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Original Article

Synthesis of MOF-5 Modified Bi_2WO_6 Polyoxometalate Accommodated on the Pores of Hollow Fiber for HF-SPME of Acetamiprid, Abamectin and Diazinon and their Determination by High Performance Liquid Chromatography-Ultraviolet

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ABSTRACT

In this study, metal organic framework-5/ Bi_2WO_6 (MOF-5/Bi_2WO_6) composite was synthesized for using in hollow fiber solid phase microextraction (HF-SPME) for separating acetamiprid, abamectin, and diazinon as the model compounds. To use the prepared adsorbent in the HF-SPME configuration, propylene hollow fiber was soaked in the methanolic mixture of adsorbent for accommodating the sorbent inside the pores of hollow fiber. In the next step, various parameters were optimized. Under optimal condition, the linear ranges for measuring acetamiprid, abamectin and diazinon were 0.2-100 µg L^{-1}, 0.2-100 µg L^{-1}, and 0.5-200 µg L^{-1}, respectively. The coefficients of determination (R^2) were 0.9961 to 0.9982. The limits of detection (LODs) of the method for acetamiprid, abamectin, and diazinon were 0.06, 0.05, and 0.14 µg L^{-1}, respectively. Moreover, the enrichment factors (EFs) were 64, 66, and 62 for acetamiprid, abamectin, and diazinon, respectively. In addition, the absolute recoveries (ARs%) were in the range of 62-64%. Relative standard deviation values (RSD%) for the concentration of 2.0 µg L^{-1}, 10 µg L^{-1}, and 100 µg L^{-1} of acetamiprid were between 1.1% and 4.7%, for abamectin between 1.1% and 4.5% and for diazinon between 1.7% and 3.0%. Finally, the proposed method was used to determine acetamiprid, abamectin and diazinon in orange, quince, pomegranate, and agricultural water. The results showed that the percentage of relative recovery of these toxins in the real samples studied was between 89 and 102.

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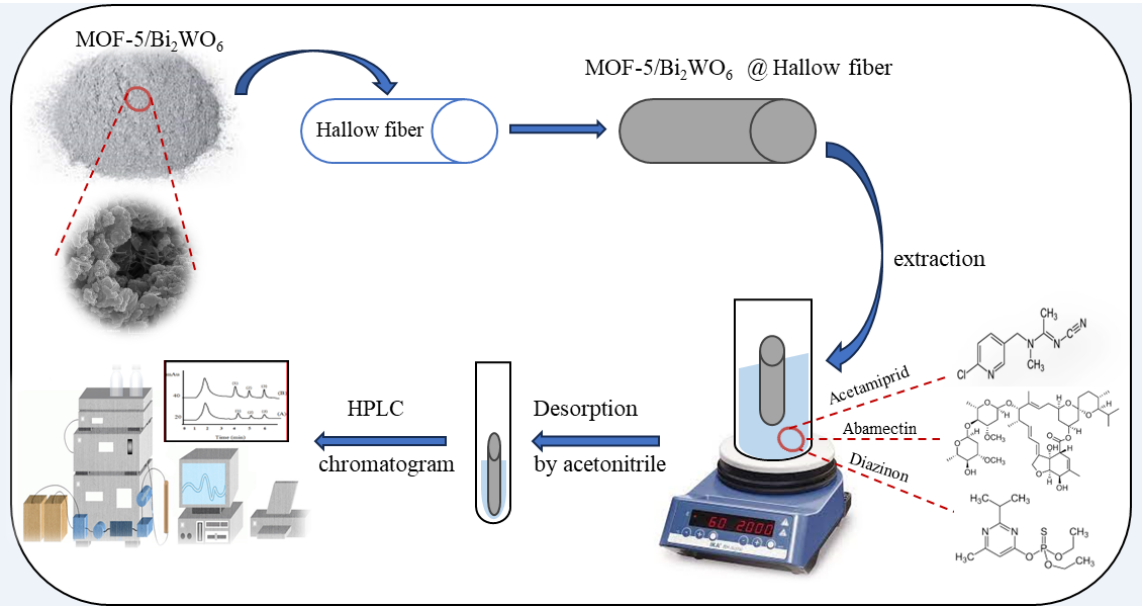
GRAPHICAL ABSTRACT



Introduction

Identifying and measuring very small amounts of various compounds in environmental samples is one of the concerns of researchers, which have attracted the attention of many scientists in recent years. In many cases, environmental samples often contain compounds that interfere with the measurement process of the target species. Therefore, the sample preparation process is necessary to remove interfering substances [1]. Sample preparation is very important, especially when the goal is to measure very small amounts of the test species. Depending on the type of extraction phase, two methods of solid phase extraction which is called SPE [2] and liquid phase extraction which is called LPE are presented [3]. SPE is popular sample extraction and traditional preconcentration technique [4]. Despite the many advantages of SPE, the presence of disadvantages such as relatively long extraction time and reduced extraction efficiency have prompted scientists to improve its performance or reduce its size. In the early 1990s, Pawlisyzn *et al.* [5] have introduced solid phase microextraction (SPME) method to eliminate the need for sample preparation, which enables simultaneous separation and preconcentration of volatile and non-volatile target compounds in samples containing complex tissue [6]. SPME is a fully balanced method that performs the extraction and preconcentration processes in one step. The most common SPME method is fiber-assisted extraction, known as fibrous solid phase microextraction (F-SPME) [7]. Although F-SPME has advantages such as short extraction time, the possibility of easy automation, no need for organic solvent, and carrying out the extraction and concentration process in one step, due to the existence of disadvantages such as the high cost of commercial fibers, the fragility of fibers, and their short life, this method needs to be developed [8-11]. HF-SPME is an efficient and effective method [12]. In HF-SPME, the prepared adsorbent is fixed in the hollow fiber (HF) pores [13]. HF can protect the synthesized adsorbents and improving performance of method. In addition, the use of HF also solves the problems of the matrix effect, which can be used once due to its cost. Imtiaz *et al.* used hollow fiber as a substrate to separate CO_2 from air [14]. Also Darvishnejad *et al.* used the HF-SPME in order to separate organophosphorus toxins from fruit samples [15]. Huijun Liu *et al.* have used the HF-SPME method for microextraction along with the injection technique with the help of micro sample collection, and the results of these works were acceptebale. Therefore, attention to this method has increased significantly in recent years [16].

Metal organic frameworks (MOFs) are consisting of metal ions or clusters connected by various organic compounds [17]. Since the first successful report about these materials by Yaghi *et al.* [18], about 20,000 different MOF compounds have been designed and synthesized by 2024, which contain various metals such as Zn, Zr, Fe, etc. and their number is constantly increasing [19-27]. The high structural potential of MOFs can be attributed to the central metal ions, the presence of open metal sites, the presence of linkers, and the modification or functionalization of MOFs. MOF-5 is a subgroup of MOFs presented in the 1990s by Yaghi *et al.* In MOF-5, Zn^{2+} is used as the central metal ion and terephthalic acid as the linker [28]. Up to now, various modifications such as MOF@MOF [29], metal organic frameworks/covalently organic framework (MOF@COF) [30], and metal organic frameworks/carbon nanotube (MOF/CNT) [31] have been introduced. One of the used modification is polyoxometalate (POM). POMs are polyatomic anionic clusters that have a structure of oxygen and metal, which can be used in electro catalysis processes due to their special characteristics, including high reduction and oxidation properties [32-34]. POMs are also used as adsorbents in separation processes [35], but due to their small surface area, their utilization faces limitations. To solve this problem, in-situ growth of POMs on other substrates such as MOFs is used. This increases the extraction efficiency and increases the absorption capacity of the sorbent [35]. The most famous types of polyoxometalates are Keggin, Anderson, Dawson, and Lindquist. Phosphotungstic acid is a type of hetero polyanion, and the first Kegin structure was discovered in 1993 by J. F. Kegin, which is a tetrahedral structure linked by 12 tungsten atoms, with the oxygen atoms centered on the phosphorus atom [36]. Phosphotungstic acid is also the strongest known heteropolyacid. Bismuth tungstate (Bi_2WO_6) is one of the simplest aurivilius oxides with a layered structure [37]. To achieve the highest extraction efficiency, factors affecting the extraction process should be investigated and optimized. In general, optimization of extraction parameters can be done in two ways, including one variable at a time and experimental design. Among these two methods, experimental design has been able to occupy the most place among researchers due to considering the interaction effects between factors and the number of experiments much less than the method of one variable at a time [38].

Pesticides are widely used in the cultivation of plants and plant products to prevent and control diseases and insect pests. Pesticides include insecticides, fungicides, and herbicides or a combination of one or more types of chemicals that are used primarily in agriculture to kill pests [39]. Pesticides enter the human body through various ways such as direct contact with the skin, swallowing or inhalation, and in this way they endanger human health. Serious side effects related to pesticides include skin diseases, nervous disorders, cancers, and respiratory diseases [39].

In the current study, we aim to prepare a sorbent base on the MOF-5 modified with POM. Herein, MOF-5/Bi_2WO_6 composite was prepared as a new sorbent to be used in HF-SPME method. The extracting device was used for the extraction of acetamiprid, abamectin and diazinon. Diazinon, acetaminophen, and abamectin have wide agricultural applications [40].

In addition, acetamiprid and abamectin are other common pesticides. In this study, the presented method was developed and used to quantify the selected analytes in orange, pomegranate, quince, and wastewater samples followed by high performance liquid chromatography-Ultraviolet detection (HPLC-UV). The obtained results showed good extraction efficiency, no memory effect, high adsorption capacity, and good reproducibility. Therefore, the desired adsorbent can be used to extract different analytes in real samples.

Experimental

Materials and Instrumentation

The information of the materials and the instrumentation is added into the supporting data.

Real Sample Preparation

To investigate the ability of the prepared adsorbent in measuring the real samples oranges, quince, pomegranates, and agricultural waste water were used. The desired samples were bought from a local market and after washing with water, they were peeled and crushed completely. 10 g of the selected samples were crushed and added to 15 mL of acetonitrile and 5 mL of water containing 1 g of NaCl followed by sonication for 1 min. Finally, 4 g of $MgSO_4$ was added to the mixture and the mixture was centrifuged for 5 min. It is worth mentioning that NaCl and anhydrous magnesium sulfate ($MgSO_4$) is commonly used as a drying agent. It is typically used to dry the organic layer after an aqueous work-up, and then 5 mL of the supernatant was removed and centrifuged again for 3 min. The resulting solution was used to extract target analytes.

Synthesis of MOF-5/Bi_2WO_6 Composite and the Preparation of HF-SPME Extracting Device

The precursor MOF-5 was prepared by the general approach [41]. Zink $(Acetate)_2{\cdot}2H_2O$ (2.19 g) and terephthalic acid (H_2BDC) (0.5 g) were added to 60 mL of DMF and stirred at 800 rpm. The obtained mixture was moved to autoclave (100 °C) for 12 h. The white powder which was MOF-5 obtained and used for further experiment. MOF-5/Bi_2WO_6 composite was also prepared by previously published strategy [41]. $H_3PW_{12}O_{40}$ (0.33 g) and (Cetyltriethylammonium bromide) CTAB (0.05 g) were dissolved in 70 mL of DI-water. MOF-5 (0.03 g) was added to the mixture under stirring, and then Bi $(NO_3)_3{\cdot}5H_2O$ (0.97g) was added to the mixture and transferred autoclave (120 °C) for 24 h. The prepared sorbent was collected and used for further experiments.
To prepare the extracting device, 0.2 mg of the prepared MOF-5-POM was dispersed in 10 mL of methanol, and then 1 cm of polypropylene HF was immersed in the solution. The solvent was sonicated for 2 h. Next, the extracting device was washed with pure water and left at room temperature to dry. After that, the prepared hollow fibers were used for the extraction process (Figure 1).

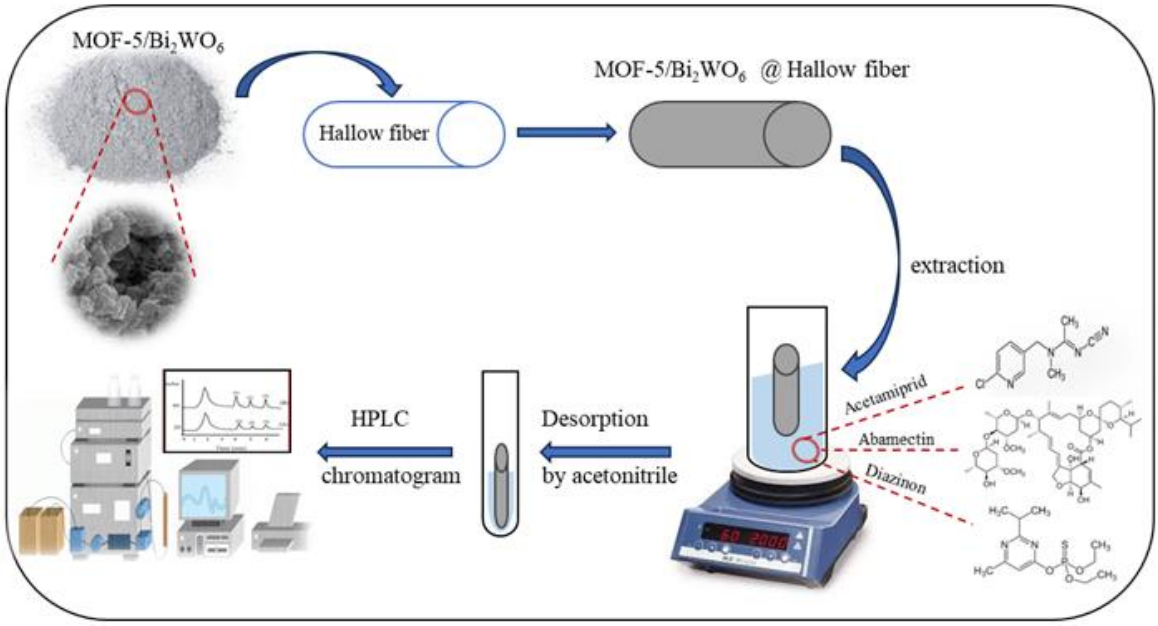


Figure 1: Synthesis of MOF-5 modified with Bi_2WO_6 polyoxometalate accommodated on the pores of hollow fiber for solid phase microextraction of acetamiprid, abamectin, and diazinon and their determination by HPLC-UV

The HF-SPME Procedure

The prepared MOF-5/Bi_2WO_6 sorbent was used for HF-SPME method of selected analytes. The information of the extraction procedure is added in the appropriate section in the supporting data (2.3.S. The HF-SPME procedure).

Design of Experiment

After screening the effective factors, the multivariable optimization method was used. Plackett-Burman design (PBD) is one of the widely used methods in the process of screening the effective factors in a process, in which each factor is examined at two levels -1 and +1. Box-Behnken design (BBD) is a three-level factorial design. In this design, a series of two-level tests are repeated among different sets of variables. The required information about the PBD, BBD, and the selected intervals is provided in the Supporting data. In BBD, the intervals selected for salt effect were 0, 7.5 and 15 (% W/V), for pH were 3, 6, and 9, and for extraction time were 5, 17.30, and 30 min. Moreover, the volumes of the eluent were 100, 200, and 300 µL, which were investigated.

Results and Discussion

Characterization of the Prepared Sorbent

Fourier transform infrared spectroscopy (FT-IR) spectra of MOF-5 and the prepared MOF-5 modified with Bi_2WO_6 were shown in Figure 2 (A).

In the spectrum related to MOF-5, the absorption band in the absorption region of 3458.34 cm^{-1} can be related to the hydroxyl (OH) groups. Likewise, the absorption peak appearing in the absorption region of 1582.50 cm^{-1} can be corresponded to the stretching vibrations related to carboxylic groups (COOH). In the absorption region 1387.24 cm^{-1}, vibrations of Zn-O, in the absorption region 1104.36 cm^{-1}, stretching vibrations related to (C-N), in the absorption region 1016.53 cm^{-1}, stretching vibrations related to (C=C) and also (C-O) groups were observed in the absorption region 825.36 cm^{-1}. In the spectrum of MOF-5 modified with Bi_2WO_6, absorption bands in the absorption region of 729.66 cm^{-1}, stretching vibrations (Bi-O) and carboxylic group (COOH) in the absorption region of 1582.50 cm^{-1} were observed, which is a confirmation of the successful synthesis of the adsorbent [41].

The crystal structures of the prepared MOF-5 and MOF-5/Bi_2WO_6 were investigated by X-ray diffraction (XRD) and the results are presented in Figure 2 (B). It can be seen that the two strong peaks in the 2Θ region at 6.9° and 9.7° corresponding to the pure MOF-5 diffraction pattern are associated with the (200) and (220) lattice planes, respectively, indicating that the MOF-5 crystalline compound has been successfully synthesized.

Furthermore, the multi-structure diffraction pattern of MOF-5/Bi_2WO_6 has characteristic peaks around 2Θ= 28.31°, 32.93°, 47.16°, and 55.83°, which are indicated by Miller indices (113), (020), (220), and (313) [41]. The obtained results were the same as the previously published results [41]. The surface morphology of the MOF-5 and MOF-5/Bi_2WO_6 synthesized as adsorbent is shown by field emission scanning electron microscope imaging (FE-SEM) at different magnifications in Figure 2C. Figure 2(C-(a-b)) shows the FE-SEM images of MOF-5 with different magnifications. The comparison of the pictures shows the preparation of each MOF-5/Bi_2WO_6 multi-structure component, and Bi_2WO_6 is well-placed on the MOF-5surface, and several MOF-5/Bi_2W_6 structures have been synthesized. The obtained results were the same as the previously published results [41]. To investigate the elemental analysis of MOF-5 and the prepared MOF-5/ Bi_2WO_6 composite, X-ray energy dispersive spectroscopy (EDX) was used. The EDX result is shown in Figure 1(D). Based on the results, MOF-5 and MOF-5/Bi_2WO_6 composites contain C, N, O, Zn, Bi, and W elements. Also, Figure 2(D) shows the map of the distribution of the selected atoms in the MOF-5 / Bi_2WO_6 composite structure. Concerning the structure of compounds MOF-5, Bi_2WO_6, and MOF-5/Bi_2WO_6 composite as well as the good dispersion of groups on the composite surface, it indicates the possibility of creating hydrogen bonds in the process of producing possible species with this sorbent [42]. N_2 adsorption and desorption isotherms of pure MOF-5 and MOF-5/Bi_2WO_6 composites are shown in Figure 1(E). It refers to non-porous materials or macro porous absorbents that can have an unlimited number of absorbent layers.

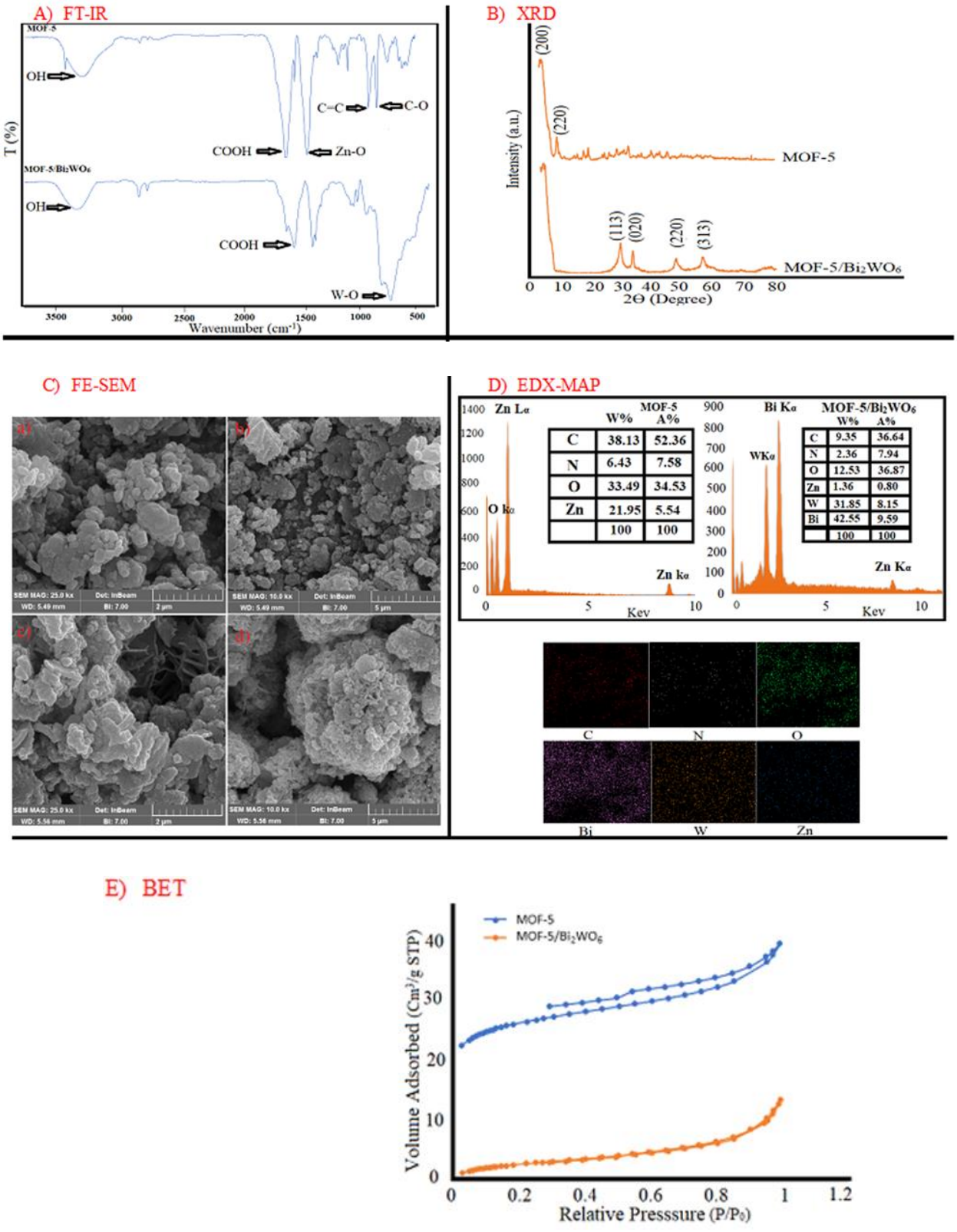


Figure 2: A) XRD patterns of MOF-5 and MOF-5/Bi_2WO_6 composite, B) FE-SEM image of (a-b) MOF-5; (c-d) MOF-5/Bi_2WO_6 composite, C) FT-IR spectra of MOF-5 and MOF-5/Bi_2WO_6, D) EDX spectra of MOF-5 and MOF-5/Bi_2WO_6 and mapping of MOF-5/Bi_2WO_6, and E) N_2 adsorption-desorption isotherms of MOF-5 and MOF-5/Bi_2WO_6 composite

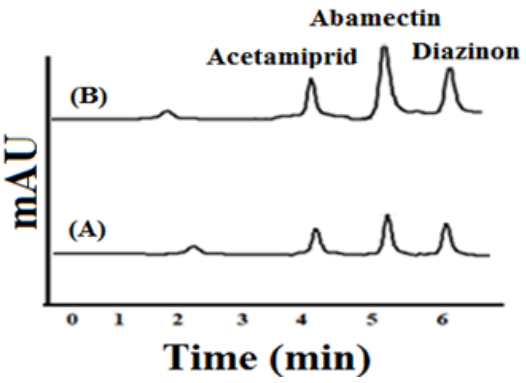


Figure 3: Chromatogram obtained from the measurement of selected analytes in pomegranate (a) before and (b) after spiking of 5 µg L^{-1} of the analytes

The turning point, which is called point B, is actually the point where the initial absorbent layer is completed and the absorption of subsequent layers begins. Type hysteresis 3 shows no absorption limitation at high relative pressures and has non-hard, plate-like shear holes. The hysteresis branch of the third type has a steep slope leading to loop closure, which occurs for nitrogen at a temperature of 77 K and at a relative pressure between 0.40-0.45. Table S1 shows the absorption data of MOF-5 and MOF-5/Bi_2WO_6 composites. The specific surface of MOF-5 increased after modification with Bi_2WO_6, which can increase the active surface to conclude and finally increase the efficiency when using the composite as a sorbent [41].

Extraction and Desorption Condition Optimization

A suitable eluent is a solvent that is high enough to penetrate into the sorbent and make a strong interaction with the investigated compounds. Among the characteristics of desorption solvent, low volatility, complete desorption of the target experimental species, and non-destruction of the sorbent and analytes have high priority. It should be noted that the determination of desorption solvent is also related to the type of mobile phase used in chromatography devices. Moreover, desorption solvent should present the acceptable chromatographic behavior. Four solvents including acetonitrile, methanol, ethanol, and isopropanol were selected and investigated. As can be seen in Figure S5, acetonitrile has a greater ability to desorb desired species from the sorbent. Considering that the mobile phase of the device is 80% acetonitrile and 20% water, it can be expected that the resulting chromatogram will have better peaks. The reason for choosing acetonitrile can be due to its greater polarity than other solvents used in this research (details of the work are provided in the supporting data). The results obtained from Box Behnken design (BBD) were used to obtain the optimization equations. In this regard, the surface area (Y) is related to, the amount of pH (A), extraction time (B), eluent volume (C), and salt effect (D) of the solution. Based on the Analysis of variance (ANOVA) results, the p-value for the model's lack of fit (LOF) was measured as 0.430. In addition, correlation coefficient (R^2), predicted R^2, and adjusted R^2 were obtained as 99.35, 98.07, and 99.98, respectively. A quadratic equation from the results of the BBD was created to predict the response at each point and is as follows:

$$Y= 38274.4 -8104.92\ A + 7473.00\ B - 8560.17\ C +20196.3\ D + 26645.2\ D^2 +31414.8\ B^2 +44210.2\ BD - 32474.0\ CD \quad (1)$$

In this equation, A, B, C, and D are pH, extraction time, eluent volume, and salt effect. Y is the total area under the peak chromatograms of abamectin, acetamiprid, and diazinon. The response procedure diagram of each pair of independent variables in supporting data was shown.

The pH of the solution (A) is also one of the experimental methods for conducting experiments. pH between 3 and 9 was investigated. The results showed that pH = 3 was chosen as the optimal pH. Diazinon is not affected by pH, but acetamiprid and abamectin are. When acetamiprid is exposed to acidic pH, its nitrogen group becomes protonated and has a small positive charge. Since the prepared adsorbent has a small negative charge, the desired species can be adsorbed by electrostatic interactions with the prepared adsorbent. Abamectin is further affected by pH due to having OH groups in its molecular structure. At acidic pH, abamectin can be adsorbed to the adsorbent by forming hydrogen bonds through OH groups. Extraction time (B) is one of the important parameters. In this study, the extraction time was investigated in the range of 5 to 30 min. The outputs indicated that with the increase of extraction time, the total peak area of the target analytes increased, which indicates the increase of the extraction efficiency. Therefore, the optimal time to reach equilibrium in the extraction process was determined as 30 min. The volume of desorption solvent (C) was investigated in the range of 100 to 300 µL. The results of BBD show that the increase in the volume of eluent also causes the dilution of the desired experimental species and the peak area decreases in high volume of the desorption solvent. Therefore, the volume of 100 µL was selected as the optimal volume. It is worth mentioning that the volume of the desorption container is one of the limiting factors in selection of the volume of eluent. Salt effect (D) is an important parameter that was optimized using experimental design. For this purpose, the effect of salt is considered as an important parameter in extraction process, by adding Na_2SO_4 to the solution. The ionic strength of the solution can be increased and the solubility of the desired species can be reduced. The effect of salt investigated in the range of 0 to 15 (% W/V). The results showed that the best conditions for conducting the experiment to reach the highest efficiency was achieved when the salt concentration is 15 (%W/V). The reason can be attributed to the effect of salt-out effect. Salt molecules stabilize them well on the adsorbent by reducing the solubility and declining the electrostatic energy between the molecules of the studied species [43].

Moreover, the stability and memory effect of the sorbent was determined. The information of the stability performance and the memory effect study is added in the appropriate section in the supporting data (2.5. S. The investigation of memory effect and stability of the sorbent). Based on the results, the sorbent is stable up to 20 times. In addition, the sorbent has no memory effect.

Evaluation of Method

Limit of detection (LOD), limit of quantitation (LOQ), linear dynamic range (LDR), enrichment factor (EF), and relative standard deviations (RSDs) were calculated. The results are shown in Table 1.

Table 1: Analytical performance characteristics of the method in water matrices

Analytes	Linear range (µg L^{-1})	Coefficient of determination (R^2)	Precision (%)						LOD	LOQ	EF	AR (%)
			Inter-day			Intra-day						
			2[c]	10	100	2	10	100				
Acetamiprid	0.2-100	0.9961	2.9	2.8	1.1	4.7	3.7	2.4	0.06	0.19	64	64
Abamectin	0.2-100	0.9965	3.3	2.3	1.1	4.5	4.1	3.1	0.05	0.18	66	66
Diazinon	0.5-200	0.9982	2.4	1.9	1.7	3.0	2.6	2.1	0.14	0.47	62	62

[a] *Spiking level*

[b] *Relative standard deviation (RSD) (n = 3)*

[C] *The units of the concentrations are µg L^{-1}*

The linear range of abamectin, acetamiprid and diazinon was obtained in the range of 0.2-100 µg L^{-1}, 0.2-100 µg L^{-1}, and 0.5-200 µg L^{-1}. The coefficients of determination (R^2) for

acetamiprid, abamectin, and diazinon were 0.9960, 0.9965, and 0.9982, respectively. The LODs which are the minimum concentration of the target analyte that can be reliably detected by the method were further obtained. LODs were obtained based on the signal-to-noise ratio of 3. Moreover, LOQs were obtained based on the S/N= 10. The LOD of the method for acetamiprid, abamectin, and diazinon was 0.06, 0.05, and 0.14, respectively. Relative standard deviation (RSD %) values for having 2 - 100 µg L^{-1} were also obtained between 1.1% and 4.7%. The EFs were 62 and 66, respectively. The absolute recoveries (ARs%) were obtained based on the following equation (Equation (2)):

$$AR(\%) = EF \times \frac{V_{eluent}}{V_{sample}} \times 100 \quad (2)$$

Where, V_{eluent} and V_{sample} are the eluent volume and sample solution volume, respectively. The volume of 100 µL was selected as the optimal volume for the eluent and the 10 mL is the volume of sample solution. The AR% values for selected analytes were 62 and 66, respectively. To evaluate and compare the proposed method with other methods provided by other researchers, Table 2 was prepared. As can be seen, the detection limit of the proposed method was better than other works done by other researchers.

Table 2: Comparison of the method with some studies conducted by others

Instrument	Method	Matrix	RSD (%)	LDR (µg L^{-1})	LOD (µg L^{-1})	Reference
HPLC- UV	MSPME[a]	Diazinon	2.5-4	0.3-50	0.090	[44]
HPLC- UV	DSPE	Diazinon	<10.1	10-100000	0.070	[45]
HPLC-UV	MHMS-MCNPs[b]	Diazinon	4.6	0.2-200	0.070-0.090	[46]
HPLC-UV	DLLME–SFO[c]	Diazinon - Abamectin	5.4-8.4	2-400	0.700	[47]
HPLC- UV	MSPE[d]	Diazinon	7.1	10-100	1.000	[48]
HPLC-UV	HF-SPME	Diazinon – Abamectin-Acetamiprid	1.1-4.7	0.2-500	0.054-0.141	This method

[a]*Multiple solid phase microextraction*
[b]*Mixed hemi micelle SDS-coated magnetic chitosan nanoparticles*
[c]*dispersive liquid-liquid microextraction based on solidification of a floating organic drop*
[d]*Magnetic solid-phase extraction*

As can be seen, the figures of merit calculated in this research, including LOD, LDR, and RSD% are better than some works done by others. The results showed that the proposed method is a simple, reproducible, easy, and sensitive method. The mechanism for the extraction of the target analytes from the sample solution to the coating might be owing to the π-π stacking interaction, hydrogen bonding, and Van der Waals interaction between selected pesticides and the synthesized sorbent.

Real Sample Analysis

The performance of the method in complicated real samples were studied (The data required for this section are provided in the supporting information). Standard addition method was used to perform the quantification tasks. In addition, relative recoveries (RR) and spiking recoveries (SR) were calculated. The relevant information for the calculation of SR and RR are written in supporting data (2.6.S. Real sample analysis). The results are presented in Table 3.
The obtained chromatograms of each target analytes are shown in Figure S6. Moreover, the chromatogram obtained from the measurement of selected analytes in pomegranate before and after spiking of 5 µg L^{-1} of the analytes is shown in Figure 3. Based on the results, it was approved

that the method is an appropriate for extraction of selected analytes in real samples.

Table 3: The results of analysis of selected analytes in real samples

		Acetamiprid			Abamectin			Diazinon		
Orange	Measured	2.50			2.10			1.90		
	Added	2.00	5.00	10.00	2.00	5.00	10.00	2.00	5.00	10.00
	Found	4.30	7.40	12.00	4.10	4.80	11.90	3.81	6.60	11.20
	SRa (%)	90.00	98.00	95.00	100.00	94.00	98.00	95.00	94.00	93.00
	RRb (%)	89.00	94.00	92.00	102.00	96.00	91.00	96.00	92.00	90.00
	RSD% n=3	4.60			4.40			2.60		
Quince	Measured	2.70			1.50			1.60		
	Added	2.00	5.00	10.00	2.00	5.00	10.00	2.00	5.00	10.00
	Found	4.60	7.40	12.30	3.30	6.10	11.70	3.50	6.40	11.10
	SR (%)	95.00	94.00	94.00	90	92.00	102.00	95.00	96.00	95.00
	RR (%)	91.00	90.00	96.00	91	90.00	100.00	93.00	91.00	90.00
	RSD% n=3	3.90			5.20			3.10		
Pomegranate	Measured	2.70			2.20			1.86		
	Added	2.00	5.00	10.00	2.00	5.00	10.00	2.00	5.00	10.00
	Found	4.54	7.40	11.80	4.21	6.90	11.20	3.81	6.60	11.20
	SR (%)	92.00	94.00	91.00	100.00	94.00	90.00	100.00	96.00	94.00
	RR (%)	91.00	92.00	90.00	95.00	91.00	90.00	98.00	92.00	90.00
	RSD% n=3	4.90			3.7			4.10		
Agricultural wastewater	Measured	2.40			3.30			3.10		
	Added	2.00	5.00	10.00	2.00	5.00	10.00	2.00	5.00	10.00
	Found	4.30	7.50	11.60	5.20	8.00	13.70	4.91	7.90	12.40
	SR (%)	95.00	102.00	92.00	95.00	94.00	104.00	90.00	96 .00	93.00
	RR (%)	97.00	94.00	89.00	93.00	93.00	95.00	95.00	93.00	91.00
	RSD% n=3	3.10			3.30			2.60		

[a]*Spiking recovery percentage*

[b]*Relative recovery percentage*

Conclusion

In this article, very capable sorbent containing Keggin type phosphotungstic acid was used for the modification of MOF. In this regard, MOF was initially synthesized, and then Bi_2WO_6 was accommodated on MOF to prepare MOF-5/Bi_2WO_6 composite. After that, the prepared MOF-5/Bi_2WO_6 was dispersed in methanol and stabilized in the pores of the hollow fiber walls to prepare the extractions device. HF-enhanced MOF-5/Bi_2WO_6 was used in HF-SPME-HPLC-UV method to extract and determine some toxins including acetamiprid, abamectin, and diazinon in orange juice, pomegranate juice, and agricultural wastewater. Under optimal condition, the linear ranges for measuring acetamiprid, abamectin, and diazinon were 0.2-100 µg L^{-1}, 0.2-100 µg L^{-1}, and 0.5-200 µg L^{-1}, respectively. The limits of detection (LODs) of the method for acetamiprid, abamectin and diazinon were 0.06, 0.05, and 0.14 µg L^{-1}, respectively. Moreover, the enrichment factors (EFs) were 64, 66, and 62 for acetamiprid, abamectin, and diazinon, respectively. In

addition, the absolute recoveries (ARs%) were in the range of 62-64%. Relative standard deviation values (RSD%) for the concentration of 2.0 μg L^{-1}, 10 μg L^{-1}, and 100 μg L^{-1} of acetamiprid were between 1.1% and 4.7%, for abamectin between 1.1% and 4.5% and for diazinon between 1.7% and 3.0%.

The proposed method has the capability of separation and preconcentration in one step. In this study, the important variables affecting the extraction performance of the method were optimized through experimental design, and then the figure of merit of the method was calculated. It is worth mentioning that memory effect has been seen because polypropylene hollow fibers are disposed and have been used once.

Please See Supporting Information.

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