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Azinphos-methyl and chlorfenvinphos pesticides determination using fabric phase sorptive extraction followed by high performance liquid chromatography-photodiode array detector

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Abbreviations: **EF**, Enrichment factor; **ER**, Extraction recovery; **FPSE,** Fabric phase sorptive extraction; **HPLC**, High performance liquid chromatography; **LLE**, Liquid-liquid extraction; **LOD**, Limit of detection; **LOQ**, Limit of quantification; **PDA,** Photodiode array detector; **RSD**, Relative standard deviation; **SPE**, Solid phase extraction

Abstract

A reliable and efficient fabric phase sorptive extraction method was developed for the rapid analysis of azinphos-methyl and chlorfenvinphos pesticide residues in wastewater and fruit juice samples using high-performance liquid chromatography-photodiode array detector. The influences of major experimental parameters were evaluated and optimized. Relative standard deviation values at two different concentrations (50 and 100 μg L^{-1}) for intra–day (n = 6) and inter–day (n = 4) precisions were less than 8%. Limits of detection for azinphos-methyl and chlorfenvinphos were calculated as 0.96 μg L^{-1} and 2.5 μg L^{-1}, respectively. The values of the enrichment factors for azinphos-methyl and chlorfenvinphos were calculated as 71 and 73, respectively. The developed analytical method has been allowed simple, specific, accurate and sensitive simultaneous determination of azinphos-methyl and chlorfenvinphos. Additionally, the superior performances and operational simplicity of fabric phase sorptive extraction method have been demonstrated by analyzing the selected pesticide residues in wastewater as well as in carrot, apple, peach, apricot, and orange juice samples.

Keywords: High performance liquid chromatography; Fabric phase sorptive extraction; Fruit Juices; Carrot juice; Wastewater; Pesticides.

1. Introduction

Organophosphorus pesticides such as azinphos-methyl and chlorfenvinphos are commonly used in agriculture to increase crop yields. However, these pesticides can cause serious neurotoxic disorders, kidney and liver damage, and asthma in addition to other health problems. Therefore, it is widely accepted that the usage of these pesticides should be kept under control due to their side effects on the ecosystem and human health [1-5]. From this point of view, there is a strong demand for the development of efficient sample preparation methods coupled with instrumental techniques to assess and control the concentration of these compounds. The aims of the sample preparation step are to minimize the impact of the complexity of real sample matrices and to eliminate possible interferences by reliably extracting the target analytes [6, 7]. To date, two main categories of extraction methods including solvent-based extraction methods [8, 9] and sorbent-based extraction methods (e.g. solid phase extraction (SPE) [10, 11], dispersive solid phase extraction [12, 13], stir bar sorptive extraction [14, 15], magnetic dispersive solid phase extraction [16, 17], matrix solid phase dispersion [18, 19], and solid phase micro extraction (SPME) [20, 21] have been introduced. Both the sample preparation approaches suffer from several limitations and benefits from many advantages. However, sorbent-based extraction methods demonstrate superiorities in terms of low solvent consumption and efficient sample clean-up over solvent-based methods [22]. More recently, fabric phase sorptive extraction (FPSE) was introduced as an efficient, facile, and promising extraction method [23]. The FPSE method has attracted much attention for the extraction of various target molecules from food, biological, and environmental samples. For example, pesticide molecules in environmental samples [24, 25], UV filters in biological samples [26], parabens in cosmetic samples [27], and anti-inflammatory drugs [28] were successfully analyzed with FPSE method. The basis of membrane preparation in this method involves the coating of a sponge-like sol-gel organic-inorganic hybrid sorbent on a permeable fabric substrate made of polyester, cellulose, or fiberglass. In contrast to the physical coating process on the substrate surface, sol-gel coating process can provide homogeneous and reproducible sorbent coating as it exploits chemical covering approach. After preparing the membrane, a small piece of it is immersed in the aqueous sample matrix to absorb the target analytes. Indeed, the satisfactory performance of the FPSE membrane not only stems from the organic-inorganic hybrid coating but also from the planar geometry and surface chemistry of the fabric substrate. Taken as a whole, a hydrophobic substrate like polyester can be a suitable choice for nonpolar analytes, while a hydrophilic substrate like cotton cellulose is commonly chosen for polar or semi-polar analytes. In comparison with the most popular sorbent-based extraction methods, FPSE is a reliable method for *in situ* sample preparation requirements. Additionally, a plethora of sol-gel-based sorbent coatings is available that can be used as the extractive phase in the preparation of the FPSE membrane. The broad range of FPSE membrane coatings including polar, medium polar, nonpolar, cation exchanger, anion exchanger, mixed mode, and zwitterionic multi-mode sorbents expand the feasibility of application of FPSE for the extraction of the enormous diversity of target analytes from different real samples. Moreover, the FPSE membrane can be easily handled using tweezers in the adsorption and desorption steps [29, 30]. In FPSE, the extraction equilibrium is attained *via* intermolecular interaction of the analytes and active sites of the porous FPSE membrane. In this article, azinphos-methyl and chlorfenvinphos were initially extracted to the methyltrimethoxysilane poly(propylene glycol)-*b*-poly(ethylene glycol)-*b*-poly(propylene glycol) (sol-gel MTMS/PPG-PEG-PPG) coated FPSE membrane and then desorbed to an elution solvent. Finally, the elution solvent was directly injected into the high-performance liquid chromatography combined with a photodiode array detector (HPLC-PDA) for the analysis of the target pesticides.

Due to the medium polarity of the analytes in this study, high extraction efficiency is attained *via* their intermolecular interaction and active sites of the selected medium polar FPSE membrane. In 2022, the same membrane was used for the analysis of adamantine analogues in urine samples with UHPLC-MS/MS [31], and in this study, the capability of this FPSE membrane for the extraction of completely different analytes from other kinds of matrices was proved for the first time and two kinds of organophosphorus pesticides were efficiently extracted from wastewater, carrot juice and fruit juice samples. It is worth mentioning that selected pesticides were used for pest control in vegetable and fruit production in Turkey and they were previously analyzed in different samples collected from this country [32-34].

2. Experimental

2.1. Chemicals

The fabric membrane substrate made from muslin cotton cellulose 100% was obtained from Jo-Ann Fabrics (Miami, FL, USA). Azinphos-methyl and chlorfenvinphos standards, trifluoroacetic acid, acetone, and phosphoric acid were obtained from Sigma-Aldrich (St. Louis, MO, USA). An MES Minipure Dest Up (Ankara, Turkey) water purification system was used to prepare ultra-pure water with a resistivity of 18.2 MΩ cm. Acetonitrile (ACN), phosphoric acid, boric acid, and sodium chloride were purchased from Merck (Darmstadt, Germany). Moreover, *iso*-propanol and acetic acid were purchased from Tekkim Chemical Company (Bursa, Turkey). In addition, methanol was purchased from Supelco (Bellefonte, PA, USA). Sodium sulfate was purchased from IsoLab Chemicals (Wertheim, Germany).

Methyltrimethoxysilane (MTMS, 98%) and poly(propylene glycol)-block-poly(ethylene glycol)-block-poly(propylene glycol) (PPG-PEG-PPG) were obtained from Sigma-Aldrich (St. Louis, MO, USA). It should be noted all reagents in this study were of analytical grade.

2.2. Preparation of solutions

A mixture stock solution of azinphos-methyl and chlorfenvinphos at a concentration of 50 mg L^{-1} (each pesticide) was prepared in methanol and stored in a refrigerator at 4 °C. Additionally, working standard solutions for all experiments (500 μg L^{-1} of each pesticide) were prepared daily by diluting the above-mentioned stock solution with deionized water. Moreover, a Britton Robinson buffer consists of a mixture of 0.04 mol L^{-1} phosphoric acid, 0.04 mol L^{-1} acetic acid, and 0.04 mol L^{-1} boric acid was prepared to adjust the pH of aqueous samples in the range of 2 to 10.

2.3. Preparation of real samples

Four fruit juice samples including apple, peach, apricot, and orange juices as well as a carrot juice sample were purchased from local stores (Sivas, Turkey). Additionally, wastewater sample was collected from a garden pond (Sivas, Turkey) in a brown glass bottle during the agrochemicals'

usage span. Carrot, apple, peach, and apricot samples were diluted at a ratio of 1:1 (*v:v*) with deionized water before the practice of FPSE. The orange juice sample was diluted at a ratio of 1:2 (*v:v*). It is also worth mentioning that the wastewater was used without dilution or any other pre-extraction sample manipulation (filtration, centrifugation, etc.).

2.4. Instruments and HPLC conditions

A Shimadzu 20-AD high performance liquid chromatography system (Tokyo, Japan) equipped with an auto sampler (SIL-20AC), a Phenomenex (Torrance, CA, USA) C_{18} column, a thermostatic oven (CTO-10 AS), a pump (LC20-AD), a software (LC Solution), and a thermostatic oven (CTO-10 AS) were used for the analysis of the target analytes. In addition, a 0.45-µm PTFE membrane filter (HNWP, Millipore) was used as a filter to prepare solutions and mobile phase solvents before their injection into HPLC system. A mixture of methanol– ACN-water containing 0.1% trifluoroacetic acid (50:20:30, *v:v:v*) at a flow rate of 1.0 mL min^{-1} was used as the optimized mobile phase-as in isocratic elution mode. The temperature of the column was kept constant at 30 °C. - Along with that, the wavelengths of azinphos-methyl and chlorfenvinphos detection were set at 222 nm and 244 nm, respectively. Furthermore, the injection volume of the autosampler was set at 10 µL. A pH meter model (Mettler Toledo MP220, Mettler Toledo, Switzerland) equipped with a glass electrode was used for pH measurements of samples. - An ultrasonic water bath (Kudos, China) was used for degasification of mobile phase components. A laboratory rotator (Fisherbrand, Thomas Scientific, Swedesboro, USA) and a Jeiotech vortex (Korea) were utilized in the adsorption and desorption steps, respectively. A scanning electron microscope (SEM) (Tescan, Brno, Czech) with an accelerating voltage of 10.0 kV was used to identify the morphology of the MTMS/PPG-PEG-PPG coated FPSE membrane. The building blocks of the FPSE membrane were characterized by Fourier transform infrared spectroscopy (PerkinElmer Lambda 25).

2.5. Preparation of MTMS/PPG-PEG-PPG coated FPSE membrane

Due to the medium polarity of the target analytes (azinphos-methyl and chlorfenvinphos) hydrophilic Muslin, 100% cellulose cotton fabric was used as the substrate for sol-gel MTMS/PPG-PEG-PPG coating. Commercial cotton cellulose fabric is generally produced in bulk for manufacturing garment products that contain surface finishing chemicals and additives to improve the overall appearance of the fabric. These chemicals obscure a large portion of the surface hydroxyl functional groups which are needed to maximize the sol-gel sorbent loading during the sol-gel sorbent coating process. The detailed surface treatment process of cellulose fabric is presented elsewhere [35, 36]. Taking the medium polarity of the target analytes into consideration, a sol solution was designed using PPG-PEG-PPG as the polymer, MTMS as the networking sol-gel precursor, trifluoroacetic acid as the catalyst and water as the hydrolytic agent and acetone: methylene chloride (50:50, *v:v*) as the solvent system. The molar ratio between sol-gel precursor, organic/inorganic polymer, acetone, methylene chloride, trifluoroacetic acid, and water was kept at 1:0.13:1.94:2.3:0.75:3.

The detailed procedure of sol solution preparation and subsequent coating and post-treatment procedures are presented -other where [37]. Briefly, the sol solution was prepared by the sequential addition of 5 g organic/inorganic polymer, 10 mL acetone: methylene chloride (1:1, *v:v*), 5.0 mL MTMS and 2.0 mL trifluoroacetic acid (containing 5% water, *v:v*). The sol solution was vortexed vigorously after adding each of the ingredients to ensure that the resulting solution becomes homogeneous and particle free. The sol solution was then subjected to sonication to remove any trapped air bubbles. Finally, the sol solution was transferred into a 30 mL amber reaction vessel and a 10 cm × 5 cm piece of clean and treated cotton fabric was gently immersed into the sol solution. The sol solution was allowed to create the sol-gel sorbent coating on the fabric substrate for 4 h at room temperature. At the end of the sol-gel sorbent coating process, the sorbent-coated fabric was removed from the reaction vessel and stored in a desiccator overnight. Subsequently, the sol-gel sorbent coated fabric was rinsed with acetone: methylene chloride (1:1, *v:v*) under sonication for 30 min. The sol-gel sorbent coated membrane was then air dried for 1 h and was cut into 1.0 cm × 2.0 cm pieces. The FPSE membranes were then stored in an air-tight container until their application in sample preparation.

2.6. Fabric phase sorptive extraction procedure

Initially, a small piece of FPSE membrane with an area of 2.0 cm^2 (1.0 cm ×2.0 cm) was immersed into the mixture of ACN/methanol (50:50, *v:v*) and vortex agitated for 2 min. After the separation of the FPSE membrane, it was rinsed with deionized water. Subsequently, 40 mL of sample solution (see Section 2.3) or deionized water containing 500 μg L^{-1} of each pesticide and 5% (*w:v)* of sodium sulfate was placed in a 50–mL test tube. After that, the aforementioned FPSE membrane was immersed into it. After then, the test tube was placed in a rotator at 100 rpm rate for 35 min. After the target analytes were absorbed onto the FPSE membrane, the membrane was separated from the aqueous solution. Following this, the supernatant was removed and 500 μL methanol was added onto the separated FPSE membrane and vortex agitated for 2 min to desorb the target analytes. Afterward, methanol containing the analytes was separated from the sorbent and samples; then, it was filtered using syringe tip and injected into HPLC (Fig. 1).

[Insert Fig. 1]

3. Results and discussion

3.1. Selection of the FPSE membrane

Due to the medium polarity of both the analytes, azinphos-methyl (log Kow 2.75) [38] and chlorfenvinphos (log Kow 3.81) [39], an FPSE membrane possessing high affinity towards medium polarity compounds would be the rational choice. The selectivity and extraction efficiency of the FPSE membrane depend on (a) the polymer; (b) the sol-gel precursor; and (c) the fabric substrate [30]. Since the polymer is considered as the most significant contributor to the selectivity and extraction efficiency attributes of the FPSE membrane, a medium polarity polymer PPG-PEG-

PPG, was selected as the organic polymer in the sol solution. MTMS was used as the sol-gel networking precursor due to its possession of methyl pendant group that also contributes to the hydrophobic characteristics of the FPSE membrane. The substrate was Muslin, 100% cotton cellulose. The very high concentration of surface hydroxide functional groups on 100% cotton cellulose fabric allowed higher loading of sol-gel sorbents during the sol-gel sorbent coating process. It is worth mentioning that the sol-gel sorbent loading is proportionate to the available surface hydroxide groups on the substrate surface.

3.2. Characterization of FPSE membrane

The MTMS/PPG-PEG-PPG membrane coating was characterized using Fourier Transform-Infrared Spectroscopy (FT-IR) and Scanning Electron Microscopy (SEM).

3.2.1. Fourier Transform-Infrared Spectroscopy (FT-IR)

FT-IR spectra provide valuable information about the functional composition of different building blocks of sol–gel sorbent coating as well as the successful integration of the building blocks into the final product, sol–gel PPG-PEG-PPG sorbent coating. The FT-IR spectra of sol-gel PPG-PEG-PPG and sol-gel MTMS/PPG-PEG-PPG sorbent FPSE membrane are presented in Fig. 2a and Fig. 2b, respectively. Major bands in PPG-PEG-PPG pristine polymer spectra include –C–H stretching at 2869 cm^{-1}, -C–H bending at 1456 cm^{-1} and –C-O-C stretching at 1095 cm^{-1} [40]. The presence of many bands in the FT-IR spectra of sol–gel PPG-PEG-PPG such as bands at 2894 cm^{-1}, 1428 cm^{-1}, 1271 cm^{-1}, 1102 cm^{-1} and 768 cm^{-1} are also present in sol-gel MTMS/PPG-PEG-PPG FT-IR spectra strongly suggests the successful integration of the sol-gel precursor MTMS and the organic polymer into the sol–gel PPG-PEG-PPG sorbent.

[Insert Fig. 2]

3.2.2. Scanning Electron Microscopy (SEM)

FPSE membranes take advantage of many beneficial features offered by sol–gel coating technology including a precisely controllable surface coating process that provides excellent coating uniformity and chemically bonded sorbent-coated film on the substrate surface. The unique architecture of FPSE membrane combines the extraction principles of SPME (characterized by equilibrium extraction) and SPE (characterized by exhaustive principle) duo to its unique design. In order to exploit the exhaustive extraction principle of SPE, the FPSE membrane must be permeable [30]. The FPSE substrate, 100% cellulose, is permeable as demonstrated in Fig. 3 (a, b). The surface morphology of sol-gel MTMS/PPG-PEG-PPG coated FPSE membrane at 100x and 500x magnifications are presented in Fig. 3 (c, d). As illustrated in the SEM images, sol-gel MTMS/PPG-PEG-PPG coated FPSE membranes maintained the through pores after the sol–gel sorbent coating. The sol-gel sorbent coating on the substrate surface is uniform.

[Insert Fig. 3]

3.3. Reusability of FPSE membranes

The reusability of the FPSE membranes was assessed after eluting the analytes from the FPSE membrane with the mixture of ACN: methanol at a ratio of 1:1 and drying after each usage in the FPSE extraction procedure. The findings in Fig. 4 illustrated that the analytes can be adsorbed on the FPSE membrane for at least six adsorption/desorption cycles. It is worthwhile to note that the relative standard deviations of the analytical signals in six consecutive adsorption/desorption cycles were lower than 9%.

[Insert Fig. 4]

3.4. Optimization of the extraction procedure

In this study, impactful factors including elution solvent kind and volume, rotation and vortex span, pH, sample volume, and salt addition should be optimized to maximize the extraction efficiency of FPSE.

3.4.1. Effect of the sample matrix pH

The aqueous solution pH is an effective factor in the stability of the analytes and their extraction efficiency. In the cases of organic ionizable analytes, the extraction efficiency of the method can be increased when their molecular forms dominate. Hence, the optimization of this parameter is fundamental [41, 42]. For this aim, the pH of the solutions was adjusted at 2, 3, 4, 5, 6, 7, 8, 9, and 10 using the Britton Robinson buffer (see section 2.2). As illustrated in Fig. 5(a), the optimum analytical signals were obtained for pH = 6 and this value was selected as the optimum pH value. The pH values of real samples in this study were adjusted to 6. The pH of the aqueous phase plays a fundamental role in FPSE, as it affects not only stability of the analytes, but also charge of the adsorbent surface.

3.4.2. Selection of elution solvent

The selection of a suitable elution solvent is a very important criterion for the desorption and elution of the analytes from the surface of the FPSE membrane. To distinguish the most suitable elution solvent for this requirement, methanol, ACN, acetone, ethanol, iso-propanol, and 1:1 mixture of ACN/methanol were used in FPSE. It is apparent from Fig. 5(b) that the usage of methanol results in higher extraction efficiency compared to the other ones. Hence, it was chosen for the rest of the study.

3.4.3. Optimum volume of the aqueous sample

The sample volume adsorbed per FPSE membrane is an important parameter that should be maximized. Hence, the volume of the aqueous solution containing a constant concentration of the analytes was optimized. Fig. 5(c) illustrates that there is a gradual increase in the analytical signals as the amount of aqueous solution increased up to 40 mL, while higher volumes of the solution have no significant effect on the extraction efficiency. Therefore, the optimization steps proceeded using 40 mL of aqueous sample solutions.

3.4.4. Optimum extraction time

The rotating mixer provides vigorous mixing of samples and improves the adsorption efficiency by increasing the contact surface area between FPSE membrane and analytes. In order to evaluate the impact of contact time between the FPSE membrane and sample, mixing time was set between 0 to 40 min. As illustrated in Fig. 5(d), the analytical signals increase until 35 min, while prolonged rotating has no remarkable effect on them. Therefore, 35 min was selected to proceed with the further optimization steps.

[Insert Fig. 5]

3.4.5. Effect of salt addition

The effect of salt addition on extraction efficiency can be considered from two contradictory aspects. From a positive point of view, salt addition may facilitate the extraction of the analytes into the FPSE membrane as it can raise the polarity of the aqueous sample and therefore reduce the solubility of the analytes in this phase. From another point of view, salt addition can increase the viscosity of the aqueous sample and reduce extraction efficiency [41]. Hereby, the effect of the type and concentration of salt on the extraction was evaluated in this step. In this study, two types of salt, namely, NaCl and Na_2SO_4 with different concentrations (2.5, 5.0, 7.5, and 10.0*%*, *w*:*v*) were added to the aqueous solutions separately and the analytical signals were compared with the experiments which were done in the absence of salt (Fig. 6(a, b)). As shown in Fig. 6(a), Na_2SO_4 addition at a concentration of 5 % (*w*:*v)* can increase the analytical signals and facilitate the extraction of the analytes, while NaCl addition has no positive effect on the extraction efficiency. Considering the results, 5% (*w*:*v)* Na_2SO_4 was added into the aqueous solutions in subsequent experiments.

3.4.6. Effect of elution solvent volume

In FPSE, elution solvent volume should be high enough to desorb the analytes from the surface of the membrane and low enough to reach high enrichment factors (EFs) and low LODs. Hence, this parameter plays a critical role in the performance of the proposed extraction method. In order to optimize the volume of methanol, its volume changed in the range of 200–1500 µL. As it is shown in Fig. 6(c), the use of 500 µL methanol leads to more efficient enrichment of the analytes and

desorption of the analytes from the surface of FPSE membrane. Thus, this volume of methanol results in higher analytical signals compared to other values.

3.4.7. Desorption time

Desorption time can be decreased by vortex agitation. To examine the effect of this factor, the samples were shaken with a vortex agitator at 0 to 160 s intervals. According to Fig. 6(d), desorption of the analytes increases up to 120 s and longer times only lead to a prolonged extraction procedure without any effect on the extraction efficiency. Therefore, 120 s was selected to desorb the analytes.

[Insert Fig. 6]

3.5. Analytical figures of merit and comparison of the proposed method with previously published methods

Under the optimized conditions, the analytical figures of merit including linear range (LR), LOD, LOQ, relative standard deviation (RSD), extraction recovery (ER), and EF values were calculated to validate the proposed method. EF equals analyte concentration in the sedimented phase (C_{org}) divided by its initial concentration in the aqueous phase (C_0) (Eq. 1). In Eq. 1, C_{org} and C_0 are the concentrations of the analytes in the organic phase and aqueous sample, respectively. ER is also should be calculated from Eq. 2, where V_{org} and V_{aq} are volumes of the organic phase and aqueous solution, respectively [41].

$$EF = \frac{C_{org}}{C_{aq}} \tag{1}$$

$$ER = \frac{n_{org}}{n_{aq}} \times 100 = \frac{C_{org} \times V_{org}}{C_{aq} \times V_{aq}} \times 100 = EF \times \frac{V_{org}}{V_{aq}} \times 100 \tag{2}$$

ERs and EFs were calculated considering the peak areas obtained from the injection of the elution solvent after the FPSE procedure and direct injection of stock solutions. In the chromatographic methods, LOD is the least concentration of the analyte in the sample in which the ratio of signal height to the background noise is equal to three by considering international guidelines. Additionally, LOQ is expressed as a concentration in which the ratio of signal height to the background noise is equal to 10. To assess the linear range, a series of aqueous solutions were prepared at different concentrations and injected into the HPLC-PDA after extraction. In addition, intra- and inter-day reproducibility of the method was evaluated by analyzing the aqueous standard solutions at specific concentrations after performing several consecutive extraction methods for one day and different days, respectively.

As highlighted in Table 1, LRs of the proposed procedure for both analytes were wide and their coefficients of determination were satisfactory (≥ 0.9991). Furthermore, the values of LOD were obtained 0.96 and 2.50 μg L^{-1} for azinphos-methyl and chlorfenvinphos, respectively. Moreover, the RSDs were obtained in the ranges of 2–6% for intra– (n = 6) and 3–8% for inter–day (n = 4) precisions, respectively. Additionally, EF values were assigned as 71 and 73 for azinphos-methyl and chlorfenvinphos, respectively. Furthermore, LOQ values were obtained 3.20 and 8.33 for azinphos-methyl and chlorfenvinphos, respectively. Extraction recoveries were also obtained 89 and 91 for azinphos-methyl and chlorfenvinphos, respectively. Moreover, LODs and EFs were extended to each sample based on their dilution ratios and reported in Table 2.

[Insert Table 1]

[Insert Table 2]

LR, RSD, EF, and LOD of the proposed procedure were compared with previously proposed analytical methods in the literature. It appears from Table 3 that MTMS/PPG-PEG-PPG based FPSE-HPLC-PDA method proposed in this study results in comparable or superior results to previously proposed methods. Therefore, the proposed FPSE-HPLC-DAD method fulfills the requirements of a suitable analytical method for the analysis of azinphos-methyl and chlorfenvinphos.

[Insert Table 3]

3.6. Real samples analysis

To analyze azinphos-methyl and chlorfenvinphos residues in real samples, FPSE-HPLC-PDA method was finally applied to four fruit juice samples (apple, peach, apricot, and orange) as well as carrot juice and wastewater samples under the optimized and validated method. It is worthwhile noting that added–found method was used to evaluate the accuracy of method and matrix effect in the aforementioned samples at 30, 50, and 100 μg L^{-1} concentrations in three replicates. Additionally, to determine the relative recovery percentages, the peak areas obtained from the spiked samples at three different concentrations were compared with those obtained from deionized water at the same spiked concentration. The results, as shown in Table 4, indicate that the relative recovery percentages of the analytes in the samples are in the range of 86–97 %. Hence, the matrix effect in the above-mentioned real samples is considered insignificant for both of the target analytes. Blank samples of wastewater and carrot, apple, peach, apricot, and orange juices were also injected into HPLC-PDA and results demonstrate that real samples lack of the analytes or the concentration of these compounds are less than the LOD values of the method. Although these samples were found to be negative at the quantitative assay of the analytes considered in the present study, the applicability of the validated proposed procedure for the extraction of azinphos-

methyl and chlorfenvinphos from the matrices of the real samples was proved on extraction of these analytes from spiked samples using added-found method.

[Insert Table 4]

[Insert Fig. 7]

4. Conclusion

In this study, sol-gel MTMS/PPG-PEG-PPG coated FPSE membrane was successfully used for the reliable analysis of azinphos-methyl and chlorfenvinphos in several fruit juice samples, a carrot juice, and a wastewater sample. The proposed equilibrium-based extraction method is efficient, simple and economical, and one of the most important gains is that it offers an environmentally friendly analysis. Additionally, the proposed extraction method exploits the advantages of the substrate surface chemistry and the FPSE membrane can be reused for several adsorption/desorption cycles. Altogether, the priorities of the method are wide linear range, satisfactory precision, low LOD/LOQ values, and good relative recoveries in complex matrices of real samples for both pesticides. Therefore, the proposed FPSE-HPLC-PDA method meets the requirements of a suitable analytical method.

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Declaration of competing interest

The authors have no competing interests to declare.

Authorship statements

Halil İbrahim Ulusoy: Conceptualization, Project administration, Funding acquisition, Formal analysis, Writing–review & editing; Masoumeh Sattari Dabbagh: Investigation, Writing–original draft, Validation, Software; Marcello Locatelli: Methodology; Songül Ulusoy: Writing–review & editing; Abuzar Kabir: Writing–review & editing, Investigation; Mir Ali Farajzadeh: Writing–review & editing.

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References

[1] H. Fu, P. Tan, R. Wang, S. Li, H. Liu, Y. Yang, Z. Wu, Advances in organophosphorus pesticides pollution: Current status and challenges in ecotoxicological, sustainable agriculture, and degradation strategies, J. Hazard. Mater., 424 (2022) 127494. .

[2] F.C. Shaffo, A.C. Grodzki, A.D. Fryer, P.J. Lein, Mechanisms of organophosphorus pesticide toxicity in the context of airway hyperreactivity and asthma, Am. J. Physiol. Lung Cell. Mol. Physiol., 315 (2018) 485-501.

[3] M. Jokanović, Neurotoxic effects of organophosphorus pesticides and possible association with neurodegenerative diseases in man: A review, Toxicology, 410 (2018) 125-131. .

[4] A.A. Malekirad, M. Faghih, M. Mirabdollahi, M. Kiani, A. Fathi, M. Abdollahi, Neurocognitive, mental health, and glucose disorders in farmers exposed to organophosphorus pesticides, Arh. Hig. Rada. Toksikol., 64 (2013) 1-8.

[5] T.O. Ajiboye, P.O. Oladoye, C.A. Olanrewaju, G.O. Akinsola, Organophosphorus pesticides: Impacts, detection and removal strategies, Environ. Nanotechnol. Monit. Manag., 17 (2022) 100655.

[6] M.A. Farajzadeh, M. Sattari Dabbagh, A. Yadeghari, Deep eutectic solvent based gas-assisted dispersive liquid-phase microextraction combined with gas chromatography and flame ionization detection for the determination of some pesticide residues in fruit and vegetable samples, J. Sep. Sci., 40 (2017) 2253-2260.

[7] S. Wahab, K. Muzammil, N. Nasir, M.S. Khan, M.F. Ahmad, M. Khalid, W. Ahmad, A. Dawria, L.K.V. Reddy, A.M. Busayli, Advancement and New Trends in Analysis of Pesticide Residues in Food: A Comprehensive Review, Plants, 11 (2022) 1106.

[8] W. Ahmad, A. Al-Sibaai, A. Bashammakh, H. Alwael, M. El-Shahawi, Recent advances in dispersive liquid-liquid microextraction for pesticide analysis, TrAC, Trends Anal. Chem., 72 (2015) 181-192.

[9] N. Brito, S. Navickiene, L. Polese, E. Jardim, R. Abakerli, M. Ribeiro, Determination of pesticide residues in coconut water by liquid–liquid extraction and gas chromatography with electron-capture plus thermionic specific detection and solid-phase extraction and high-performance liquid chromatography with ultraviolet detection, J. Chromatogr. A, 957 (2002) 201-209.

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

[11] G. Amendola, P. Pelosi, R. Dommarco, Solid-phase extraction for multi-residue analysis of pesticides in honey, J. Environ. Sci. Health., Part B, 46 (2010) 24-34.

[12] P. Zhao, P.J. Alvarez, X. Li, C. Pan, Development of an analytical method for pesticide residues in berries with dispersive solid phase extraction using multiwalled carbon nanotubes and primary secondary amine sorbents, Anal. Methods, 10 (2018) 757-766.

[13] D. Yang, X. Li, D. Meng, Y. Yang, Carbon quantum dots-modified ferrofluid for dispersive solid-phase extraction of phenolic compounds in water and milk samples, J. Mol. Liq., 261 (2018) 155-161.

[14] H. Baša Česnik, Š. Velikonja Bolta, Stir bar sorptive extraction methods for determination of pesticide residues in wine and a study of storage wines from Slovenia, J. Cent. Eur. Agric., 22 (2021) 557-570.

[15] H. Ying, C. Qiue, X. Xiaoguang, W. Baoxing, X. Jicang, Y. Lei, Y. Yan, Y. Yong, Determination of pyrethroid pesticide residues in tobacco leaves and tea using stir bar sorptive extraction-thermal desorption and gas chromatography-mass spectrometry, Chin. J. Chromatogr., 25 (2007) 25-29.

[16] M. Majd, S. Nojavan, Magnetic dispersive solid-phase extraction of triazole and triazine pesticides from vegetable samples using a hydrophilic-lipophilic sorbent based on maltodextrin- and β-cyclodextrin-functionalized graphene oxide, Microchim. Acta, 188 (2021) 1-12.

[17] X. Yang, K. Qiao, Y. Ye, M. Yang, J. Li, H. Gao, S. Zhang, W. Zhou, R. Lu, Facile synthesis of multifunctional attapulgite/Fe_3O_4/polyaniline nanocomposites for magnetic dispersive solid phase extraction of benzoylurea insecticides in environmental water samples, Anal. Chim. Acta, 934 (2016) 114-121.

[18] J. Liu, C. Ji, X. Liu, X. Li, H. Wu, D. Zeng, Fe_3O_4 nanoparticles as matrix solid-phase dispersion extraction adsorbents for the analysis of thirty pesticides in vegetables by ultrahigh-performance liquid chromatography-tandem mass spectrometry, J. Chromatogr. B, 1165 (2021) 122532.

[19] L.F.S. Santos, R.A. de Jesus, J.A.S. Costa, L.G.T. Gouveia, M.E. de Mesquita, S. Navickiene, Evaluation of MCM-41 and MCM-48 mesoporous materials as sorbents in matrix solid phase dispersion method for the determination of pesticides in soursop fruit (Annona muricata), Inorg. Chem. Commun., 101 (2019) 45-51.

[20] X.C. Huang, J.K. Ma, R.X. Feng, S.L. Wei, Simultaneous determination of five organophosphorus pesticide residues in different food samples by solid-phase microextraction fibers coupled with high-performance liquid chromatography, J. Sci. Food Agric., 99 (2019) 6998-7007.

[21] E.F. Valenzuela, F.G. de Paula, A.P.C. Teixeira, H.C. Menezes, Z.L. Cardeal, A new carbon nanomaterial solid-phase microextraction to pre-concentrate and extract pesticides in environmental water, Talanta, 217 (2020) 121011.

[22] N. Casado, J. Gañán, S. Morante-Zarcero, I. Sierra, New advanced materials and sorbent-based microextraction techniques as strategies in sample preparation to improve the determination of natural toxins in food samples, Molecules, 25 (2020) 702.

[23] V. Samanidou, I. Kaltzi, A. Kabir, K.G. Furton, Simplifying sample preparation using fabric phase sorptive extraction technique for the determination of benzodiazepines in blood serum by high-performance liquid chromatography, Biomed. Chromatogr., 30 (2016) 829-836.

[24] A.G. Canlı, B. Sürücü, H.I. Ulusoy, E. Yılmaz, A. Kabir, M. Locatelli, Analytical methodology for trace determination of propoxur and fenitrothion pesticide residues by decanoic acid modified magnetic nanoparticles, Molecules, 24 (2019) 4621.

[25] H.İ. Ulusoy, K. Köseoğlu, A. Kabir, S. Ulusoy, M. Locatelli, Fabric phase sorptive extraction followed by HPLC-PDA detection for the monitoring of pirimicarb and fenitrothion pesticide residues, Microchim. Acta, 187 (2020) 1-11.

[26] M. Locatelli, K.G. Furton, A. Tartaglia, E. Sperandio, H.I. Ulusoy, A. Kabir, An FPSE-HPLC-PDA method for rapid determination of solar UV filters in human whole blood, plasma and urine, J. Chromatogr. B, 1118 (2019) 40-50.

[27] S. Gülle, H.I. Ulusoy, A. Kabir, A. Tartaglia, K.G. Furton, M. Locatelli, V.F. Samanidou, Application of a fabric phase sorptive extraction-high performance liquid chromatography-photodiode array detection method for the trace determination of methyl paraben, propyl paraben and butyl paraben in cosmetic and environmental samples, Anal. Methods, 11 (2019) 6136-6145.

[28] A. Tartaglia, A. Kabir, F. D'Ambrosio, P. Ramundo, S. Ulusoy, H.I. Ulusoy, G.M. Merone, F. Savini, C. D'Ovidio, U. De Grazia, Fast off-line FPSE-HPLC-PDA determination of six NSAIDs in saliva samples, J. Chromatogr. B, 1144 (2020) 122082.

[29] A. Kabir, R. Mesa, J. Jurmain, K.G. Furton, Fabric phase sorptive extraction explained, Separations, 4 (2017) 21.

[30] A. Kabir, V. Samanidou, Fabric phase sorptive extraction: a paradigm shift approach in analytical and bioanalytical sample preparation, Molecules, 26 (2021) 865.

[31] G. Sidiropoulou, A. Kabir, K.G. Furton, F.S. Kika, K. Fytianos, P.D. Tzanavaras, C.K. Zacharis, Combination of fabric phase sorptive extraction with UHPLC-ESI-MS/MS for the determination of adamantine analogues in human urine, Microchem. J., 176 (2022) 107250.

[32] B. Çakmak Sancar, M. Akhan, M. Öztürk, Ö. Ergün, Pesticide residues in vegetables and fruits from Istanbul by LC-MS/MS, Harran Tarım ve Gıda Bilimleri Dergisi, 26 (2022) 303-315.

[33] C. Erkmen, S. Kurbanoglu, B. Uslu, Fabrication of poly (3, 4-ethylenedioxythiophene)-iridium oxide nanocomposite based tyrosinase biosensor for the dual detection of catechol and azinphos methyl, Sensors Actuators B: Chem., 316 (2020) 128121.

[34] E.T. Özer, B. Osman, B. Parlak, An experimental design approach for the solid phase extraction of some organophosphorus pesticides from water samples with polymeric microbeads, Microchem. J., 154 (2020) 104537.

[35] A. Tartaglia, A. Kabir, F. D'Ambrosio, P. Ramundo, S. Ulusoy, H.I. Ulusoy, G.M. Merone, F. Savini, C. D'Ovidio, U. De Grazia, K.G. Furton, M. Locatelli, Fast off-line FPSE-HPLC-PDA determination of six NSAIDs in saliva samples, J. Chromatogr. B, 1144 (2020) 122082.

[36] E. Zilfidou, A. Kabir, K.G. Furton, V. Samanidou, An improved fabric phase sorptive extraction method for the determination of five selected antidepressant drug residues in human blood serum prior to high performance liquid chromatography with diode array detection, J. Chromatogr. B, 1125 (2019) 121720.

[37] A. Kabir, R. Mesa, J. Jurmain, K. Furton, Fabric phase sorptive extraction explained, Separations, 4 (2017) 21.

[38] K. Knauer, N. Homazava, M. Junghans, I. Werner, The influence of particles on bioavailability and toxicity of pesticides in surface water, Integr. Environ. Assess. Manage., 13 (2017) 585-600.

[39] P. Zawadzki, Visible Light–Driven Advanced Oxidation Processes to Remove Emerging Contaminants from Water and Wastewater: a Review, Water, Air, Soil Pollut., 233 (2022) 374.

[40] S. Sundararajan, A.B. Samui, P.S. Kulkarni, Synthesis and characterization of poly(ethylene glycol) acrylate (PEGA) copolymers for application as polymeric phase change materials (PCMs), React. Funct. Polym., 130 (2018) 43-50.

[41] M. Sattari Dabbagh, M.A. Farajzadeh, Introduction of a new procedure for the synthesis of polysulfone magnetic nanoparticles and their application in magnetic solid phase extraction for the extraction of some pesticides from fruit and vegetable juices, Microchem. J., 158 (2020) 105238.

[42] V. Doroschuk, I.Y. Matsenko, Y. Mandzyuk, O. Makukha, N. Grytsyk, Cloud point extraction combined with liquid chromatography coupled to tandem mass spectrometry for the determination of verapamil in urine, J. Anal. Chem., 74 (2019) 701-706.

[43] K. Seebunrueng, Y. Santaladchaiyakit, P. Soisungnoen, S. Srijaranai, Catanionic surfactant ambient cloud point extraction and high-performance liquid chromatography for simultaneous analysis of organophosphorus pesticide residues in water and fruit juice samples, Anal. Bioanal. Chem., 401 (2011) 1703-1712.

[44] T.T. Hu, C.M. Lu, H. Li, Z.X. Zhang, Y.H. Zhao, J. Li, Determination of Eleven organophosphorus pesticide residues in textiles by using HPLC-HRMS, Anal. Sci., 33 (2017) 1027-1032.

[45] M. Soodi, A. Garshasbi, S. Eskandari, Development a HPLC method for simultaneous determination of Azinphose methyl, Diazinon, Phosalone and Chlorpyrifos residues in fruit, J. pharm. health care sci., 4 (2012) 79-87.

[46] V. Muckoya, P. Nomngongo, J. Ngila, Determination of organophosphorus pesticides in wastewater samples using vortex-assisted dispersive liquid–liquid microextraction with liquid chromatography–mass spectrometry, Int. J. Environ. Sci. Technol., 17 (2020) 2325-2336.

[47] Z. Ghoraba, B. Aibaghi, A. Soleymanpour, Ultrasound-assisted dispersive liquid-liquid microextraction followed by ion mobility spectrometry for the simultaneous determination of bendiocarb and azinphos-ethyl in water, soil, food and beverage samples, Ecotoxicol. Environ. Saf., 165 (2018) 459-466.

[48] S. Jan, F. Waqar, S.W. Ali, M.A. Malik, B. Mohammad, M. Khan, W. Yawar, Synthesis and application of a bi-functional sorbent derived from ethylacrylate-divinylbenzene copolymer for the solid-phase extraction of pesticides from water, J. Liq. Chromatogr. Rel. Technol., 35 (2012) 700-711.

[49] L.Y. Gemechu, Analysis of multiclass pesticide residues in vegetables using microwave assisted extraction followed by high performance liquid chromatography with ultraviolet detection, Int. j. sci. res. eng. trends., 6 (2020) 2395.

[50] P. Zhao, L. Wang, L. Zhou, F. Zhang, S. Kang, C. Pan, Multi-walled carbon nanotubes as alternative reversed-dispersive solid phase extraction materials in pesticide multi-residue analysis with QuEChERS method, J. Chromatogr. A, 1225 (2012) 17-25.

[51] D.K. Singha, P. Majee, S.K. Mondal, P. Mahata, Highly Selective Aqueous Phase Detection of Azinphos-Methyl Pesticide in ppb Level Using a Cage-Connected 3D MOF, ChemistrySelect, 2 (2017) 5760-5768.

[52] T. Eskandari, A. Niazi, M.H. Fatemi, M.J. Chaichi, Determination of azinphos-methyl in environmental samples using alkaline hydrolysis combined with spectroflourimetry and response surface modelling, Int. J. Environ. Anal. Chem., 101 (2021) 2963-2974.

[53] M.A. Alhamami, J.S. Algethami, M.A. Rizk, A.M. Abbas, G.M. Khairy, A New Chemosensor Based on a Luminescent Complex for the Investigation of Some Organophosphorus Pesticides in Environmental Samples, Chemosensors, 10 (2022) 391.

Figure captions:

Figure 1. Schematic flow diagram of fabric phase sorptive extraction procedure.

Figure 2. FT-IR spectra of (a) Pristine PPG-PEG-PPG; (b) sol-gel MTMS/PPG-PEG-PPG coated FPSE membrane.

Figure 3. Scanning electron microscopy images of (a, b) uncoated Muslin, 100% cotton cellulose at 100x and 500x magnifications, respectively; (c, d) sol-gel MTMS/PPG-PEG-PPG coated FPSE membrane at 100x and 500x magnifications, respectively.

Figure 4. Reusability of FPSE membranes.

Figure 5. (a) Effect of pH. Extraction conditions: aqueous sample, 50.0 mL deionized water spiked with 500 μg L^{-1} of azinphos-methyl and chlorfenvinfos; pH, 6; rotating time in adsorption step, 40 min; vortex time in adsorption step, 120 s; kind of elution solvent, methanol; elution solvent volume, 1 mL; without salt addition. The error bars show the standard deviation of three repeated determinations. (b) Impact of elution solvent selection on desorption efficiency. Extraction conditions: aqueous solution pH was adjusted at 6. Other conditions were the same as those used in Fig. 5(a). (c) Amount of the aqueous sample. Extraction conditions: methanol was used as elution solvent. Other conditions were the same as those used in Fig. 5(b). (d) Study of sorption time. Extraction conditions: aqueous solution volume was 40 mL. Other conditions are the same as those used in Fig(c).

Figure 6. Effect of salt addition (a) Na_2SO_4 addition (b) NaCl addition. Extraction conditions: are the same as those used in Fig. 5 (d), except rotating time was 35 min. (c) Study of elution solvent volume. Extraction conditions: are the same as those used in Fig. 6(a), except 5%, *w/v* Na_2SO_4 was added into the aqueous sample. (d) Study of vortex time in desorption step. Extraction conditions: are the same as those used in Fig. 6(c), except 500 μL methanol was used as the elution solvent.

Figure 7. HPLC–PDA chromatograms of unspiked carrot juice (a), carrot juice spiked with 50 μg L^{-1} of each pesticide (b), and standard solution (3 mg L^{-1} of each pesticide in methanol) (c). The proposed procedure was implemented in (b) and (c) chromatograms while the standard solution was directly injected into the HPLC-PDA. Peaks identification: (1) azinphos-methyl, (2) chlorfenvinphos.

Conflict of Interest

The authors have no conflict of interests to declare

Authorship statements

Halil İbrahim Ulusoy: Conceptualization, Project administration, Funding acquisition, Formal analysis

Masoumeh Sattari Dabbagh: Investigation, Writing–original draft, Validation,Software

Marcello Locatelli: Methodology

Songül Ulusoy: Resources

Abuzar Kabir: Writing–review & editing, Investigation,

Mir Ali Farajzadeh: Writing–review & editing

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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683 **Highlights**

684 ➢ A polymeric-coated fabric membrane was prepared by sol-gel method.

685 ➢ The prepared membrane was used as the adsorbent in FPSE method.

686 ➢ FPSE method was followed by the analysis of target analytes with HPLC-PDA.

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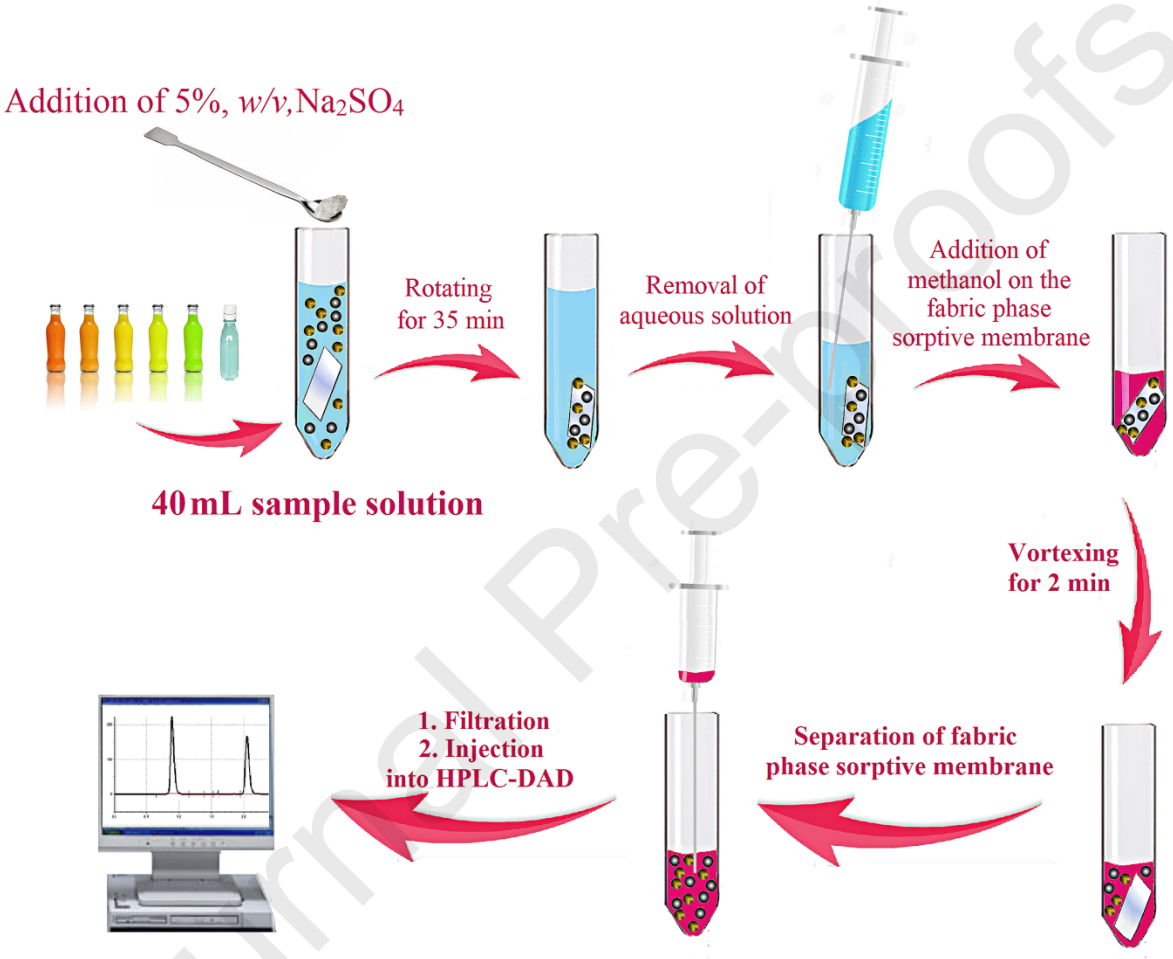

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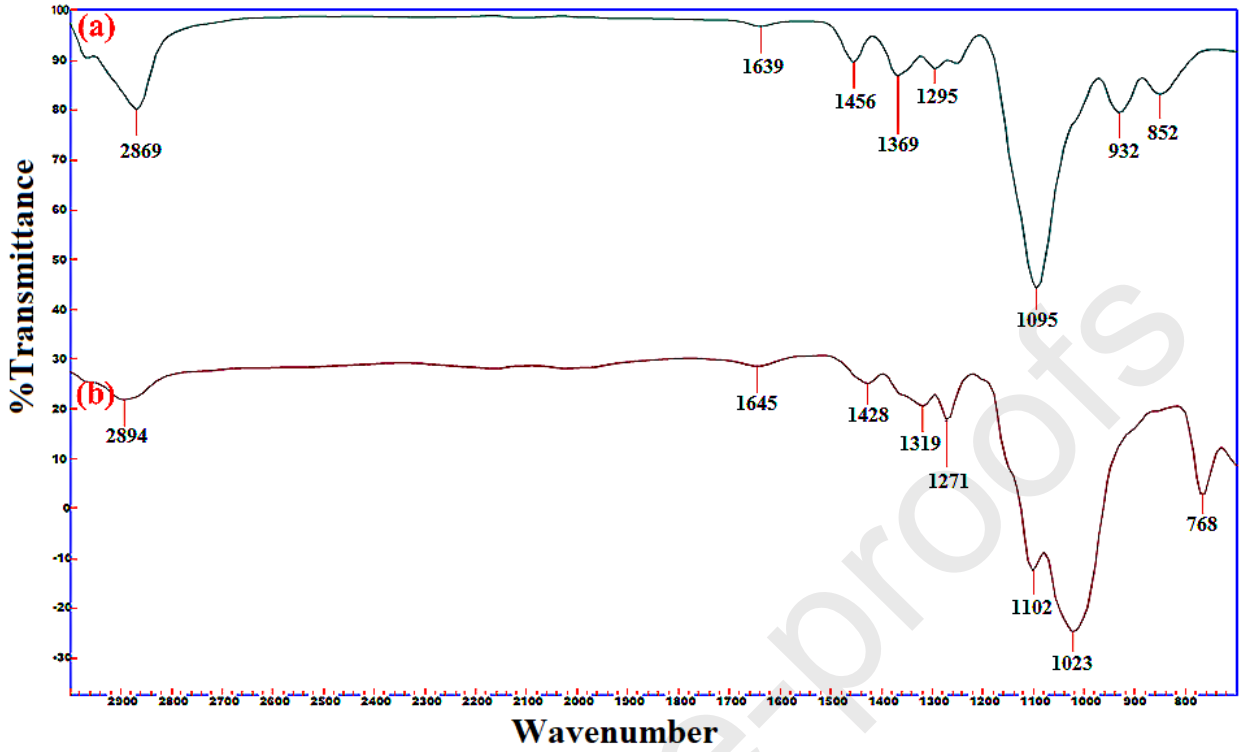

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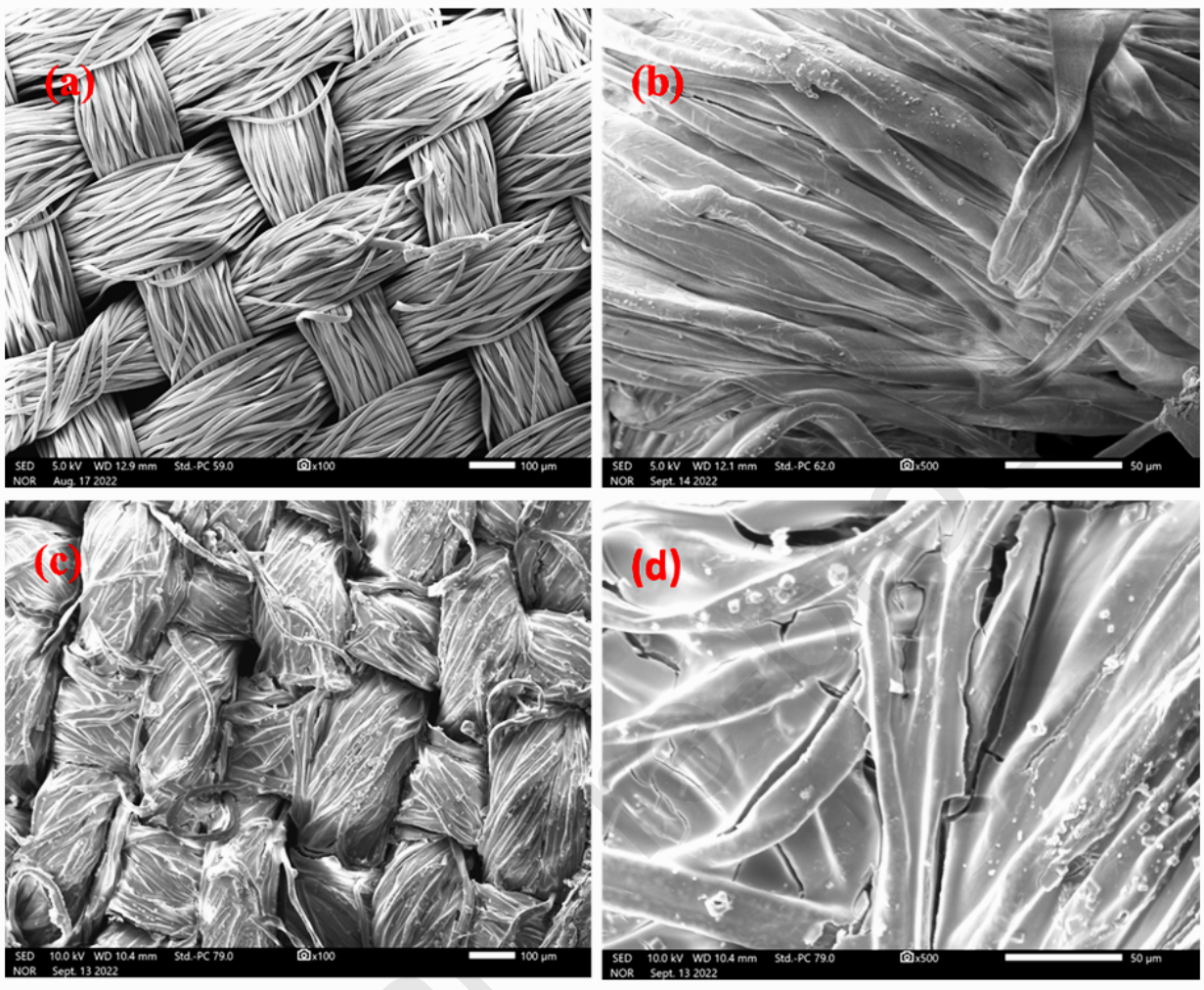
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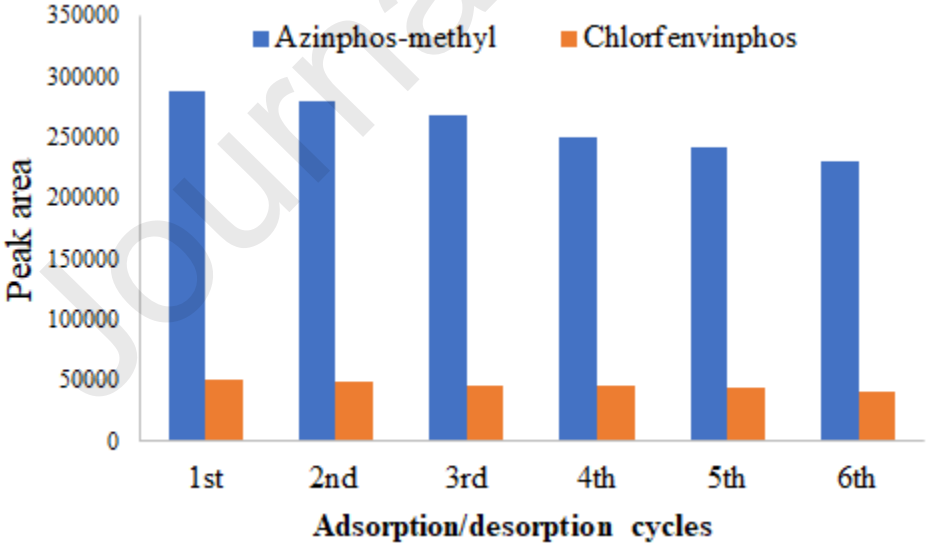
Azinphos-methyl
Chlorfenvinphos
Peak area
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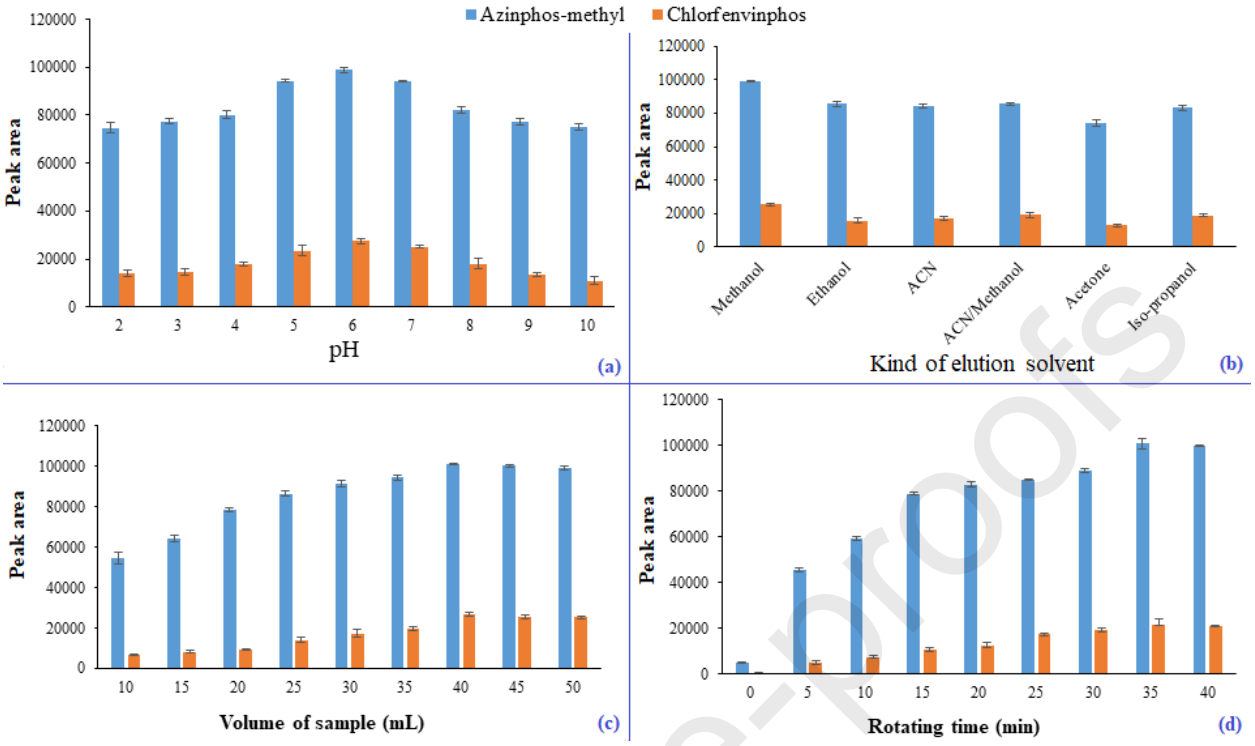

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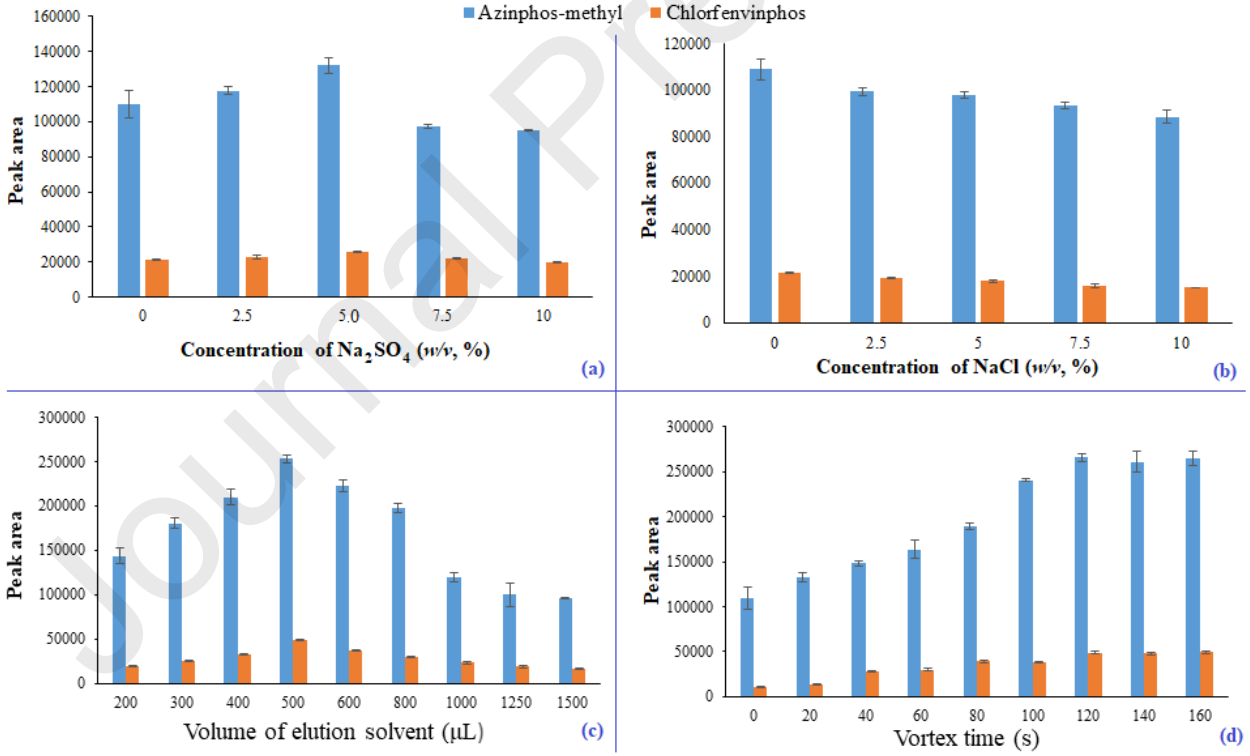

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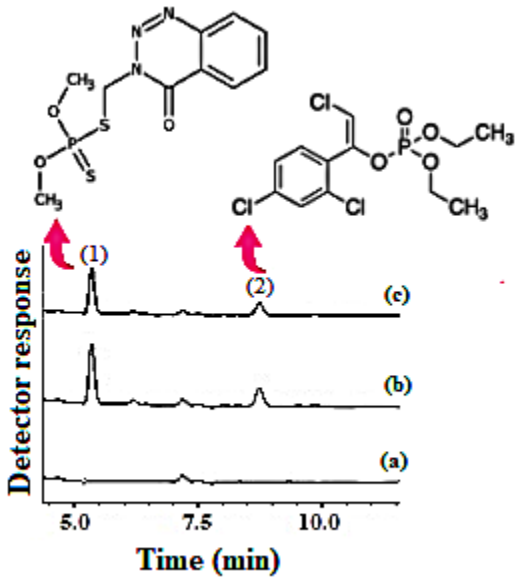

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Table 1. Summary of the figures of merit of the proposed method

Analyte	LOD [a]	LOQ [b]	LR [c]	r^2 [d]	RSD% [e]		RSD% [f]		EF ± SD
					Intra–day	Inter–day	Intra–day	Inter–day	
Azinphos-methyl (222 nm)	0.96	3.20	5-700	0.9993	4	5	2	3	71 ± 4
Chlorfenvinphos (244 nm)	2.50	8.33	10-700	0.9991	6	8	5	5	73 ± 6

a) Limit of detection (S/N=3) (µg L^{-1}).

b) Limit of quantification (S/N=10) (µg L^{-1}).

c) Linear range (µg L^{-1}).

d) Coefficient of determination.

e) Relative standard deviation for intra– (n=6) and inter–day (n=4) precisions at a concentration of 50 µg $L^{-1}$of each analyte.

f) Relative standard deviation for intra– (n=6) and inter–day (n=4) precisions at a concentration of 100 µg L^{-1} of each analyte.

g) Enrichment factor ± standard deviation (n=3).

h) Extraction recovery ± standard deviation (n = 3).

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Table 2. EFs and LODs for the extraction of the selected pesticides

Analyte	EFs of analytes in the samples based on their dilution ratios		LODs (S/N=3) (µg L^{-1}) in the samples based on their dilution ratios	
	Azinphos-methyl	Chlorfenvinphos	Azinphos-methyl	Chlorfenvinphos
Wastewater	71 ± 4	73 ± 6	0.96	2.50
Carrot	35.5 ± 2	36.5 ± 3	1.92	5.00
Apple	35.5 ± 2	36.5 ± 3	1.92	5.00
Peach	35.5 ± 2	36.5 ± 3	1.92	5.00
Apricot	35.5 ± 2	36.5 ± 3	1.92	5.00
Orange	23.6 ± 1	24.3 ± 2	2.88	7.50

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Table 3. Comparison of the FSPE- HPLC–UV method with published methods for the analysis of azinphos-methyl and chlorfenvinphos.

Analyte	Method	Sample	LR [a)]	LOD [b)]	RSD% [c)]	Ref.
Azinphos-methyl	CPE-HPLC-PDA [d)]	Water and fruit juice samples	50-5000 (μg L^{-1})	30 (μg L^{-1})	1.6	[43]
Azinphos-methyl	QuEChERS-HPLC-HRMS [e)]	Textile samples	5–500 (μg L^{-1})	5 (μg kg^{-1})	-	[44]
Azinphos-methyl	SPE-HPLC-UV [f)]	Fruit samples	50–1000 (μg L^{-1})	15 (μg L^{-1})	0.06-1.7	[45]
Azinphos-methyl	VA-DLLME–UHPLC [g)]	Wastewater samples	5-100 (μg L^{-1})	0.83 (μg L^{-1})	7.89	[46]
Azinphos-methyl	UA-DLLME-IMS [h)]	Water, Soil, Potato, Tomato, Orange juice	6-100 (μg L^{-1})	1.31 (μg L^{-1})	1.1-3.5	[47]
Chlorfenvinphos	SPE–HPLC–UV [i)]	Water	0.035–20.10 (mg L^{-1})	36.9 (μg L^{-1})	9.5	[48]
Chlorfenvinphos	MAE-HPLC-UV [j)]	Potato and pepper	-	1263	17.6	[49]

				(μg kg^{-1})		
Chlorfenvinphos	QuEChERS-r-DSPE-GC–MS [k)]	Fruit and vegetables	20-500 (μg L^{-1})	3-6 (μg kg^{-1})	-	[50]
Azinphos-methyl	Luminescence based on metal-organic frameworks	Apple	-	16 (μg L^{-1})	-	[51]
Azinphos-methyl	Alkaline hydrolysis combined with spectroflourimetry and response surface modelling	River water	5.0–1000 (μg L^{-1})	1.013 (μg L^{-1})	1.36	[52]
Chlorfenvinphos	Luminescence based on Europium (III)–(vitamin B1)$_2$	Water samples	0.95–20 (μmol L^{-1}) equal to 341.59-7191.40 (μg L^{-1})	0.31 (μmol L^{-1}) equal to 111.46 (μg L^{-1})	-	[53]
Azinphos-methyl (222 nm)	FSPE- HPLC–UV [l)]	waste water and fruit juice samples	5-700 (μg L^{-1})	0.96 (μg L^{-1})	2-4	This method
Chlorfenvinphos (244 nm)			10-700 (μg L^{-1})	2.50 (μg L^{-1})	5-6	

[j)] Linear range (μg L^{-1}).

[k)] Limit of detection (S/N=3) (μg L^{-1}).

[l)] Relative standard deviation.

702 d) Cloud point extraction-high performance liquid chromatography-photodiode array detection.

703 e) Quick, easy, cheap, effective, rugged and safe-high performance liquid chromatography-high-resolution mass
704 spectrometry.

705 f) Solid-phase extraction-high performance liquid chromatography-ultraviolet detection.

706 g) Vortex-assisted dispersive liquid–liquid microextraction-ultra-high performance liquid chromatography–tandem mass
707 spectrometry.

708 h) Ultrasound-assisted dispersive liquid-liquid microextraction-ion mobility spectrometry.

709 i) Solid-phase extraction-high performance liquid chromatography-ultraviolet detection.

710 j) Microwave assisted extraction-high performance liquid chromatography-ultraviolet detection.

711 k) Quick, easy, cheap, effective, rugged and safe-reversed-dispersive solid phase extraction-gas chromatography–mass
712 spectrometry.

713 l) Fabric phase sorptive extraction-high performance liquid chromatography-ultraviolet detection.

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Table 4. Study of matrix effect and calculation of mean relative recoveries. 30, 50, and 100 µg L^{-1} of each pesticide were spiked into deionized water and real samples.

Analytes	Waste water	Apple juice	Orange juice	Carrot juice	Peach juice	Apricot juice
	Mean relative recovery ± standard deviation (n=3)					
	All samples were spiked with each analyte at a concentration of 30 µg L^{-1}					
Azinphos-methyl	86 ± 4	93 ± 5	89 ± 5	90 ± 5	93 ± 4	89 ± 5
Chlorfenvinfos	87 ± 5	92 ± 4	89 ± 4	88 ± 4	92 ± 3	88 ± 3
	All samples were spiked with each analyte at a concentration of 50 µg L^{-1}					
Azinphos-methyl	93 ± 4	93 ± 4	92 ± 4	93 ± 3	94 ± 4	90 ± 4
Chlorfenvinfos	96 ± 3	94 ± 3	92 ± 5	92 ± 3	92 ± 2	88 ± 3
	All samples were spiked with each analyte at a concentration of 100 µg L^{-1}					
Azinphos-methyl	94 ± 3	97 ± 3	94 ± 4	95 ± 4	95 ± 3	93 ± 4
Chlorfenvinfos	96 ± 3	97 ± 3	95 ± 4	91 ± 2	95 ± 2	92 ± 3

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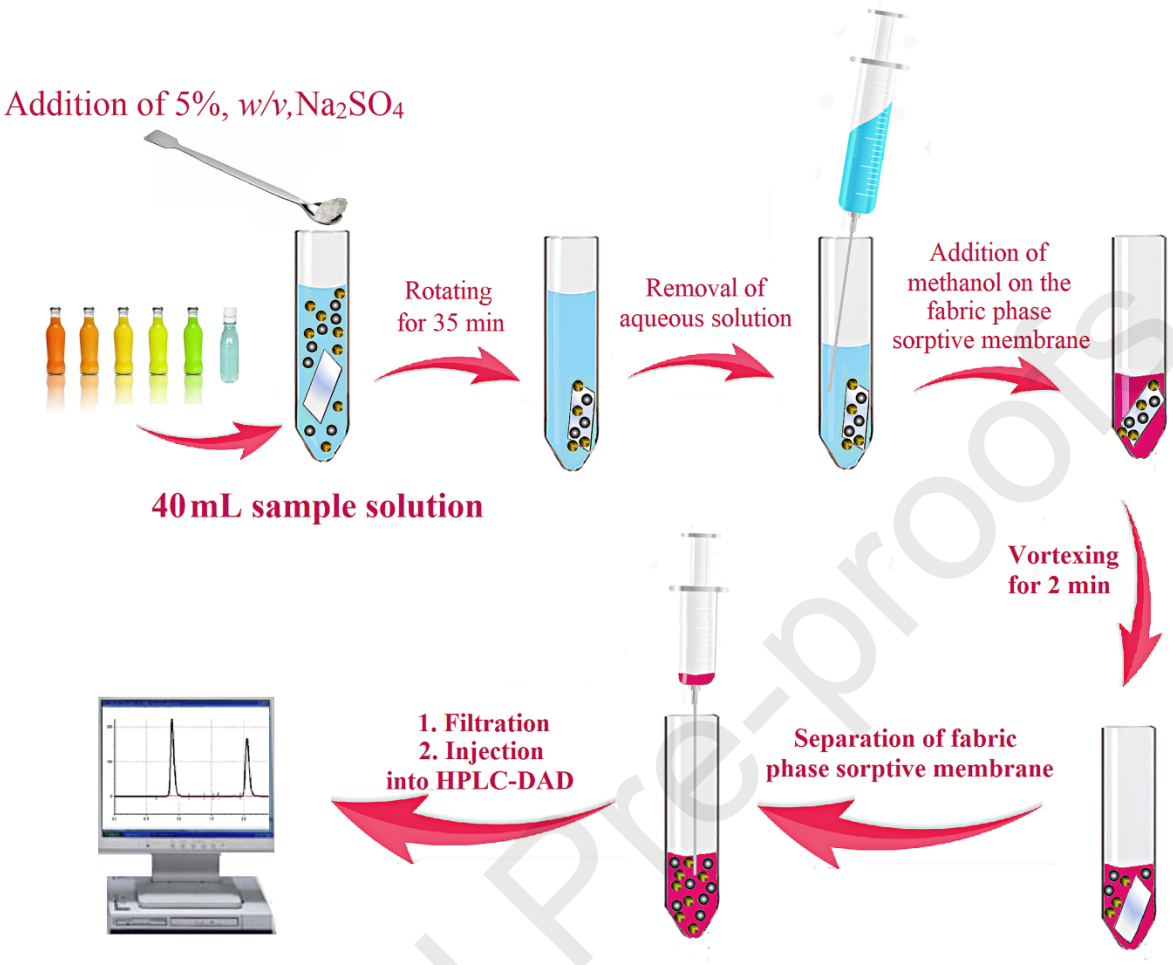

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