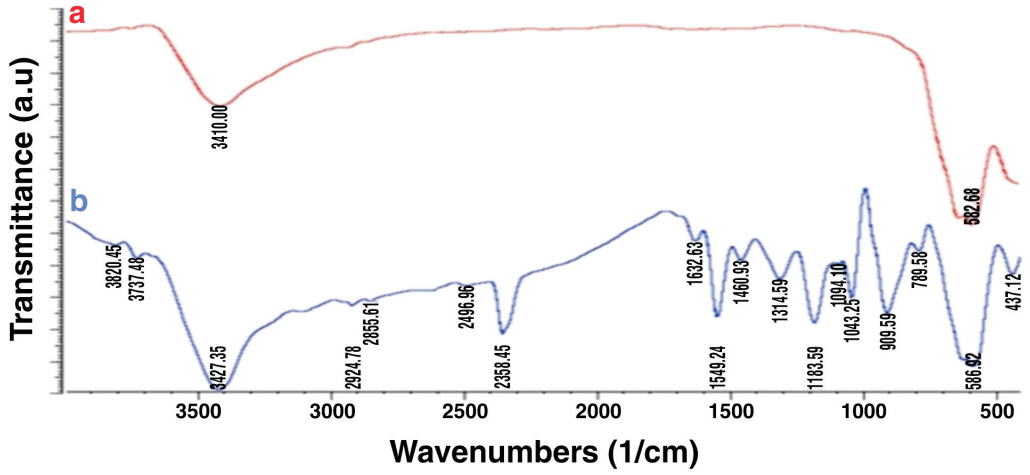

Figure 5 FT-IR spectra of (a) Fe_3O_4, (b) Fe_3O_4@PPy.

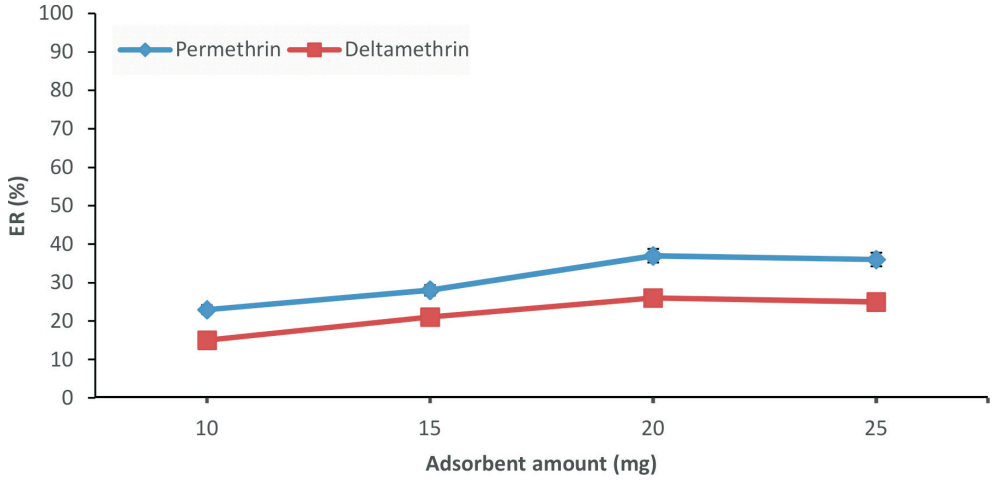

Figure 6 Effect of adsorbent amount on the extraction efficiency of permethrin and deltamethrin using MSPE-DLLME. Extraction conditions used were methanol as disperser or eluent solvent; tetrachloroethylene as the extraction solvent; desorption time of 1 min; extraction time of 10 min; sample volume of 10 mL; and adsorbent amounts of 10, 15, 20 and 25 mg (n = 3).

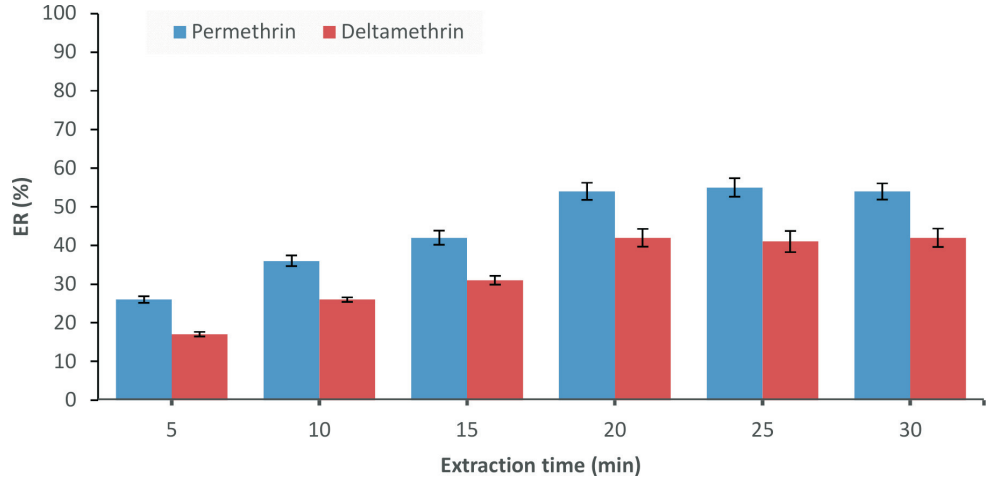

Figure 7 Effect of extraction time on the extraction efficiency of permethrin and deltamethrin using MSPE-DLLME. Extraction conditions were methanol as the disperser or eluent solvent; tetrachloroethylene as the extraction solvent; desorption time of 1 min; extraction time of 5, 10, 15, 20, 25 and 30 min; sample volume of 10 mL; and 20 mg of adsorbent amount (n = 3).

effectively. Also, at lower volumes of methanol the emulsion does not form, thereby the recovery is low. At methanol volumes higher than 800 μL, the extraction efficiency decreases, due to the increasing solubility of the target analytes in the water phase. Therefore, a volume of 800 μL was chosen as the optimum volume for the elution solvent.

3.5. Effect of Extraction Solvent Type and its Volume

The extraction solvent must possess certain properties, including higher density than water, high extraction capability of the analytes, and low solubility in water. To investigate the effect of the extraction solvent, chloroform, tetrachloroethylene, chlorobenzene, and 1,1,2- trichloroethane were tested. The results

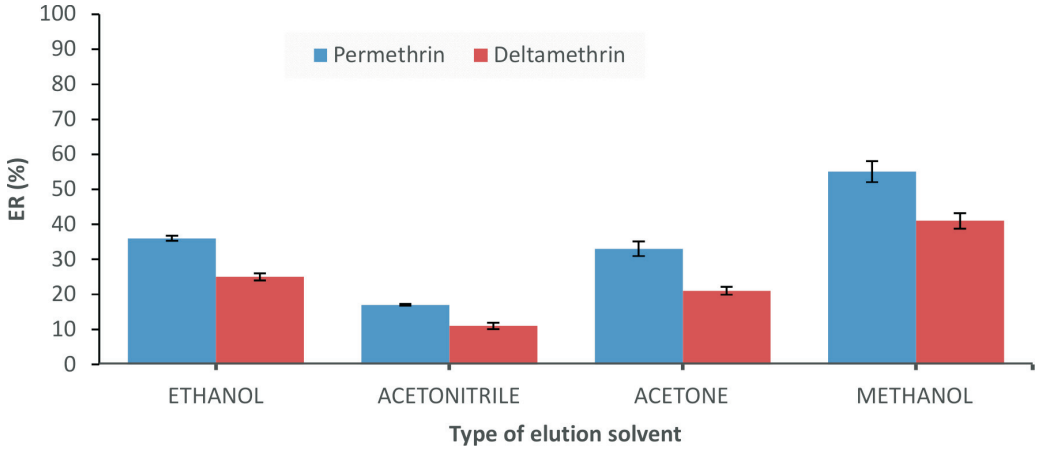

Figure 8 Comparison of several types of elution and disperser solvent for MSPE-DLLME procedure. Extraction conditions were tetrachloroethylene as the extraction solvent; desorption time was 1 min; extraction time of 20 min; and sample volume of 10 mL (n = 3).

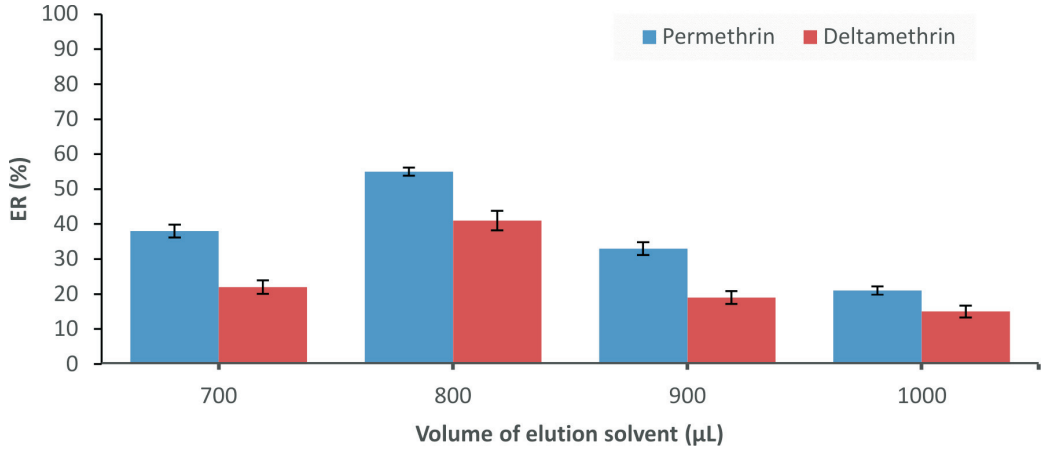

Figure 9 Varying the volume of elution solvent using tetrachloroethylene as the extraction solvent, desorption time of 1 min, an extraction time of 20 min, and a sample volume of 10 mL (n = 3).

(Fig. 10) clearly indicate that the extraction efficiency obtained using 1,1,2-trichloroethane was higher than that of the other extraction solvents. It is probably because of the higher solubility of the analytes in 1,1,2-trichloroethane in comparison with the other tested solvents. Therefore, 1,1,2-trichloroethane was selected as the extraction solvent in further experiments.

To examine the effect of the volume of the extraction solvent, additional experiments were carried out using 800 μL methanol (elution solvent) and different volumes of the extraction solvent (20–90 μL), and the results as presented in Fig. 11. It was found that with an increase in the volume of 1,1,2-trichloroethane from 20.0 to 40.0 μL, extraction efficiency increases and after that decreases, because of increasing the volume of the organic (sediment) phase. According to the results, 40.0 μL of 1,1,2-trichloroethane was selected as the optimum extraction solvent volume.

3.6. Desorption Time

The influence of desorption time was also investigated. It was observed (Fig. 12) that after 5 min, no notable changes occurred in the extraction efficiencies. Therefore, 5 min was considered as the optimal desorption time of the analytes in subsequent experiments.

3.7. Quantitative Aspects

The analytical characteristics of the proposed method was validated under the optimized conditions in terms of linearity, precision and limit of detection to estimate the efficiency and feasibility of the method for its application in analysis of environmental samples. The results are listed in Table 1 under optimum conditions. The analytes demonstrated good linearity in the range of 0.5–100 μg L^{-1} with good correlation coefficients r^2 = 0.989 and r^2 = 0.979 for permethrin and deltamethrin, respectively. The limits of detection (LODs), based on signal-to-noise ratio (S/N) of 3, was 0.01 μg L^{-1} for both. The limits of quantification (LOQs), based on signal-to-noise ratio (S/N) of 10, was 0.6 μg L^{-1} for both.

The precision of the method was evaluated by carrying out five independent measurements of the studied compounds at three concentration levels. The results are shown in the Table 2.

Table 3 compares the proposed method with other extraction methods for the determination of the target analytes in water samples. The quantitative results of the proposed method are better than those of homogeneous liquid–liquid microextraction via flotation assistance (HLLME-FA),[59] or micro liquid–liquid extraction.[60] Comparison of the proposed method with micro liquid–liquid extraction and competitive enzyme-linked immunosorbent assays (C-ELISAs)[61] for the extraction and determination of the analytes indicates that this novel method has a short extraction time for determination of the analytes. C-ELISAs is expensive and requires more organic solvents and time. Also, micro liquid–liquid extraction requires more toxic organic solvent and time. Moreover, the proposed method has potential for the determination of the target analytes in complex matrices such as waste water due to clean up of the MSPE before DLLME method. In addition, it can be used in the large volumes of sample in contrast to the DLLME method. The recovery of

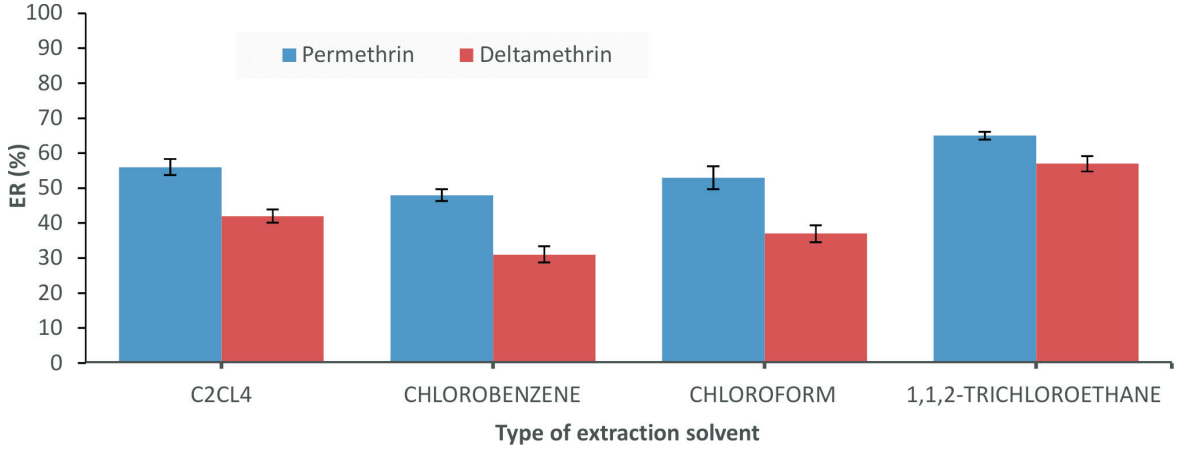

Figure 10 Effect of extraction solvent on recovery of the analytes using methanol as the eluting solvent, a desorption time of 1 min, an extraction time of 20 min, and a sample volume of 10 mL (n = 3).

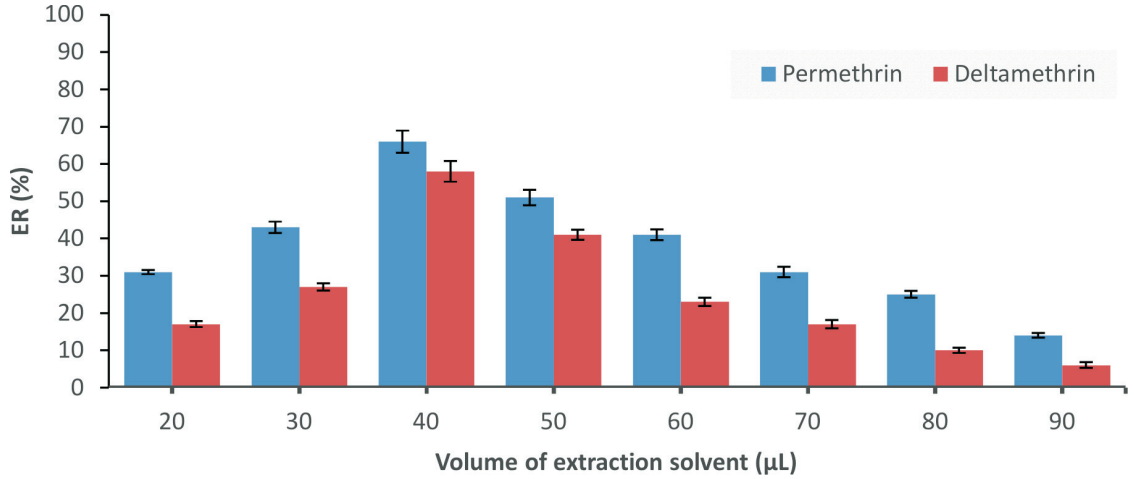

Figure 11 Varying the volume of the extraction solvent during the DLLME step. Methanol was used for the MSPE stage with a desorption time of 1 min, the extraction time was 20 min, and the sample volume was 10 mL (n = 3).

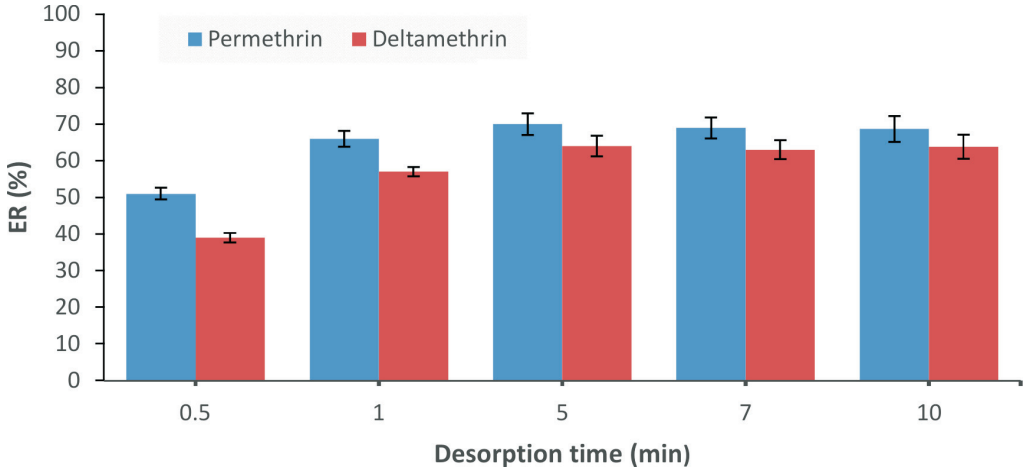

Figure 12 Effect of desorption time on the extraction efficiency of MSPE-DLLME of permethrin and deltamethrin using methanol as the disperser or eluent solvent; 1,1,2-trichloroethane as the extraction solvent; desorption time of 0.5, 1, 5, 7 and 10 min; extraction time of 20 min; and a sample volume of 10 mL (n = 3).

the proposed method are comparable with other extraction methods[59–61]. Finally, the proposed method has exciting potential to determine the selected analytes at trace levels in water samples.

3.8. Analysis of Real Samples

During the present investigation, matrix effects on the extraction were also evaluated by investigating the applicability of the proposed method to determine permethrin and deltamethrin concentrations in waste water, river, tap and well water samples. These samples were extracted using MSPE-DLLME method and analyzed by GC-FID. The results from waste water, tap, river and well water samples showed that they were free of permethrin and deltamethrin contamination. These samples were spiked with permethrin and deltamethrin standard solution (10.0 μg L^{-1} concentration level) to assess matrix effects. The results of relative recoveries were between 88 to 95 %. These results (Table 4) show that the waste water, tap, well and river water matrices, in our present context, had negligible effect on MSPE-DLLME method.

Table 1 Quantitative results of MSPE-DLLME and GC-FID method for permethrin and deltamethrin.

Analyte	Linear range /μg L^{-1}	LOD[a] /μg L^{-1}	LOQ[b] /μg L^{-1}	R^{2}[c]
Permethrin	0.5–100	0.01	0.6	0.989
Deltamethrin	0.5–100	0.01	0.6	0.979

[a] LOD, limit of detection for S/N = 3.
[b] LOQ, limit of quantification for S/N = 10.
[c] Coefficient of determination.

4. Conclusion

This paper describes the application of the MSPE-DLLME method combined with GC-FID for determination of trace amounts of permethrin and deltamethrin in water samples. The relative recoveries were in the range of 88–95 % and showed that waste water, tap, well and river waters matrices had negligible effect on the MSPE-DLLME. The method is precise, reproducible and linear over a wide range and require small volumes of organic extractant. Moreover, the proposed method is promising

Table 2 Relative standard deviation at three different concentration levels by using proposed method.

Analyte	Relative standard deviation (R.S.D.%), n = 5		
	5.0 μg L^{-1}	10.0 μg L^{-1}	50 μg L^{-1}
Permethrin	6.5	4.6	1.0
Deltamethrin	8.6	5.3	1.5

Table 3 Comparison of the proposed method with other extraction methods for determination of deltamethrin and permethrin.

Method	R.S.D.%	Dynamic linear range /μg L^{-1}	Limit of detection /μg L^{-1}	Extraction time /min	Recovery /%
HLLME-FA-GC-FID[59]	6.9–7.8	1.0–200	0.2–0.3	1	90–98
Micro-liquid–liquid extraction-GC-MS[60]	1.9–11.7	1.0–9.0	0.003–0.035	13	>93
Competitive enzyme-linked immunosorbent assays (C-ELISAs)[61]	–	0.2–150	1.1	72 h	92–100
MSPE-DLLME-GC-FID	1.0–1.5	0.5–100	0.01	1	88–95

Table 4 Determination of permethrin (PRM) and deltamethrin (DLM) in waste water, river, tap and well water and relative recovery of spiked permethrin and deltamethrin in them.

Sample	Concentration of PRM and DLM /μg L^{-1} ± S.D., n = 3		Added PRM and DLM /μg L^{-1}		Found PRM and DLM /μg L^{-1} ± S.D., n = 3		Relative recovery /%	
	PRM	DLM	PRM	DLM	PRM	DLM	PRM	DLM
Tap water [a]	n.d [b]	n.d [b]	10	10	9.2 ± 0.1	9.3 ± 0.2	92	93
Waste water [c]	2.1	1.8	10	10	10.9 ± 0.5	10.7 ± 0.6	88	89
Well water [d]	n.d [b]	n.d [b]	10	10	9.4 ± 0.2	9.1 ± 0.3	94	91
River water [e]	n.d [b]	n.d [b]	10	10	9.5 ± 0.3	9.2 ± 0.4	95	92

[a] From drinking water system of Tehran, Iran.
[b] Not detected.
[c] From Tehran, Iran.
[d] From Tehran, Iran.
[e] Kolakchal River water, Tehran, Iran.

for trace analysis of permethrin and deltamethrin in natural water samples.

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