

Supporting Information

Synthesis of MOF-5 Modified Bi₂WO₆ 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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2.1. S. Standard Solutions, Material, Reagents and Chemical

Selective analytes acetamiprid, abamectin and diazinon were obtained from Sigma-Aldrich (Milwaukee, WI, USA). HPLC grade methanol, HPLC grade acetonitrile, isopropanol (>99.5%) and ethanol (>99%), hydrochloric acid (HCl 37%), terephthalic acid (C₈H₆O₄), sodium hydroxide (NaCl), zinc acetate.2H₂O, bismuth (III) Nitrate.5H₂O, Cetyltriethylammonium bromide (CTAB), N,N-dimethylformamide (DMF, >99.5%), and phosphotungstic acid (H₃PW₁₂O₄₀) were purchased from Merck (Darmstadt, Germany). Zinc acetate dihydrate (Zn(Ac)₂·2H₂O), terephthalic acid (H₂BDC), N,N-dimethylformamide (DMF), absolute ethanol (C₂H₅OH), Phosphotungstic acid (H₃PW₁₂O₄₀), Cetyltrimethylammonium Bromide (CTAB), Bismuth Nitrate Pentahydrate (Bi(NO₃)₃·5H₂O), and the water used in the experiment is deionized water. Propylene hollow fiber was also purchased from Membrane, Germany.

Standard solutions of selected pesticides (1000 mg L⁻¹) were prepared by dissolving each analyte in acetonitrile and stored at 4 °C. A mixed standard solution (10.0 mg L⁻¹) was prepared by diluting the stock solutions in acetonitrile. Working solutions (100 µg L⁻¹) were prepared by diluting the standard solution mixed with deionized water (DI-water). DI water was obtained using a pure Smart-2 ultrapure water system from TKA, Germany.

2.2. S. Instrumentation

Different techniques, including Fourier Transform Infra-Red (FT-IR (model: JASCO FT-IR 4600 spectrophotometer (JAPAN))), were utilized for recording the infrared spectrum of the prepared sorbent. X-ray diffraction (XRD) data were achieved by an X-ray diffractometer (XRD Explorer GNR 2020(ITALY)) in Cu Kα (λ = 1.540598 Å) radiation source. The morphology of prepared sorbent was investigated through field emission scanning electron

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microscope (model: SEC-SNE-4500) and Energy Dispersive X-ray spectroscopy (EDX JEOL 7600F). The specific surface area, pore size distribution, and pore volume measurements were carried out at 77 K using a surface area analyzer (model BELSORP mini 100 instruments). The pH values of the sample solutions were adjusted using a pH meter model Analyzer 250 Corning (England). Barrett-Joyner-Halenda and Brunauer-Emmett-Teller (BET) (model: BEL JAPAN, INC) was assessed to evaluate the pores' structure and the specific surface.

Separation, detection and quantification of the extracted analytes were performed using a Waters high-performance liquid chromatography instrument equipped with a dual UV-Vis detector model 2487 (Waters Assoc, Milford, MA, USA), a binary solvent pump model 1525 and an injection valve (Rheodyne 7725i (Cotati, CA, USA)) containing a 20- μ L sample loop. Separation of the selected analytes was performed at room temperature on a Waters Symmetry $\text{\textcircled{R}}$ reversed phase C18 column (25 mm $\times$ 4.6 mm I.D., 5 μ m particle size). The analytes were eluted by an isocratic program at the flow rate of 1.0 mL min⁻¹. The mobile phase consisted of acetonitrile and water (80:20). The UV detector was set at 239 nm. Acetamiprid, Abamectin, and Diazinon, were eluted at 4.3, 5.8 and 6.1 min, respectively.

2.3.S. The HF-SPME Procedure

The prepared MOF-5/Bi₂WO₆ HF was used as extractive phase for HF-SPME method of selected analytes. To perform HF-SPME, the extraction device was immersed in 10 mL of the prepared sample solution (pH=3 and Na₂SO₄=15%) for 30 min. The prepared solution was stirred at 1100 rpm. After the extraction process, HF was removed from the sample solution and immersed in a homemade glass vial containing 100 μ L of a suitable eluent (acetonitrile). The glass vial was sonicated for 1 min to complete the elution step. Finally, 25 μ L of the eluent enriched with the target analytes was injected into the HPLC-UV for analysis.

2.4. S. The Optimization Approach

HF-SPME-HPLC-UV was used to extract and measure acetamiprid (Figure S1), abamectin acetamiprid (Figure S2), and diazinon (as a model analyte) (Figure S3) in environmental water and fruit juice samples. Based on our preliminary studies and experiments, at least six factors, including solution pH, stirring speed, extraction time, desorption time, and elution solvent volume and salt effect, affected the experimental response. According to the studies, the mentioned factors were selected at two levels (low and high) for 12 implementations in PBD. Symbols, low and high levels, and coded values for factors in screening experiments are summarized in Table S2. Analysis of variance (ANOVA) was used to determine the effects. Important variables were selected based on the number of their evaluation effects, which were shown as a Pareto chart. Significant factors were evaluated based on the Pareto

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diagram (Figure S2). Bars extending beyond each column correspond to effects that are statistically significant at the 95% confidence level. Based on the obtained results (Table S3), salt effect, extraction volume, extraction time and pH of the sample solution respectively had the greatest effect on the extraction of toxins, and the extraction time is not significant in the intervals of their changes. According to PBD (Equation 1 and Table 3), stirring speed and desorption time were fixed at 1100 rpm and 1 min, respectively, for subsequent experiments.

Table S1: The adsorption data of MOF-5 and MOF-5/Bi₂WO₆ composites

Sample name	Specific surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Pore size (nm)
MOF-5/Bi ₂ WO ₆	964.666	0.060478	2.5077
MOF-5	106.09	0.020292	7.6511

Table S2: Experimental variables and levels of the Plackett–Burman design

Factor	Name	Level	
		Min (-1)	Max (+1)
A	pH	3	9
B	Extraction time (min)	5	30
C	Eluent volume (μL)	100	300
D	Salt effect	0	%15
E	String rate (rpm)	300	800
F	Desorption time	1	5

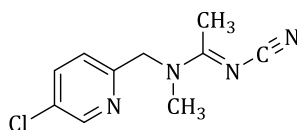


Figure S1: The structure of Acetamiprid

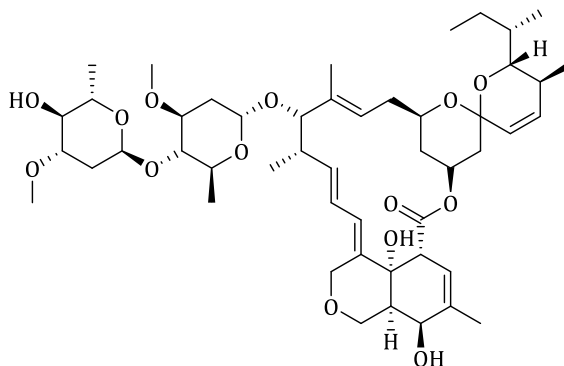


Figure S2: The structure of Abamectin

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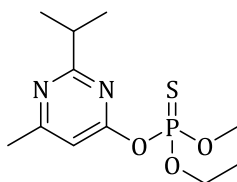


Figure S3: The structure of Diazinon

Table S3: The matrix of the Plackett–Burman design experiments obtained from MINITAB and the response

Experimental number	Factors						Response
	A	B	C	D	E	F	Response
1	1	1	-1	1	1	-1	28557
2	1	-1	1	-1	-1	-1	63891
3	-1	1	1	-1	1	-1	84181
4	-1	1	-1	-1	-1	1	83182
5	1	1	-1	1	-1	-1	24168
6	1	-1	1	1	-1	1	54567
7	1	1	1	-1	1	1	83649
8	-1	-1	1	1	1	-1	73153
9	-1	-1	-1	-1	-1	-1	74600
10	-1	1	1	1	-1	1	85903
11	-1	-1	-1	1	1	1	73647
12	1	-1	-1	-1	1	1	70565

To optimize the level of these four important parameters and estimate their mutual effect, BBD-based response surface method was used as a multivariate statistical technique. BBD is a class of rotatable second-order design with respect to three-level factorial design. The data points lie on a hypersphere equal to the central point in the BBD, which has three levels (-1, 0, +1). The numerical value of the total test points (Y) is obtained from the following Equation (1):

$$Y=2X(X-1) + y_0 \quad (1)$$

Where X is the number of parameters and y_0 is the number of central points. A total of 27 test runs are required, which were conducted randomly. The matrix of BBD experiments obtained from MINITAB and the response (peak area of total analytes) are shown in Table S4. The polynomial model created to predict mine performance in terms of main factors and variable interaction is according to Equation 2. Model analysis was performed using ANOVA (Table S5). The importance of each coefficient was checked with F-test and P-value (probability). P-values higher than 5% showed that the variable has no significant effect on the model and can be removed. Based on ANOVA, the lack of fit (LOF) was measured to be

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0.430. A high R^2 indicates that the predicted response was completely correct. A high adjusted R^2 value indicates the correlation between the experimental response and the fitted model (Table S6). It can be seen from the data that the response equation provides a reasonable model for BBD. Finally, desorption time: 1 min, sample solution pH: 3, extraction time: 30 min, stirring speed: 1100 rpm, washing solvent volume: 100 μ L and salt effect: 15% (W/V). Were selected as the optimal conditions of the method (Table S7).

Table S4: Analysis of the variance for the fit of the experimental data to Plackett–Burman design

Source	Degree of freedom (D.F)	Sum of squares (SS)	Adjusted sum of squares (adj. SS)	Adjusted mean squares (adj. MS)	F-value	p-Value
pH	1	684407552	684407552	684407552	36.16	0.002
Extraction Time	1	1856769530	1856769530	1856769530	98.10	0.000
Stirring rate	1	62750707	62750707	62750707	3.32	0.128
Desorption Time	1	35994424	35994424	35994424	1.90	0.226
Desorption volume	1	1201460444	1201460444	1201460444	63.48	0.001
Salt effect	1	883448281	883448281	883448281	46.68	0.001
Main effect	6	4724830938	4724830938	787471823	41.61	0.000
Residual Error	5	94634979	94634979	18926996		
Total	11	4819465917				

Table S5: The matrix of the Box-Behnken design experiments obtained from MINITAB and the responses

Experimental number	Factors				Response
	Salt effect	Extraction Time	Desorption volume	pH	
1	0	0	0	0	38412
2	-1	-1	0	0	115650
3	1	0	1	0	46031
4	0	1	0	1	87774
5	0	0	-1	-1	58675
6	1	0	-1	0	124953
7	1	1	0	0	166854
8	0	1	-1	0	83731
9	-1	1	0	0	40550
10	0	0	0	0	34074
11	-1	0	0	-1	51963
12	0	0	-1	1	39433
13	1	0	0	1	80808
14	-1	0	-1	0	20511
15	0	-1	-1	0	71190
16	0	1	1	0	63416
17	0	0	1	1	22518
18	0	1	0	1	73939

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19	0	0	1	-1	39243
20	1	0	0	-1	89766
21	0	-1	0	1	52011
22	0	-1	0	-1	69546
23	-1	0	1	0	71485
24	0	0	0	0	38395
25	-1	0	0	1	31011
26	1	-1	0	0	65113
27	0	-1	1	0	53078

Table S6: Analysis of the variance for the fit of the experimental data to response surface model

Source	Degree of freedom (D.F)	Sum of squares (Seq SS)	Adjusted sum of squares (adj. SS)	Adjusted mean squares (adj. MS)	F-value	p-Value
Regression	8	28348890376	28348890376	3543611297	345.93	0.00
Linear	4	7232209941	7232209941	1808052485	176.50	0.00
Salt effect	1	4894662169	4894662169	4894662169	477.82	0.00
Extraction time	1	670148748	670148748	670148748	65.42	0.00
Solvent volume	1	879317440	879317440	879317440	85.84	0.00
pH	1	788081584	788081584	788081584	76.93	0.00
Square	2	9080252911	9080252911	4540126455	443.21	0.00
AA	1	2764141500	4543793166	4543793166	443.57	0.00
BB	1	6316111410	6316111410	6316111410	616.58	0.00
Interaction	2	12036427524	12036427524	6018213762	587.50	0.00
AB	1	7818184820	7818184820	7818184820	763.21	0.00
AC	1	4218242704	4218242704	4218242704	411.79	0.00
Residual Error	18	184387669	184387669	10243759		
Lack-of-Fit	16	171891144	171891144	10743197	1.72	0.430
Pure Error	2	12496525	12496525	6248262		
Total	26	28533278045				

Table S7: Estimated determination coefficient of the BBD design

R ²	R ² (pred)	R ² (adj)
99.88%	99.74%	99.33%

Table S8: Optimized value of the factors obtained from BBD design (coded and un-coded values)

Factor	pH	Extraction time	Salt effect	Solvent volume
Coded value	-1	+1	+1	-1
un-coded values	3	30	% 15	100

2.5. S. The Investigation of Memory Effect and Stability of the Sorbent

The performance of the synthesized sorbent can be investigated by examining stability, which was determined through the reusability investigation. For this purpose, repeated

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extractions were performed according to extraction procedure. According to the mentioned method, extraction and elution were done successively. After analyte desorption and before analyte re-extraction by the sorbent, the sorbent was washed well with methanol and TFA (90:10, v/v) to completely remove the target analytes. The results showed that the sorbent extracted the analyte up to 20 times with little changes in the ER (90 ± 1.5). Memory effect was also checked. For this purpose, the extraction and desorption process of the target analytes were performed by a sorbent. After washing the sorbent, the sorbent was once again immersed in acetonitrile to perform the desorption process. The solvent containing the analytes was injected into the HPLC-UV. Based on the results, the proposed sorbent has no memory effect.

2.6.S. Real Sample Analysis

In order to quantify the analytes, standard addition method was also used. In this context three different concentration levels (2, 5, and 10 $\mu\text{g L}^{-1}$) were spiked to samples and three replicates were done for each concentration ($n = 3$). In addition, relative recoveries and spiking recoveries were also calculated. Relative recovery was defined as the ratio of the measured analyte in real samples and the measured concentration in pure water samples spiked with the same amount of analyte. The spiking recoveries were also measured using the following Equation (2):

$$\text{Spiking Recovery} = \frac{C_{\text{found}} - C_{\text{real}}}{C_{\text{added}}} \quad (2)$$

In the equation, C_{real} , C_{added} , and C_{found} are the concentrations of the analyte ($\mu\text{g L}^{-1}$) in the real sample, the spiked concentration into the real sample and the concentration after TFME, respectively. Also, RSD% values were calculated after performing three repeated tests under these conditions, and the results are presented in Table 3. Since the hollow fiber used in the HF-SPME method has a very high porosity as well as a pore size of about 0.2 μm , it can prevent entrainment of the unappropriated and large particles, which in this case provides high performance in the sample purification process. Therefore, there is no need to filter the sample solution before extraction. The obtained chromatograms of each target analytes are shown in Figure S6. Based on the obtained results, it was confirmed that the proposed method is a suitable method for extraction of selected analytes in real samples.

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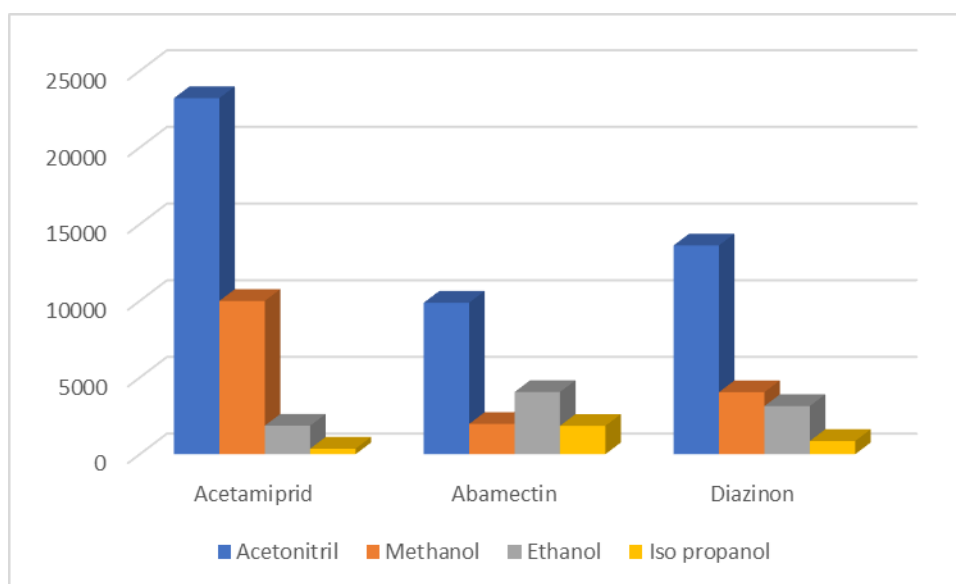


Figure S4: Pareto chart of the standardized effects obtained from a Plackett-Burman design.

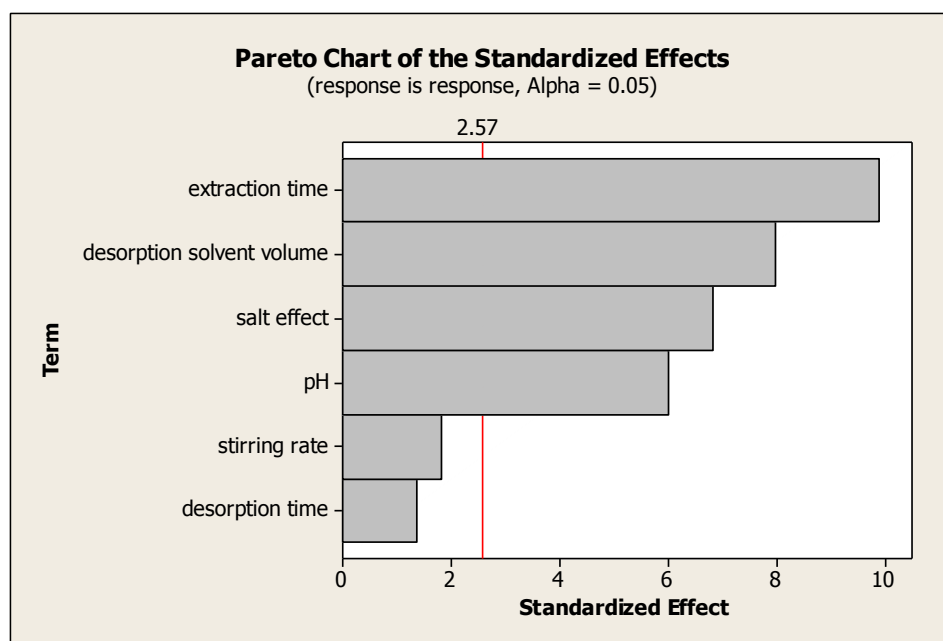


Figure S5: Effect of desorption solvent type on the extraction efficiency.

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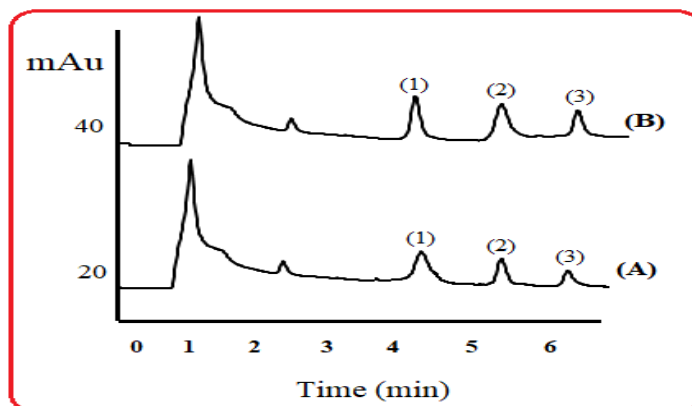


Figure S6 (A): Chromatogram obtained from the extraction and measurement of acetamiprid (4.3 min), abamectin (5.8 min) and diazinon (6.1 min) in pomegranate juice.

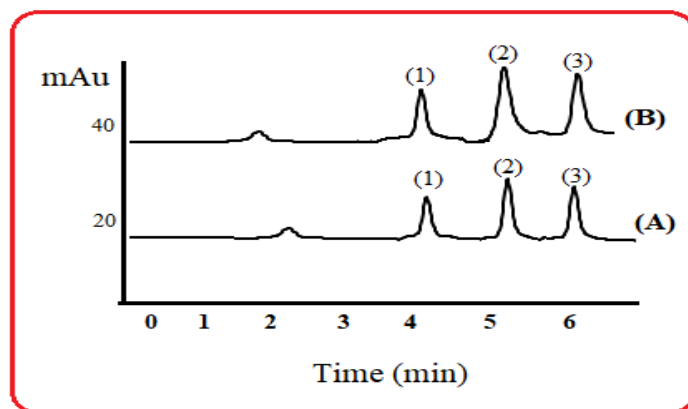


Figure S6 (B): chromatogram obtained from the extraction and measurement of acetamiprid (4.3 min), abamectin (5.8 min) and diazinon (6.1 min) in agricultural wastewater.

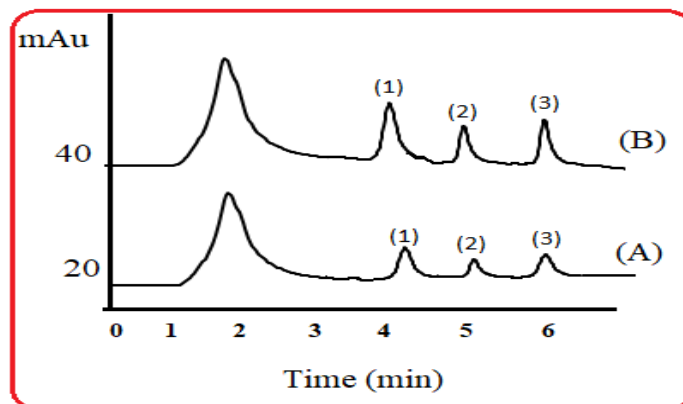


Figure S6 (C): Chromatogram obtained from the extraction and measurement of acetamiprid (4.3 min), abamectin (5.8 min) and diazinon (6.1 min) in Quince juice.

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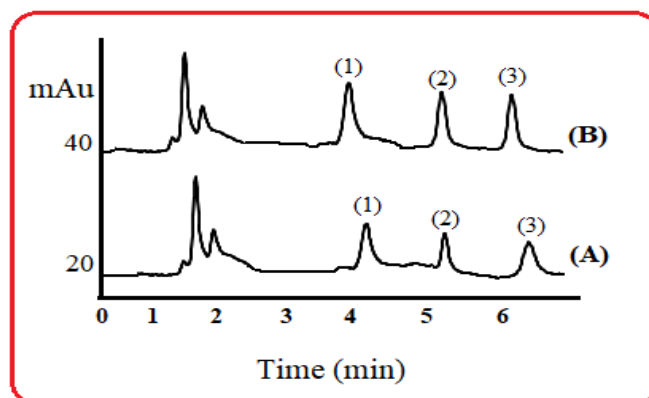


Figure S6 (D): Chromatogram obtained from the extraction and measurement of acetamiprid (4.3 min), abamectin (5.8 min) and diazinon (6.1 min) in orange juice.