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Research Paper

Preparation of Ionic Liquid-Silica Nanoparticles Nanocomposite Film Coated Porous Copper Wire for Solid-Phase Microextraction of Pesticides from Tomato Samples

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Abstract:
In this study, a new solid phase micro extraction (SPME) fiber coated by sol-gel technology based on polyethylene glycol (PEG) grafted ionic liquids (ILs), and silica nanoparticles (silica NPs) on a porous copper substrate was fabricated. The as-prepared fiber (PEG-ILs-silica NPs) was then used to extract a variety of pesticides in tomato samples before prior to their gas chromatography-flame ionization detection (GC-FID). The key parameters influencing extraction efficiency containing including extraction time, stirring rate, extraction temperature, pH, ionic strength, and desorption temperature, and time were investigated and optimized. The relative standard deviations (RSDs) for single fiber repeatability ranged from 1.2 to 4.6% (n=6), and the RSDs for fiber-to-fiber reproducibility (n=6) were 3.3–6.8%, respectively. The proposed method based on the PEG-ILs-silica NPs fiber was successfully applied for the determination of targeted pesticides in tomato samples with good recoveries from 89.8 to 103.5% (RSDs=2.1-6.9).

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1. INTRODUCTION

Pesticides, which are biologically active compounds, are employed in agriculture to get rid of various plant and animal pests. These substances may, however, be hazardous to species that are not their targets (Abd Wahib et al. 2016; AL-Ahmadi 2019). The pesticide residues can accumulate in the organs of living organisms, and gradually their concentration increases due to contact with a contaminated environment. This phenomenon will be harmful not only to humans but also to all living organisms (Pathak et al. 2022). The continuous research performed in this field indicates the presence of the remains of these toxic substances in most agricultural products, and various cases of infection to different diseases and even death have been reported as a result of their consumption by humans (Andraščíková and Hrouzková 2015; Barata et al. 2004; Sarkar et al. 2021). Diverse methods like Supercritical Fluid Extraction, Accelerated Solvent Extraction, Microwave-Assisted Extraction, Matrix Solid Phase Dispersion, Ultrasonic Extraction, et Cetra. have been reported to separate and measure these substances in various tissues (Lawal et al. 2018; Liu et al. 2022; C. Yu et al. 2022). In agriculture, various plant and animal pests are eradicated using pesticides, which are biologically active compounds. These substances may, however, harm species that are not their intended targets (Aghdam et al. 2022; Kottadiyil et al. 2023; Pareja et al. 2022).

Solid-Phase Microextraction was raised for the first time in 1990 by Powlyszin and his colleagues as a sample preparation and pre-concentration method and, at the time, as a new solvent-free technique for importing the sample into the chromatography systems [16]. The basis of this extraction method is a counterbalance between the analyte in the sample solution and fiber coating, in which the analyte is desorbed inside an analytical device like gas chromatography or high-performance liquid chromatography after extraction (Abbasalizadeh et al. n.d.; Chiluwal et al. 2022). Commercial fibers used in solid-phase microextraction have a number of drawbacks, including large thickness, fragility, high cost, and absence of chemical link between stationary phase and substrate surface (which results in the fiber's poor heat stability) (Abdulra'uf et al. 2012; de Andrade et al. 2021). A large number of various fibers have been made in different ways to overcome these disadvantages. Some of these methods include the electrochemical deposition of conductive polymers, sol-gel technology, and using of ionic liquids and nanoparticles (Feng et al. 2022; F. Wang et al. 2022; Y. Wang et al. 2022; Zhang et al. 2018). The sol-gel process is a simple method for preparing the silica and silicates from the metal alkoxide precursor. Sol is the colloids suspended in liquid, and gel is a suspension that preserves its appearance. Sol-gel is a suspension of solid suspended particles in liquid that maintains its shape. In general, a sol-gel process includes simultaneous reactions of hydrolysis and condensation. In this process, the metal alkoxide is replaced by the hydroxyl group during the hydrolysis reactions. Afterward, the condensation reactions are performed, and the hydroxyl groups produce the siloxane bands. The drawbacks of commercial fibers used in solid-phase microextraction include their high thickness, fragility, high cost, and lack of a chemical bond between the stationary phase and the surface of the substrate (which results in the fiber's poor heat stability) (Aberoomand Azar et al. 2013; Manousi et al. 2022).

The fragility of the used sublayers is another significant disadvantage of commercial fibers of the solid-phase micro-extraction. The copper metal substrate was used in this project to improve the extraction increase. The lack of chemical bonds between the polymer network and the copper substrate is another disadvantage of commercial fibers, which decreases fiber efficiency. In this project, to overcome this problem, 3-Mercaptopropyltrimetoxysilane was used as an intermediate compound to create a bond between the substrate surface and polymer network (Feng et al. 2022; Hasani et al. 2022; Hayat et al. 2022; Zang et al. 2022).

In recent years, using ionic liquids in micro-extraction methods has been very well received. Ionic liquids are compounds that have been made up from the connection of a large organic cation and a relatively large anion so that their melting point is low (lower than 200°C). Ionic liquids have unrivaled physical and chemical properties to organic solvents. Commercial fibers used in solid-phase microextraction have several drawbacks, including high thickness, fragility, high cost, and absence of chemical link between stationary phase and substrate surface (which results in the fiber's poor heat stability) (Delińska et al. 2022; Feng et al. 2022; Rosa et al. 2022; Zeger et al. 2022).

In this study, to create the fiber of solid-phase micro-extraction, at the beginning, a piece of copper wire with a thickness of 24 micrometers and a length of 1.5 centimeters became porous by the electrochemical method. Then, the surface of this porous copper wire was modified by creating a covalent bond with a 3-Mercaptopropyltrimethoxysilane substance in the self-assembled monolayer (SAM) technique. Next, using the sol-gel procedure, different polymers modified with ionic liquids and silica nanoparticles were placed on the sublayer modified in the previous step. They were used to investigate and compare the extraction efficiency of pesticides. The immersion mode was used for extraction because of the low volatility of the studied pesticides. In the last step, the fiber with the highest extraction efficiency was utilized to analyze the value of the pesticides in the actual tomato sample.

2. EXPERIMENTAL

A. Apparatus and Reagents

A gas chromatography device model HP6890 equipped with a flame ionization detector (FID) with split/splitless injection valve, armed with a capillary column of CP-Cil8 CB equivalent to SPB-5, bought from the Varian company with a length of 30 meters, an inner diameter of 0.25 millimeters, and a thickness of 0.25 micrometers was used to separate and determine the amount of the pesticides. The Lab Solution software version 2.30 was used for collecting the chromatography data, and the GC Post run software version 2.3 was used for processing the chromatography data. A Hydrogen generator, a model of 1500-OPGU, made by the Shimadzu Company from Japan, was used to produce hydrogen gas. Also, helium gas with a purity of 99.999% was used. The other utilized equipment was a syringe for solid-phase micro-extraction made in the laboratory and a magnetic stirrer made by the Gerhardt Company of Germany, a scale model AEL-220, an ultrasonic bath (model Trs-420) made in the England Grant Company, a water bath, IKA heater made in Germany, an Eppendorf 5417R centrifuge machine for separating the gel from the sol-gel solution, a Double tracking v/3A30 power supply, a desktop PH meter, and the Ohmmeter made in Switzerland.

Without any purification, all ingredients were employed with analytical rigor. The pesticides used in this research are: Terbutylazine (C9H16ClN5, Mw= 229.710), Desethyl atrazine (C6H10ClN5, Mw= 187.63), Phorate (C7H17O2S3, Mw= 260.36), Parathion (C10H14NO5PS, Mw= 291), and Phosmet (C11H12NO4PS2, Mw= 317.323). These pesticides were purchased from the Sigma-Aldrich company. Other used chemical compounds include 1-butyl-4-methyl pyridinium tetrafluoroborate (BMPT), polydimethylsiloxane, (3-mercaptopropyl)Trimethoxysilane (3MPTS), polydimethylsiloxane with terminal hydroxyl groups, poly(methyl hydro siloxane), tetraethoxysilane, dichloromethane, acetonitrile, trifluoroacetic acid, sodium hydroxide, ethanol, sulfuric acid, copper(II) sulfate, and polyethylene glycol prepared from the Merck company. Tomato samples were grown in a greenhouse of one of the villages around Lahijan.

B. General Procedure

1) Preparation of the porous copper wire

First, the copper wire (with a length of 2 cm and a diameter of 200 micrometers) was washed in acetone, ethanol, and distilled water to remove its impurities. A two-electrode system including copper anode and cathode immersed in the electrolyte containing 10% solution (volume-volume) of sulfuric acid and 5% solution (volume-volume) of copper (II) sulfate was used to produce the porous copper wire. A 500 millivolts current was applied for 5 minutes in this system. Thus, a thin layer of copper sat on the copper wire, and the copper wire became porous. After the precipitation, the wire was shaken violently and kept in pure ethanol for later use.

Figure 1 shows the Electron Microscope image from the surface of the copper wire before and after creating the porosity. The wire was placed in the 0.001 molar solution of 3-mercaptopropyl Trimethoxysilane in ethanol for two hours to form the self-assembled monolayer of 3-mercaptopropyl Trimethoxysilane on the copper wire. Then, that wire was put in one molar solution of soda for one hour and the 0.01 molar solution of hydrochloric acid for half an hour, and at the end, was washed with distilled water. Thus, a self-assembled monolayer of 3-mercaptopropyl Trimethoxysilane was precipitated on the copper wire.

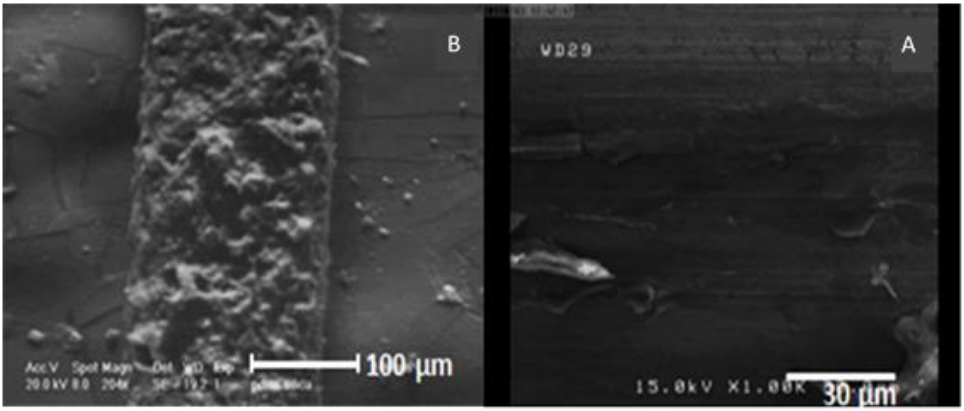

Figure 1. SEM image of copper surface A. before porosity and B. after porosity.

2) Preparation of the solid phase Microextraction fiber

Preparing the polyethylene glycol fiber was done according to the following procedure: first, methyl Trimethoxy silane (400 µL), hydroxyl-terminated poly (dimethylsiloxane) (OH-TSO) (100 mg), tetraethoxysilane (TEOS) (100 µL), Suprax polyethylene glycol (200 mg), acetone (200 µL), and 95% trifluoroacetic acid (TFA) (200 µL), (containing 5% of distilled water) were added to a microtube and were shaken intensely by a shaker. The microtube was placed in a centrifuge at the speed of 12000 rpm and at a temperature of 20 °C for 8 minutes to separate the sol from the gel. Finally, the modified copper wire was immersed for 30 minutes in the separated sol sample.

Preparing the PEG-ILs fiber (polyethylene glycol–ionic liquid) was performed in the following order: BMPT ionic liquid (50 mg) was added to acetonitrile (400 µL) and was stirred with a stirrer for one minute. Afterward, OH-TSO (180 mg), Suprax polyethylene glycol (100 µL), and TEOS (100 µL) were added to the above mixture and put in the ultrasonic device for 3 minutes. Then, polymethyl hydro siloxane (PMHS) (40 mg) and 95% TFA (containing 5% of distilled water) (300 µL) were added to the above mixture and put in a centrifuge at a speed of 12000 rpm and a temperature of 20 °C for 8 minutes. The modified copper wire was submerged in the aforementioned clear solution for 20 minutes, causing a layer of fiber to develop on the porous copper wire. As soon as the generated fiber emerged from the sol solution, it was dipped into the silica nanoparticle powder to deposit the tiny particles (Kumar et al. 2008; J. Yu et al. 2004).

3) Extraction of Pesticides by prepared Fibers

After the manufacturing process, all produced fibers were placed under the passage of helium gas at 280 °C for an hour. For the sample extraction, 300 grams of the tomatoes prepared in the greenhouse were crushed and homogenized with liquid nitrogen and got to the volume with distilled water so that in the spiking stage of pesticides, the pesticides get to all tomato samples equally. Tomato samples without pesticides were crushed, homogenized, and diluted with 500 mL of distilled water. For preparing the tomato solution of the specific values of pesticides, 50 mL of tomato solution with appropriate amounts of standard solutions of the pesticides (each pesticide with a concentration of 100 ppm was poured into a 100 mL flask and brought to volume with distilled water) were daily mixed in a 100 mL flask and brought to volume with double-distilled water and were homogenized in the ultrasonic bath for 30 minutes. 10 mL of the above uniform mixture was transferred to the falcon tube and centrifuged at 8000 rpm for 10 minutes. 10 mL of the supernatant solution in the test tube was transferred to a glass container. The syringe of solid-phase micro-extraction with hand-made fibers was used to extract the pesticides. The needle tip passed through the plastic layer of the glass cover, the fiber was put in the solution, and the direct extraction of pesticides was performed. Then, the fiber was pulled into the syringe, and the syringe was injected into the GC device.

3. RESULTS AND DISCUSSION

A. *Preparation of the PEG-ILs-silica NPs Fiber*

First, the electrochemical deposition method was used to prepare the porous copper wire. The electro-purification method is used widely for purifying (99.8 % <) several metals such as copper. The higher the applied voltage is, the more the nucleation rate will be towards the crystal growth rate. Hence, a finer precipitate will be formed, and its surface area will be greater. On the other hand, the higher the applied voltage is, the adhesion of the sediment formed on the wire will reduce. Therefore, an optimal voltage should be used, of which 500 mV was chosen in this work. It is obvious that the longer the duration of applying the voltage is, the thickness of the formed layer will be higher. In this study, to ensure that a continuous layer has been formed on the entire surface of the wire, the desired voltage was applied for 5 minutes (Galán-Cano et al. 2013; Zarzycki 1997).

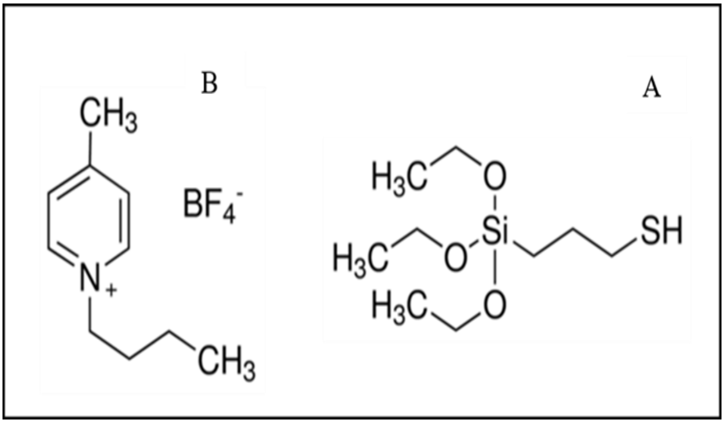

Figure 2. A. Structure of 3- mercaptopropyl trimethoxysilane (3MPTS). B. Structure of ionic liquid 1-butyl-4-methyl pyridinium tetrafluoroborate (BMPT).

In the natural state, the sol-gel materials don't tend to the metal surface. In other words, the adhesion of dielectric materials such as glass or sol-gel on the metals is very low, more physical, and too weak. Creating a firm and stable bond between metal and dielectric materials (such as glass and ceramic) is very important due to the wide range of applications, such as preparing the modified electrodes and producing the different optical components. In this method, an organic substance with two functional groups called (3-mercaptopropyl) Trimethoxysilane was used to create a chemical bond between the metal surface and the polymer network obtained from sol-gel. The structure of the 3MPTS is shown in figure 2-A.

In this work, initially, a 0.001 molar solution of 3MPTS was prepared in pure ethanol. Then, the copper wire washed with acetone, ethanol, and water was placed in the 3MPTS solution for two hours. As it turns out from the chemical formula of 3-mercaptopropyl Trimethoxysilane, this material has two functional groups: alkoxy and mercapto (with-SH moiety). During this period, the mercapto group, which has free electron pairs, established a covalent bond with the empty orbitals of copper and created a chemical bond between 3MPTS and the surface of the copper wire. Next, the above compound was placed in soda. This way, the other end of the 3MPTS compound, which has an alkoxy group, was hydrolyzed and obtained a Si-O- group. Finally, the hydrolysis was completed by putting it in the hydrochloric acid, and the Si-OH group was gained. This action led to the establishment of a chemical bond between the Si-OH groups in the 3MPTS structure and the Si-OH groups in the polymer network. Thus, the polymer network resulting from the sol-gel chemistry was attached to the surface of the porous copper wire by forming silanol bonds (Si-O-Si).

The initiators with more polarity can be used in producing them to increase the absorbent efficiency and extract pesticides with more water stability. Polyethylene glycol is one of these initiators. Polyethylene glycol increases the polarity and surface area of the absorbent by having hydroxyl groups (-OH) in its structure. In addition, hydroxyl groups cause the formation of more chemical bonds with initiators of methyl Trimethoxysilane (MTMS), tetraethoxysilane (TEOS), and hydroxyl-terminated polydimethylsiloxane (OH-TSO). Therefore, in the continuation of this research, a polyethylene glycol initiator was used in making the fiber to increase the extraction efficiency. Otherwise, using ionic liquids is one of the ways to enhance the extraction efficiency in solid-phase micro-extraction. Figure 2 shows the structure of the ionic liquid used in this work. The organic-inorganic structural nature of the ionic liquid caused increasing analyte extraction and raised the surface area of the absorbent. In BMPT-polyethylene glycol fiber, the polar nature of the polyethylene glycol absorbent increased the extraction efficiency by adding an ionic liquid. Some BMPT ionic liquid was poured into the acetonitrile solvent and dissolved with a stirrer to provide this absorbent. Next, hydroxyl-terminated polydimethylsiloxane (OH-TSO), polyethylene glycol, and tetraethoxysilane initiators were used to form and grow the polymer network. These initiators have alkoxy and hydroxyl groups and create a polymer network using hydrolysis and condensation steps. In the end, a trifluoroacetic catalyst was added to accelerate the polymerization reaction. Also, a deactivator was used to terminate the polymerization. After centrifugation, the clear sol solution was separated from the gel, and a porous copper wire was placed inside it. Finally, the prepared fiber was modified with silica nanoparticles. For adding silica nanoparticles to the prepared fibers, the produced fiber was dipped into the silica nanoparticles after placing the polymer layer on the modified wire by the sol-gel method. The number of these immersions is very significant for adding nanoparticles because, concerning the thin inner diameter of the solid-phase micro-extraction syringe, the repetition of this process thickens the layer of nanoparticles and causes removing the fiber from the substrate when working with the syringe. Figure 3 shows the electron microscope image from the absorbent surface of the polyethylene glycol-ionic liquid-silica nanoparticles.

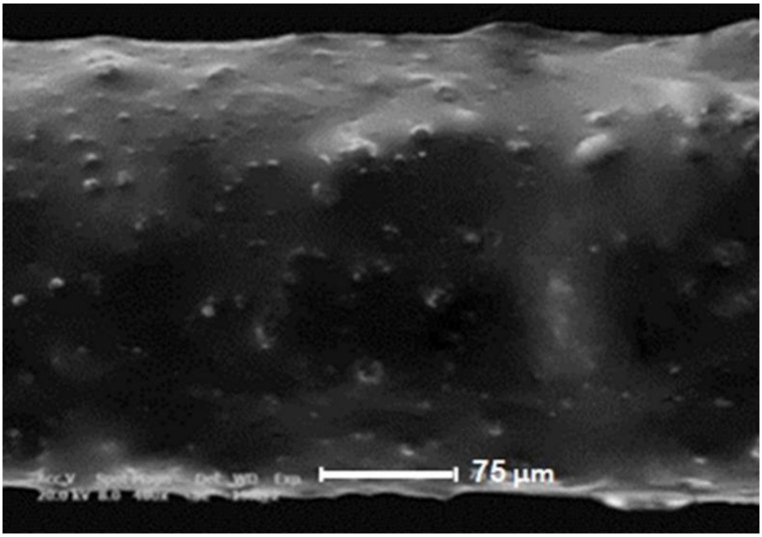

Figure 3. Image of SEM OF fiber Polyethylene glycol-ionic liquid extraction modified with silica nanoparticles.

The performance of different fibers prepared for the extraction of target pesticides (with a concentration of 500 ng/mL) was compared to achieve the highest extraction efficiency and choose the appropriate fiber. According to the results in the table I, which indicates the recovery percentage for different types of the mentioned fibers, the PEG-Ils-silica NPs fiber had the highest extraction efficiency of the pesticides compared to other fibrous tissues. Subsequently, it was used to separate and analyze the number of pesticides in the tomato sample.

Table I

Comparison of different sorbents prepared by sol-gel method to select the appropriate fiber for extraction of pesticides.

Fiber type	Desethyl-atrazine	Phosmet	Terbuthylazine	Phorate	Parathion
PEG-ILs	92.1	94.4	95.8	86.6	94.8
PEG	91.0	86.8	81.8	76.8	84.4
PEG-ILs-Silica NPs	100.0	92.4	93.2	98.0	95.7

B.Optimization of extraction conditions

The 300 grams of tomatoes were crushed and homogenized with liquid nitrogen and got to the volume with distilled water so that in the pesticide spiking phase, the pesticide would reach all tomato samples equally. Next, the mixture is stirred and stored in the refrigerator. This mixture should be agitated every time before use.

Stock standard solutions of pesticides with a concentration of 10 ppm were made with methanol solvent and kept in a refrigerator. For preparing tomato solution containing specific amounts of pesticides, 50 mL of chopped and homogenized tomato solution was mixed with suitable values of standard solutions of pesticides in a 100 mL flask and was brought to the volume by double distilled water and became uniform in an ultrasonic bath for 30 minutes. 10 mL of the above-uniformed mixture was transferred to a falcon tube and centrifuged at 8000 rpm for 10 minutes. Some supernatant solution in the test tube was transferred to a glass vial, and the manufactured fibers were placed inside it for 45 minutes at a temperature of 25 °C. Then, mentioned fibers were removed and injected into the GC machine with a special SPME syringe. The technique of comparison of the recovery percentage for one of the studied pesticides in the chromatogram obtained from the direct injection of fiber made by a special syringe of solid-phase micro-extraction into the GC device was used to achieve optimum conditions in separation and final measurement of pesticides value.

1) Effect of extraction temperature

Temperature is one of the principal parameters which plays a significant role in extraction efficiency. The extraction temperature has two different effects. On the one hand, increasing the temperature increases the emission coefficient of the analyte, but since the absorption phenomenon in the stationary phase is an exothermic process in most cases, increasing the temperature decreases the distribution constant of the analyte and causes reducing the extraction efficiency. In this research, to investigate the temperature effect on extraction efficiency, the temperature was changed from 10 to 50 °C in increments of ten. Figure 4 shows the chart resulting from a comparison of the recovery percentage of the chromatogram obtained from the extraction of pesticides to find an optimum extraction temperature. As depicted in this figure, for most species, the extraction efficiency increases with increasing temperature, but increasing the temperature beyond a specified limit causes decreasing the extraction efficiency. According to figure 4, the best temperature for extracting pesticides from the sample solution was chosen at 30 °C. The higher the analyte distribution constant between the sample matrix and the absorbent, the more analyte is absorbed in the absorbent phase, and the extraction efficiency increases (Merkle et al. 2015; Ratnaningsih et al. 2022).

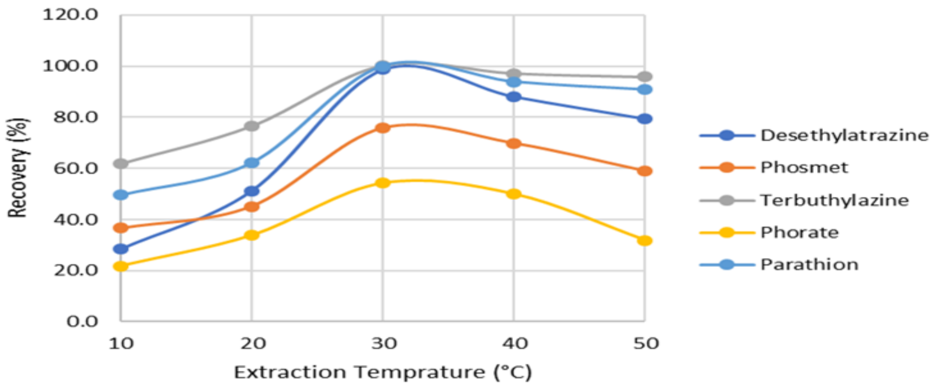

Figure 4. The effect of temperature on pesticides extraction to achieve optimal temperature using fiber PEG-IL-Silica NPs.eTh: (Pesticide Conc.; 500 PPb, Extraction Time; 30 min, NaCl Conc.; 0, pH;7.0, Extraction Stirring Speed; 200rpm, Desorption Temperature; 200 °C, Desorption Time; 3 min.).

2) Effect of the extraction time

In the solid-phase micro-extraction method, achieving the equilibrium conditions is critical in the extraction process. In the equilibrium state, the extractive system has a steady state condition, and mass changes do not affect the results (Figure 5). As seen in figure 5, the highest increase in extraction efficiency after enough extraction time was related to the Desethylatrazine pesticide, and the lowest efficiency increase was obtained for the Terbutylazine pesticide, which is probably due to the difference in their water solubility and different relative polarity. With increasing time, the extraction rate increased, and after 45 minutes, the equilibrium state was gained for all species. Therefore, 45 minutes was chosen as the required time to reach equilibrium.

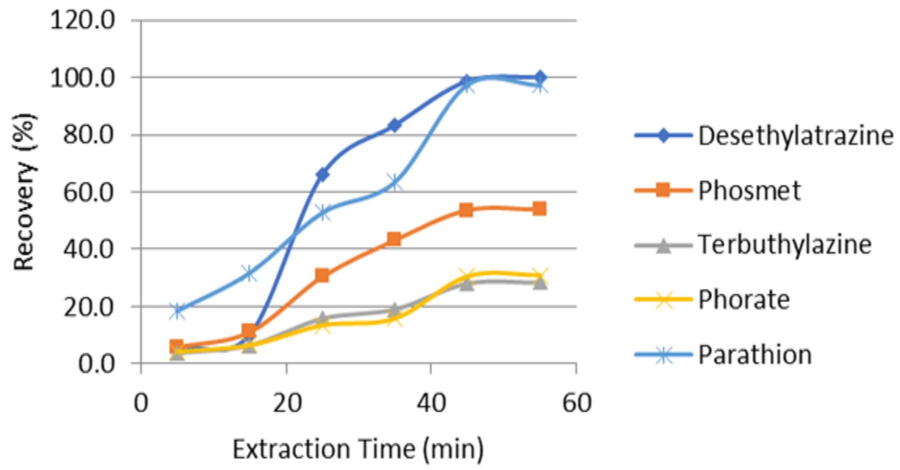

Figure 5. investigation of the amount of analyte extraction using PEG-IL-Silica NPs during different times. (Pesticide Conc.; 500 PPb, Extraction Temperature; 30 °C, NaCl Conc.; 0, pH;7.0, Extraction Stirring Speed; 200rpm, Desorption Temperature; 200 °C, Desorption Time; 3 min.).

3) Effect of ionic strength of the solution

Salting can increase or decrease the extraction rate. Adding salt or buffer increases the ionic strength of the solution. This phenomenon reduces the solubility of volatile organic compounds in water and increases the partition coefficient of the analyte several times (Kouchakinejad et al. 2022; Morcillo Pérez 2022). Usually, sodium chloride, potassium bicarbonate, and ammonium sulfate are used for this purpose. Although it should be noted that in the direct solid-phase micro-extraction, adding the salt may damage the fiber coating during extraction, while adding the salt in the headspace does not disturb the fiber (Delińska et al. 2022; Najarzadekan et al. 2022). The modified copper wire was submerged in the aforementioned clear solution for 20 minutes, causing a layer of fiber to develop on the porous copper wire. As soon as the generated fiber emerged from the sol solution, it was dipped into the silica nanoparticle powder to deposit the tiny particles (Alves et al. 2006; Chai and Tan 2008). As shown in figure 6, the impact degree of the ionic strength of the environment on the extraction efficiency of various pesticides is different, such that after the concentration of 15% salt, the extraction of Terbutylazine, Phorate, and Parathion increased when the extraction efficiency of Phosmet and Desethylatrazine did not increase significantly. This event is probably due to the difference in polarity and physicochemical properties of pesticides. Therefore, the concentration of 15% salt was selected as the optimum value at this stage.

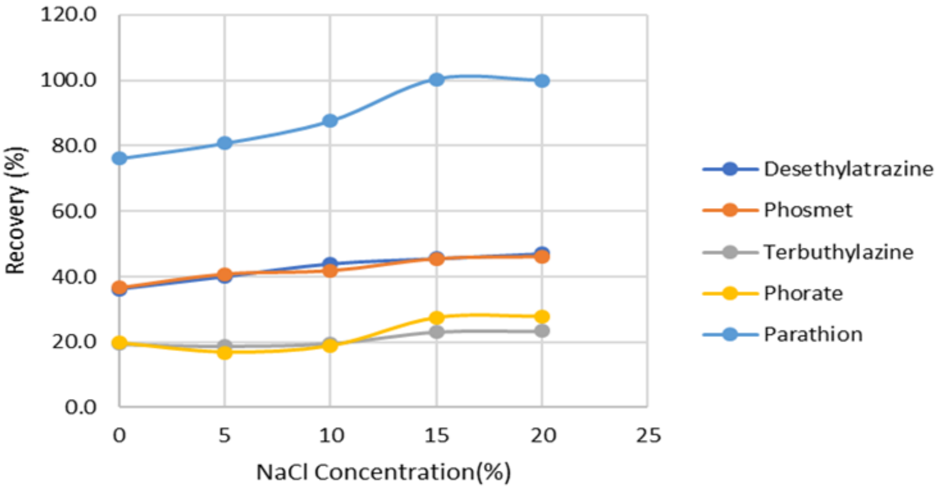

Figure 6. The effect of salt concentration on content of extracted pesticides using fiber PEG-IL-Silica NPs (Pesticide Conc.; 500 PPb, Extraction Temperature; 30 °C, Extraction Time; 30 min, pH;7.0, Extraction Stirring Speed; 200rpm, Desorption Temperature; 200 °C, Desorption Time; 3 min.).

4) Effect of the pH solution

The pH must be adjusted when the analytes are ionic, acidic, alkaline, or compounds whose formation or decomposition are affected by the pH of the environment. The nature of the analyzed chemical species may change at different pHs. Then, to investigate the effect of pH on the extraction rate of the studied pesticides, the pH of the environment was altered between 2 and 12 by adding hydrochloric acid or sodium hydroxide. The diagram obtained from the extraction of pesticides at different pHs is shown in figure 7. As can be seen, some pesticides like Terbutylazine, Desethylatrazine, and Parathion showed a very noticeable drop in recovery percentage at basic pHs. Although, Phosmet and Phorate pesticides had far fewer losses in recovery percentage during the pH increase from the neutral state. Therefore, pH = 7 was chosen as the optimum pH.

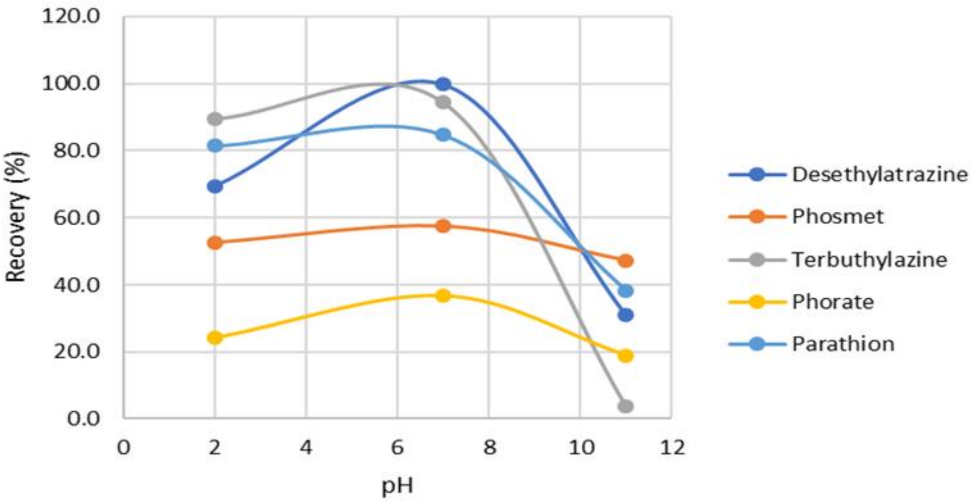

Figure 7. The effect of pH on the extraction efficiency of fiber PEG-IL-Silica NPs. (Pesticide Conc.; 500 PPb, Extraction Temperature; 30 °C, Extraction Time; 30 min, NaCl Conc.; 15%, Extraction Stirring Speed; 200rpm, Desorption Temperature; 200 °C, Desorption Time; 3 min.).

5) Effect of stirring speed

The solution is stirred in the solid-phase micro-extraction method to hasten the mass transfer from the solution mass to the fiber and shorten the extraction time. The speed of the agitation was varied from 100 to 800 rpm with intervals of 100 rpm in order to examine the impact of agitation on the extraction effectiveness of the manufactured fibers and hasten equilibrium. By increasing the stirring speed of the solution to more than 400 rpm, no significant change was observed in the increase of the extraction efficiency, and the changes were almost constant. Therefore, the speed of 400 rpm was selected to achieve the equilibrium between the solution containing pesticides and the fiber absorbent surface as quickly as possible.

6) Effect of temperature and time of desorption

The pesticide molecules are absorbed into the fiber structure using the fiber to extract the analyte in the sample container. The desorption process should be performed by a repeatable approach to measure the amount of these pesticides and calculate the extraction efficiency. In this study, fiber was directly imported into the injection chamber of the GC apparatus using a specialized syringe for solid-phase micro-extraction. Additionally, the solid-phase micro-extraction fiber's retention period and injection chamber temperature were both tuned. Analyte molecules are desorbed during desorption, after which they enter the gas space of the injection valve. As the temperature rises, so does the rate at which absorbed molecules are released and diffused in the gas environment surrounding the injection point. The process has the effect of raising the corresponding recovery percentage. As a result, the vapor pressure and diffusion rate of the absorbed compound have a big impact on the desorption process (Langore and Nikumbh 2022; Najarzadekan et al. 2022; X. Wang et al. 2022).

The results of figure 8 showed that increasing the temperature from 150 °C increased the amount of desorption, and the recovery percentage reached its maximum value at 250 °C. For all of the pesticides under study, the enhanced rate of recovery % was essentially the same. Although parathion with the lowest vapor pressure experienced the lowest increase in recovery %, desethylatrazine with the highest vapor pressure experienced the largest increase in recovery percentage. The recovery % fell as the injection chamber temperature was raised further to 300 °C. The outcomes of the experiments for the desorption period showed that as time went on, the compound recovery percentage first went up and then stayed constant. A desorption time of four minutes was deemed appropriate for carrying out the correct desorption procedure based on the percent of recoveries discovered from the data.

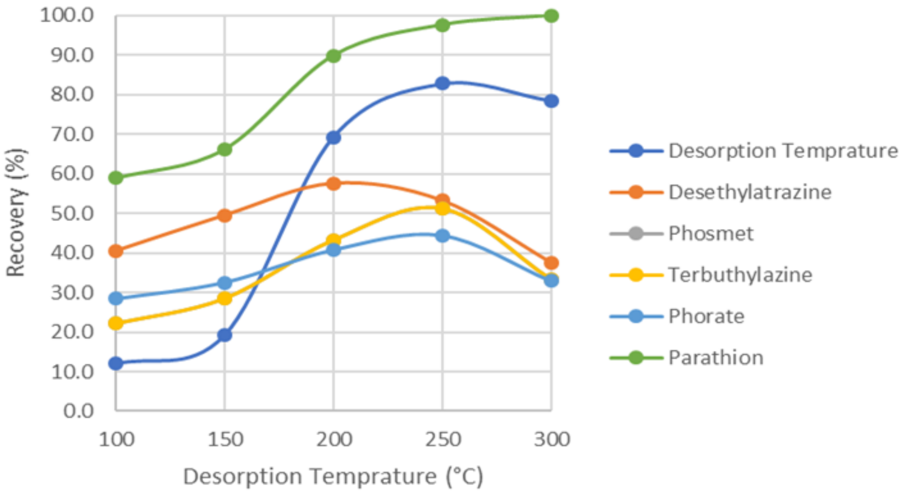

Figure 8. The effect of desorption temperature on the efficiency of PEG-IL-Silica NPs fiber extraction using the peak area of extraction chromatogram of pesticides by PEG-IL-Silica NPs fiber. (Pesticide Conc.; 500 PPb, Extraction Temperature; 30 °C, Extraction Time; 30 min, NaCl Conc.; 15%, pH;7.0, Extraction Stirring Speed; 200rpm, Desorption Time; 3 min.).

C.Method validation

According to the results obtained from the optimization stage, the optimum conditions for extracting pesticides are as follows an extraction temperature of 30 °C, extraction time of 45 minutes, a salt concentration of 15%, a stirring speed of 400 rpm, pH=7.0, desorption temperature of 250 °C, and desorption time of 4 minutes. To validate the exhibited method, specific concentrations (50, 100, 200, and 500 ppb) of each of the pesticides were spiked into the tomato sample as the final density of each of them was placed between 5 to 1000 ng/mL. To achieve the linear range of any pesticide, the extraction stages (under ideal conditions) and measurement were carried out on all samples. Drawing the height of the peaks against the analyte concentration produced calibration curves. The merit figures were calculated based on the obtained results and have been shown in Table II. Detection and quantitative limits of the method were acquired based on the best signal-to-noise ratio. A suitable linear range was observed for all pesticides in the region of 1000-0.6 ng mL-1 with good coefficients of determination (R2). Also, the method's repeatability (for one fiber) was examined at a concentration of 500 ng/mL for each pesticide with five repeated measurements and was obtained between 1.2 and 4.6%. The reproducibility of the method (fiber to fiber) was also evaluated based on the relative standard deviation of the areas under the peak obtained from repeated measurements (n= 6) with six fibers made in the same way, that its values varied between 3.3% and 6.8%.

Table II
Analysis parameters of pesticide compounds measurement in tomato samples.

Pesticide	(RSD[a]%) (n=6)		$(R^2)^b$	L.R[c] (ng mL^{-1})	D.L[d] (ng mL^{-1})	LOQ (ng mL^{-1})
	A fiber	Fiber to fiber				
Desethyl-atrazine	1.2	4.4	0.989	6-1000.0	2.0	6.0
Phosmet	2.5	5.6	0.998	15-1000.0	5.0	15.0
Terbuthylazine	4.6	2.1	0.997	27-1000.0	9.0	27.0
Phorate	2.3	3.5	0.995	12-1000.0	4.0	12.0
Parathion	3.8	6.8	0.996	24-1000.0	8.0	24.0

[a] Relative standard deviation, [b] Coefficient of determination, [c] Linear range, [d] Detection limit

D. Real sample analysis

Two types of cultivated tomatoes (tomatoes with and without pesticide) were prepared from the desired greenhouse, and the amount of pesticide in them was measured to check the applicability of the presented method. The results are shown in Table III. As can be seen, no residue of any toxins was found in the tomato samples. All specimens were spiked with the standard solution of pesticides at two concentrations of 100 and 500 ng/mL to determine the accuracy of the process. Then, the percent recovery values were obtained for three repetitions and summarized in table III. The results indicated that the percentage of recoveries was in the range of 89.8 to 103.5%, with a relative standard deviation between 2.1 and 6.5%.

Table III
Pesticide residues in tomato samples.

Pesticide	Conc. (ng mL^{-1})	Tomato 1		Tomato 2	
		Detected (ng mL^{-1})	Recovery (%) (RSD%)	Detected (ng mL^{-1})	Recovery (%) (RSD%)
Phosmet	0.0	_	_	_	_
	100.0	92.4	92.4 (3.8)	97.3	97.3 (4.3)
	500.0	467.8	93.6 (4.6)	449.1	89.8 (3.9)
Parathion	0.0	_	_	_	_
	100.0	95.7	95.7 (2.1)	101.4	101.4 (4.4)
	500.0	477.3	95.5 (3.3)	453.3	90.7 (5.6)
Phorate	0.0	_	_	_	_
	100.0	98.0	98.0 (5.4)	103.5	103.5 (3.7)
	500.0	503.1	100.6 (4.1)	472.9	94.6 (6.5)
Desethyl-atrazine	0.0	_	_	_	_
	100.0	102.5	102.5 (5.2)	90.2	90.2 (3.1)
	500.0	488.9	97.8 (3.6)	491.6	98.3 (4.8)
Terbuthylazine	0.0	_	_	_	_
	100.0	93.2	93.2 (6.2)	99.5	99.5 (2.3)
	500.0	510.6	102.1 (2.7)	482.7	96.5 (5.5)

A chromatogram of tomato sample analysis before and after adding pesticides at a concentration of 500 ng mL^{-1} is shown in Figure 9.

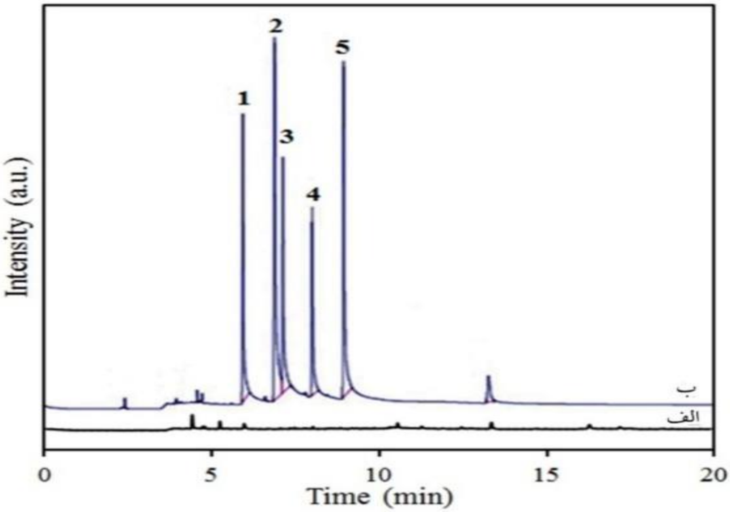

Figure 9. Chromatogram of tomato analysis (a) not spiked. B: spiked at a concentration of 500 ngL-1 of pesticide standards. The numbers are respectively: 1.Desethyl-atrazine; 2. Phosmet;3. Terbuthylazine; 4. Phorate; 5. Parathion

4. CONCLUSION

In this study, a new solid-phase micro-extraction fiber was made using sol-gel technology based on the ionic liquids on a porous copper substrate by silica nanoparticles. Various effective parameters in the extraction process of the pesticides from tomato solution containing these analytes, such as temperature and time of extraction, stirring speed of the mixture, pH, ionic strength of the environment, temperature, and time of desorption, were optimized. The extraction of pesticides from the tomato samples using the manufactured fibers showed that the PEG-Ils-silica NPs fiber had the highest efficiency in the extraction and measurement of pesticides, which was due to the similarity of the polar and absorbent nature of the fiber with the polar conformation of the studied pesticides. The new fiber coating obtained in this research has higher thermal stability than commercial fibers and is not brittle. Also, it has a larger surface area and higher extraction efficiency than commercial fibers. Using the porous copper wire increased the adhesion of the substrate surface to the polymer coating. Consequently, it caused increasing the durability and created a stronger chemical bond between the metal surface and the sol-gel network. The obtained results proved that the fiber prepared with the coating of ionic liquid and silica nanoparticles is a proper absorbent for extracting pesticides from complicated samples and can be used commercially for the conventional tracking of pesticide residues in food samples (in the quality control section).

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