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Ultrasound assisted extraction combined with NH_2-MIL-101(Cr)/polysulfone thin film-μSPE for determination of pesticides in food samples

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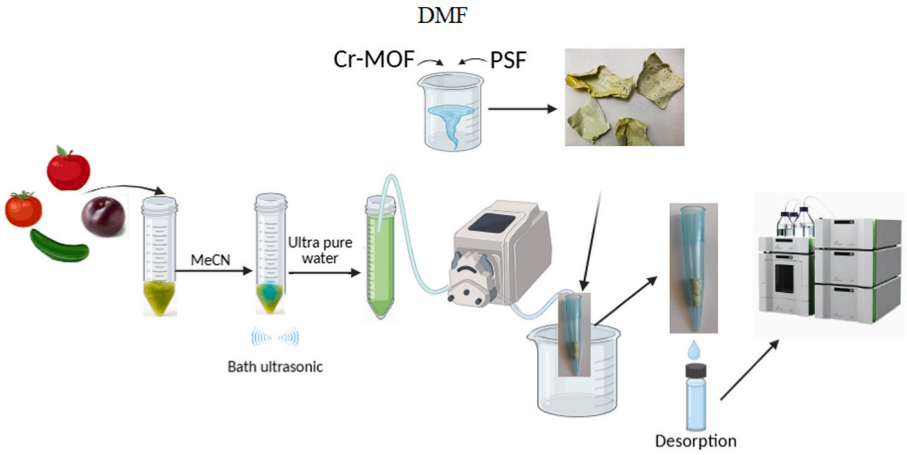
HIGHLIGHTS

- Ultrasound assisted extraction combined with micro-SPE for extraction of pesticides from fruits and vegetables.
- Rolled NH_2-MIL-101(Cr)/polysulfone thin film was used as sorbent in pipette tip-micro SPE.
- Extraction of pesticides from fruits and vegetables using 1.5 mL of acetonitrile.
- Increased stability of the adsorbent and non-clogging of the pipette tip containing the adsorbent film.

GRAPHICAL ABSTRACT



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ABSTRACT

Background: In this research, for the first time combination of ultrasound-assisted extraction and thin film micro-solid phase extraction (UAE-TF-μSPE) was developed, and applied to extract the acetamiprid and thiacloprid from foods. This procedure was shaped to resolving the analytical challenges that arise from analyzing food samples that display matrix effects on analyte recovery. Here, UAE extracts analytes from food matrices using less extraction solvent and is then coupled with TF-μSPE, where the latter performs clean-up and preconcentration of the target compound. NH_2-MIL-101(Cr) was synthesized through hydrothermal method, embedded in a polysulfone thin film, and utilized as an adsorbent in μSPE technique.
Results: The optimization of factor affecting of procedure was established based on response surface methodology (RSM). The critical parameters, such as pH, volume of extraction solvent, and ultrapure water volume were optimized. The method demonstrated outstanding analytical performance, with a detection limit established at 0.2 μg kg^{-1}, a linearity range of (1.0-200.0) μg kg^{-1}, very good repeatability characterized by relative standard

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deviation values between 2.7 % and 4.0 %, and excellent relative recovery from 85.0 to 102.0 % spiked levels 30.0-100.0 μg kg^{-1}.
Significant: The present method was able to extract pesticides from fruit and vegetable matrices using 1.4 mL of organic solvent. The presence of NH_2-MIL-101(Cr) in packed thin film at the pipette tip without clogging and back pressure preconcentrated the insecticide with high extraction efficiency. The adsorbent also exhibited a remarkable durability, contributing to repeated use without performance degradation.

1. Introduction

Antioxidants predominantly come from fruits and vegetables and are an essential part of the human diet due to the existence of macronutrients such as carbohydrate, vitamins, and minerals [1]. Tomatoes and cucumbers are among the most commonly grown vegetables worldwide and play an important role in the food processing industry, while apples and plums are valued for their rich nutritional content and health-promoting properties. However, tomatoes, cucumbers, and apples are susceptible to numerous pests and diseases that are controlled with pesticides [2–4]. At the same time, however, fruits and vegetables could be contaminated with very harmful substances such as pesticides [5]. Among different classes of pesticides, neonicotinoids (NEOs) insecticides, have gained the greatest popularity in the last decade because of their high water solubility, systemic action, and easy up-take by plant tissues, resulting in long-term residual, also, being commonly found in fruit and vegetables at concentrations of 4.0 to 500.0 μg kg^{-1} [6,7]. NEOs have been frequently detected in vegetables, fruits, and environmental matrices due to their systemic nature and high mobility within plant tissues and environmental matrices [8]. Thiacloprid and acetamiprid are two neonicotinoid compounds widely used in agriculture [9]. Their unique properties make them the most commonly used NEOs, including high bending affinity for insect nicotine receptors of acetylcholine (nAChRs), low hydrophobicity, and high penetrability [9].

At present, global food control programs for pesticides are organized towards consumer health, agricultural-resource management at a global level, and prevention of economic losses [10]. Thus, almost all such countries and institutions, including the European Union (EU), have adopted arrangements in form of standards and laws to set maximum residue limits (MRLs) for products. The MRLs of NEOs insecticides vary from 0.01 to 1.50 mg kg^{-1} [11]. Trace neonicotinoid residues in fruits and vegetables must therefore be determined for food safety and ensuring human health [12].

Pesticides are usually present in fruits and vegetables at extremely trace levels, with complexity in the sample matrix serving as the major hindrance to their extraction [13]. Much effort has, therefore, been put in by researchers to develop and optimize simple, sensitive, efficient, environmentally friendly, and reliable sample preparation methods for direct extraction and enrichment of pesticides prior to their injection into the analytical equipment [14]. The literature has widely quoted the application of the following methods in their extraction and identification of NEOs from different matrices, including magnetic solid-phase extraction(MSPE) [15], continuous sample drop flow microextraction (CSDF-ME) [16], solid-phase extraction (SPE) [17,18], solid-phase micro extraction (SPME) [19], micro solid phase extraction(μ-SPE) [20], dispersive micro solid-phase extraction (DMSPE) [21], and QuEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe) [22]. Every one of the approaches mentioned above has its merits and demerits as well. However, SPE and QuEChERS methods have been more widely used in the extraction and cleanup of pesticide residues from fruits and vegetables than the other methods [23]. QuEChERS has become one of the most popularly used sample preparation methods for pesticide extraction from fruits, vegetables, or animal matrices [24]. The limited sensitivity of QuEChERS, with a low enrichment factor, leaves this method open to further improvements [25]. Further, the consumption of organic solvents is high, and the extraction procedure takes more time. Numerous unwanted and interfering compounds coexisting with the target analytes in a sample matrix have been successfully removed using the SPE method, thereby increasing the sensitivity of the method. Very often, the SPE techniques would entail slow extraction, generate large amounts of waste, and consume excessive amounts of samples, sorbent materials, reagents, and solvents, with often minimal sensitivity [26]. This therefore calls for a sensitive, rapid, and low solvent-consuming extraction method with minimal analyte loss to improve the speed and lower the cost of sample preparation [27].

Pipette-tip micro solid phase extraction (PT-μSPE) is one of the very promising miniaturized SPE alternatives, with all the advantages of simplicity, lower solvent consumption, minimum requirements of the adsorbent, portability, remarkable efficiencies in extraction, and very low cost, making it a very preferred method of analysis [28]. Nevertheless, chemical and physical characteristics of the sorbent have remained the most important factor for obtaining the highest enrichment and sufficient recovery in micro-SPE [29]. Metal-organic frameworks (MOFs) have been gaining momentum as new types of adsorbents in recent years [29]. These materials are defined as porous organic–inorganic compounds in which a regular array of positively charged metal ions is joined together with different organic linker [30]. However, the direct use of MOFs packed in pipette tip-μSPE presents challenges (high backpressure, heterogeneity, etc.) [30] that compromise ease and reproducibility of the method while increasing the clogging possibilities of the packed pipette tip. These limits can be lifted by adding the MOF particles to a polymeric organic support to produce hybrid material with superior properties compared to those of the individual components [31].

Polysulfone (PSF) is one of the most widely used polymers for membranes owing to its high mechanical strength, great thermal stability, and excellent chemical resistance over the entire pH range [32]. In this study, we homogeneously incorporated the synthesized MOFs inside ultra-thin PSF film, mainly for the following two reasons: to ensure to avoid clogging and back pressure in the pipette tip. The thin films (TFs) of MOFs/PSF were rolled and inserted into the pipette tip, considerably reducing the time for sample extraction and allowing reuse of the adsorbent, which would no longer lead to tip blockage for real samples. In addition, it was found that analytes of interest were adsorbed by PSF itself, contributing further to extraction efficiency. TF-μSPE is not possible to be applied for the solid food samples directly. First, the pesticides in the fruit and vegetable samples must be extracted from the sample tissue into a solution so that they can contact the adsorbent. There is the important step to be done in this research, to lessen the matrix effect and contaminating interference such as fat, protein and pigments that is done by conducting the extraction of the analytes from the food matrix and into an appropriate solvent before preconcentrating analytes by TF-μSPE. In previous work has been investigated by our research group in respect of the extraction of analytes by ultrasound-assisted extraction (UAE) from the site of the fruit and vegetables-in-matrix extract into an aqueous solution [33]. The extract thus obtained can then undergo efficient treatment by TF-μSPE for clean-up and preconcentration before instrumental analysis.

In present study, we combined ultrasound-assisted extraction with micro solid-phase extraction for the first time, using NH_2-MIL-101(Cr)/PSF-thin film as sorbent, to determine acetamiprid and thiacloprid in cucumber, tomato, apple, and plum samples. The compounds of interest are then concentrated in very small volumes (several tens of microliters) of organic solvent which desorption from NH_2-MIL-101(Cr)/PSF-TF-

μ-SPE. Also in ultrasound-assisted extraction, organic solvents have a minimal amount because extraction was performed using ultrapure-water in combination with acetonitrile solvent (1.4 mL). The factors that had stronger effects on extraction efficiency, e.g., pH of the aqueous solution, volume of acetonitrile as extraction solvent, and the volume of aqueous solution, were studied and optimized in this work. Optimization of the effective parameters affecting the analytical signal was conducted via Response Surface Methodology (RSM). Next, the levels of factors of lesser influence-ultrasonic time and the type of extraction solvent were optimized.

2. Experimental

2.1. Materials

2-Aminoterephthalic acid was procured from sigma-aldrich (China). The chromium (III) nitrate nonahydrate was bought from Biochemopharma in (Cosne-sur-Loire, France). N,N-Dimethylformamide (DMF) was obtained from (Carlo-Erba, France). Methanol and sodium hydroxide are obtained from Ambernath, India. Polysulfone was given by BASF (Germany). Extraction solvents of acetonitrile for liquid chromatography, methanol for analysis and standard preparation, and hydrochloric acid for pH adjustment were purchased from Merck (Darmstadt, Germany). Acetamiprid was it purchased from Sigma-Aldrich (Seelze, Germany), while thiacloprid came from Sigma-Aldrich (St. Louis, MO, USA). A solution standard containing 1000 ppm of each pesticide was prepared in methanol and kept at −4 °C.

2.2. Instrumentation

Kindly see the supplemental information (ESI) for specific information regarding the instrumentation.

2.3. HPLC condition

All studied pesticides, along with their respective extracts, were subjected to HPLC-PDA system (PerkinElmer, Flexar-15, USA) analysis. The HPLC comprised a C18 column (150 × 4.6 mm, 5 μm; Restek, USA) along with PDA detection (PerkinElmer, Flexar-15, USA) was used for the separation and detection of the insecticides at 244 nm. HPLC-grade water and acetonitrile were degassed and was used as the mobile phase with a flow rate of 1.0 mL min^{-1}. An autosampler (PerkinElmer, USA) injected exact samples of 15.0 μL each. The gradient elution procedure was as follows: mobile phase A: water and mobile phase B: acetonitrile. First, an initial gradient of 23.0% B was maintained for 1.0 min, then increased to 30.0% B in 1.0 min and held for 2.5 min, ramping from 30.0% to 40.0% B in 3.0 min, then increased from 40.0% to 62.0% B in 2.0 min and held at this concentration for another 1.5min before its final return to 23.0% B within 1.0 min. The entire chromatographic run lasted 12.0 min.

2.4. Synthesis NH_2-MIL-101(Cr)

The synthesis of NH_2-MIL-101(Cr) was followed by the method explained by Moinfar and Khodayari [34]. Initially, a Teflon reactor was filled with eight mmol (3.20 g) of Cr $(NO_3)_3 \cdot 9H_2O$ and eight mmol (1.44 g) of 2-amino terephthalic acid. Then, 60.0 mL of 0.33 M NaOH was added dropwise. The solution was then homogenized by stirring it at 700 rpm for 60 min. Following 16 h of heating to 160 °C, the reactor was returned to its normal temperature. The solid powder was isolated using a centrifuge operating at 7000 rpm for 15 min. The resulting powder was washed three times with deionized water. The samples were centrifuged for about 50 min at 7000 rpm after a wash with DMF. To eliminate DMF residue, MOFs were washed with methanol. The processed powder was ultimately dried at 70 °C for approximately 12 h.

2.5. Synthesis PSF-TF and NH_2-MIL-101(Cr)/PSF-TF

Initially, DMF (8.0 mL) was added to dissolve 15 % PSF (1.2 g of PSF) with continuous stirring at 45° for 12 h (approximately 250 rpm) until a homogeneous casting solution was achieved [35]. After that, 0.4 gm of NH_2-MIL-101(Cr) was introduced into the casting solution, and was mixed until homogeneous. The casting solution was applied to a glass substrate (microscope slides, 0.8 - 1.2 mm thickness, and 25 * 75 mm dimensions, and microscope cover glass (22 * 22 mm plain, 0.13-0.16 mm thickness)) thoroughly pre-cleaned, and then evenly spread using a glass rod. To prepare of the thin films, mixture of PSF and NH_2-MIL101 (Cr) were spread onto a glass substrate. The resultant ultrathin of PSF-TF, and NH_2-MIL101 (Cr)/PSF-TF were immersed in deionized water for 24 h to remove any residual DMF solvent [36]. Then, the MOF/polymer thin films were washed three time with methanol under sonication for 30 min. Finally, they were placed in an oven at 140 °C for 48 h to dry.

2.6. Preparation of the tip

50 mg of NH_2-MIL-101(Cr)/PSF-TF sheet was rolled and fixed at the end of a 1-mL conical pipette tip. Due to the very narrow conical end of the pipette tip, it is not possible to remove the rolled polymer film. Then, the pipette tip containing the thin films was washed with 600.0 μL of MeCN followed by 1 mL of ultrapure water. The resulting tip was used to extract the target pesticides from fruit and vegetable samples.

2.7. Preparation of a spiked sample

Kindly see the supplemental information (ESI) for specific information considering the preparation of spiked samples.

2.8. Extraction and preconcentration method

The method of operation has two essential parts: a) modified UAE and b) TF-μSPE.

a) Modified UAE:
   As per the literature published in Refs. [33] mL test tubes were initially filled with a weight of 6.0 g uniform unspiked sample or spiked sample. Then, 1.4 mL of MeCN was put as extraction solvent into tube, and the tube was placed into an ultrasonic bath and remained at room conditions for 20 min. Afterward, it was added with 40.0 mL of ultra-pure water and shook for 20 s, and the mixture was filtered through filter paper.
b) TF-μSPE procedure:
   The aqueous solution collected after filtration step in the previous stage was measured for pH and adjusted at 5.0 to 6.0 using 0.1 M NaOH and 0.1 M HCl solutions. After adjustment of pH, the resulting solutions (40 mL) were passed through a pipette tip containing rolled thin film-MOF (NH_2-MIL-101(Cr)/PSF-TF) at a flow rate of 2.6 mL min^{-1}. The adsorbed pesticides on the NH_2-MIL-101(Cr)/PSF-TF were desorbed with about 150.0 μL of pure MeCN, followed by further injection of 15.0 μL of the resulting MeCN containing the extracted pesticides into HPLC. After every extraction, the pipette tip containing thin films was washed with 600 μL of pure MeCN and then by 1.0 mL of ultrapure water.

2.9. Experimental design

To achieve optimal extraction conditions and maximum enrichment factor for target analytes, several parameters affecting UAE-TF-μSPE were analyzed using Box-Behnken Design (BBD). Choose a BBD approach to optimize process parameters for better recovery of acetamiprid and thiacloprid from various vegetable and fruit samples including tomato, cucumber, apple, and plum. In this fashion,

experimental efficiency in terms of chemical waste and total cost is maximized with a statistical approach [37]. Three variables in BBD or BBD-influenced UAE-TF-μSPE method to examine certain influences were important process parameters: pH (A) (4.5, 6.5, and 8.5), extraction solvent volume in (B) (1.0, 1.4, and 1.8 mL), and aqueous volume (C) (20.0, 30.0, and 40.0 mL). All investigated parameters were classified under numerical variables, thus forming an experimental matrix with 17 experimental runs Table S1 with varying values for the process variables. The model design is quadratic optimization done using Design Expert software version 13.0.5.0. For response, the peak area obtained from HPLC-PDA results was taken. The results for pesticide sorption were analyzed by ANOVA and presented in three-dimensional modeling.

3. Results and discussion

3.1. Characterization

3.1.1. SEM analysis

The morphologies of the NH_2-MIL-101(Cr), PSF-TF, and NH_2-MIL-101(Cr)/PSF-TF were investigated following preparation by SEM. The results for Fig. S1(a and b) present SEM images for NH_2-MIL-101(Cr) of thus fairly crystalline morphology of the sample that was mostly a very regular octahedron particle structure in accordance with these reports [38]. As can be seen in Fig. S1 (a and b), the crystal particle of NH_2-MIL-101(Cr) had a dimensions range of about 62-127 nm, which appeared to be more uniform. The surface images were also taken to manifest possible size variations in the surface of the outer pores [39], of PSF-TF and NH_2-MIL-101(Cr)/PSF-TF. The surface view SEM images of PSF-TF and NH_2-MIL-101 (Cr)/PSF-TF are shown in Fig. S1 (c and d), and as can be seen from the surface, there is broad complex porous networks. Much more uniformly distribution of the MOFs is shown in Fig. S1 (d), which means they are free from aggregation; hence, it facilitates much easier transfer of target analyte to adsorbent surface. While cross-sectional analysis confirmed internal porosity [40]. The results, respectively, for PSF-TF and NH_2-MIL-101(Cr)/PSF-TF cross-sectional images and thickness are presented in Fig. 1(a–d). As observed in Fig. 1a and c, cross-sectional views of PSF-TF and NH_2-MIL-101(Cr)/PSF-TF, respectively, depict a very porous topography encompassing pores of variable diameters and irregular geometries, serving for the combined single effect: that of large macropores promoting rapid sample and solvent flow [41]. Besides, the accessibility of adsorbent within thin polymer film to target analytes increases. The NH_2-MIL-101(Cr) particles were seen to be well distributed throughout the network of polymer penetrating the pore walls as shown in Fig. 1c. This homogenous distribution maximizes the number of active adsorption sites possible during TF-μSPE. Furthermore, the thickness of TF is about 110.0-120.0 μm as shown in Fig. 1 (b and d) resulting in very good equilibrium between structural stability and functional performance [42]. Such thickness would be sufficient for maintaining mechanical integrity during handling. In this way, the thinness maintains rapid solvent diffusion and creates low-flow resistivity, thus improving the performance efficiency for extraction [42].

3.1.2. XRD analysis

A thorough X-ray diffraction (XRD) investigation was followed for estimating crystallinity, crystal structure, and purity of the synthesized MOFs [43]. The XRD patterns of PSF-TF, NH_2-MIL-101(Cr)/PSF-TF, and NH_2-MIL-101(Cr) are shown in Fig. 2a in the 5–80 Å range. The XRD pattern of NH_2-MIL-101(Cr) demonstrated characteristic diffraction peaks at 2Θ values of 9.03°, 16.72°, 24.92°, and 42.77° in accordance

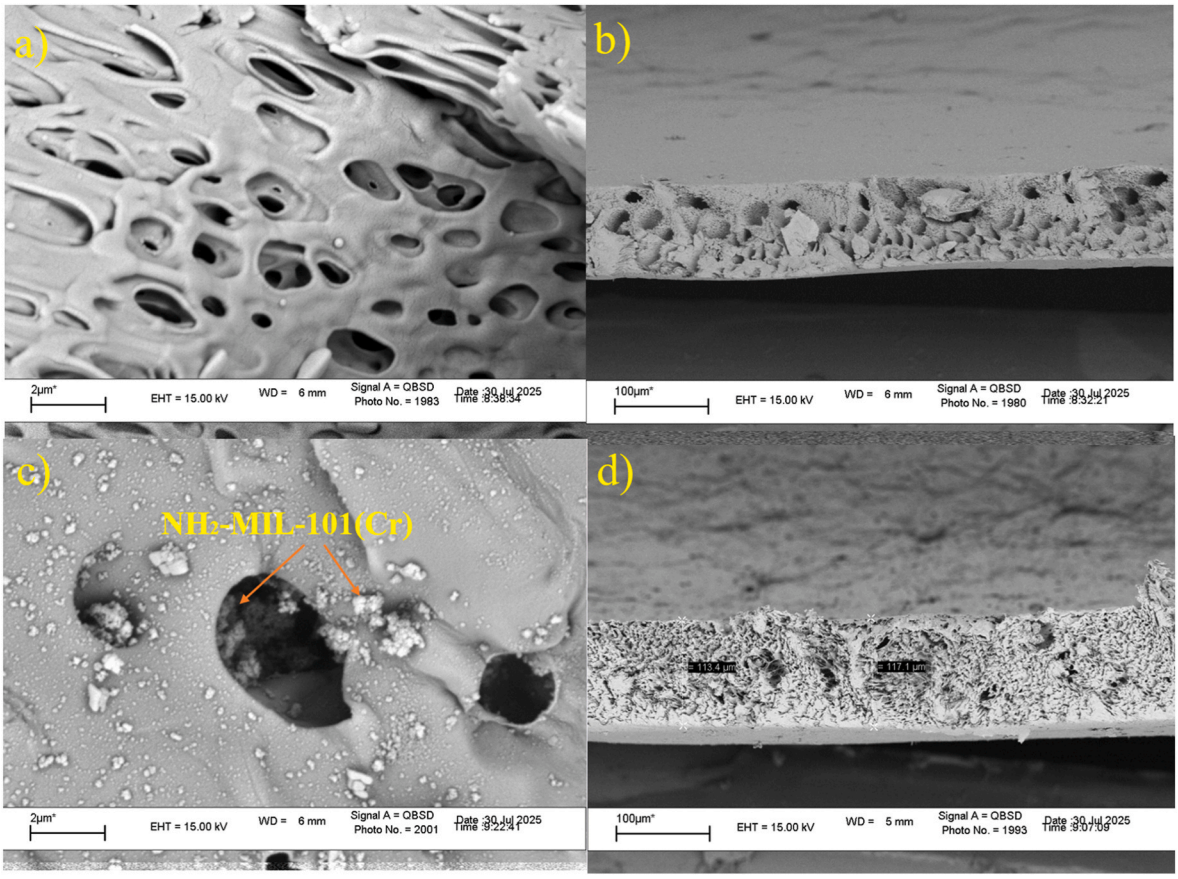

Fig. 1. shows the SEM cross-sectional images: (a) PSF-TF, (b) thickness of the PSF-TF, (c) NH_2-MIL-101(Cr)/PSF-TF, and (d) thickness of the NH_2-MIL-101(Cr)/PSF-TF.

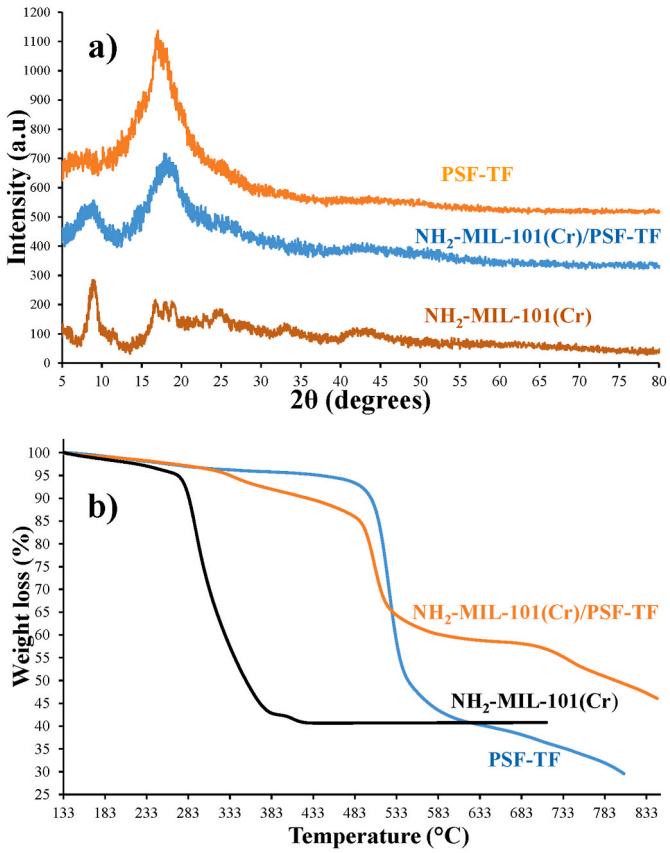

Fig. 2. (a) XRD pattern of NH_2-MIL-101(Cr)/PSF-TF, PSF-TF, and NH_2-MIL-101 (Cr), and (b) TGA pattern of NH_2-MIL-101(Cr), NH_2-MIL-101(Cr)/PSF-TF, and PSF-TF.

with previous reports [34]. These sharp diffraction peaks indicate that the NH_2-MIL-101(Cr) was synthesized with high efficiency and point to long-range ordering and crystallinity of the framework. The XRD pattern of PSF-TF is characterized by a broad band in the range of 10-25° 2Θ. This is indicative of the amorphous nature of the polymer, as shown in Fig. 2a. The XRD profiles of NH_2-MIL-101(Cr)/PSF-TF are shown in Fig. 2a, and they prove that the intensity of the diffraction peaks corresponding to the MOF in the hybrid form was reduced with respect to pure MOFs. This reveals the fact that the introduced polymer makes the change in crystallinity of the MOFs.

3.1.3. FT-IR analysis

Kindly see the supplemental information (ESI) for specific information regarding the FT-IR analysis.

3.1.4. Thermal gravimeter analysis (TGA) interpretation

The TGA was used to evaluate the thermal stability of NH_2-MIL-101 (Cr), PSF-TF, and NH_2-MIL-101(Cr)/PSF-TF. The curve was recorded in an air environment at a temperature up to 800 °C with a heating rate of 10 °C per minute. From the TGA curves Fig. 2b, two major loses of weight were recorded for NH_2-MIL-101(Cr). Approximately 3 % weight loss in this system was observed within the temperature range of 233.0-280.0 °C due to the removal of organic solvent residues and residual 2-aminoterephthalic acid that could be confined between the smaller pores, leaving NH_2-MIL-101(Cr) intact. The second weight loss, ranging from 283 °C to 383 °C, seems to be 54 %, accounted to the thermal degradation of 2-aminoterephthalic acid associated with the chromium oxide clusters. At 720 °C, the sample would have retained (40.8 %) of its original weight as a result of chromium oxide formation. The thermal stability of PSF-TF is excellent until 499 °C. It started to degrade thereafter, and the mass was changed by about (50 %) in the temperature range of 500 to 577 °C, as depicted in Fig. 2b, indicating the degradation of PSF. After that, there is a slight decline in mass of around (12 %) in temperature range between 533 and 600 °C. In addition, at temperatures over 790 °C, a further (29 %) of mass is preserved or stabilized [44]. Fig. 2b revealed the TGA curve for the NH_2-MIL-101 (Cr)/PSF-TF which was stable in the temperature range of 133-345 °C. Between 345 and 500 °C, there was approximately a 10 % weight loss, which is characteristic of thermal degradation of polysulfone, particularly involving sulfonic group losses from the polymer chains [45]. A sharp decline in the curve at 500 to 533 °C signified a total of approximately 25 % weight loss, which indicates degradation of polysulfones and perhaps part of the Cr-MOF. The mass is stabilized at temperatures over 833 °C, about 46 %, which might be attributed to the presence of chromium oxide. This confirms that MOFs were distributed evenly in the polysulfone solution.

3.2. Optimization of the extraction condition

This study's sample preparation was divided into two sections: section one included a few mL of acetonitrile and ultrasound assisted extraction were used in extracting acetamiprid and thiacloprid from food sample; then added ultra-pure water dissolves the extraction solvent on it. The water added to the sample in this step is to collect the acetonitrile solvent containing pesticides from the fruit and vegetable sample and avoid the use of more organic solvent. Meanwhile, in the next step, which is the preconcentration of the analytes with the adsorbent, the absorption of pesticides from the aqueous solution is carried out with much higher efficiency. The three parameters affecting extraction efficacy in this section were the type of solvent, the volume of solvent, and the time of sonication. In this section, the type of solvent and time of sonication were optimized. According to the modified UAE, the extraction solvent should be one that is miscible with water and low in toxicity but has a great extraction ability towards pesticides [33]. In accordance with the earlier studies, among various solvents having these features were chosen and studied-three solvents, namely acetonitrile, ethanol, and methanol [33]. For this purpose, 1.4 mL of each solvent was transferred to tubes containing 6.0 g of spiked cucumber sample with acetamiprid and thiacloprid were extracted and determined using the method described in Section 2.8 under the same conditions. As shown in Fig. S3, extraction efficiency was observed to be the best in the case of MeCN, which may be attributed to its relatively higher polarity and aprotic compared to the other two solvents [33]. Notably, acetonitrile exhibited minimal volume reduction during ultrasonication, due to its much higher boiling point, consequently, solvent evaporation was limited, resulting in improved extraction repeatability compared with the other two solvent. The second factor that seemed to have an effect upon extraction and intensity of the analytical signal was that of sonication time. As indicated in Fig. S4, extraction efficiency increased with sonication time until 17.0 min and stayed constant afterward. The ultrasound energy facilitated solvent penetration into the sample matrix and the concurrent extraction of the pesticides into the extracting solvent [33]. Hence, a longer period of sonication led to higher pesticide extraction. Finally, to ensure complete extraction of the target analytes, the sonication time for subsequent experiments was selected at 20.0 min.

In this study, the volume of extraction solvent (MeCN) was optimized on BBD since the optimal volume depended on the amount of sample. The second factor was optimized before the second section, which was the volume of ultrapure water and which was optimized by the BBD. In section two, parameters that exert different effects on the extraction efficiency of the sorbent (NH_2-MIL-101(Cr)/PSF-TF) were optimized. The pH of the aqueous solution was thus optimized by BBD as the factor greatly influencing the overall extraction performance. Furthermore, volume of desorption solvent post TF-μSPE which was the critically significant factor that could tremendously affect extraction performance. As the extraction solvent volume decreases, the extraction

efficiency increases because with the increased volume of desorption solvent, the analyte gets diluted. Hence, it was decided that a desorption solvent volume of at least 150.0 μL is required for complete immersion of the adsorbent inside the pipette tip. A lower volume of desorption solvent could not be considered, as complete immersion of the adsorbent in the solvent is crucial for desorption.

3.3. Optimization of extraction conditions by Box-Behnken

RSM is a very appropriate and accurate optimization process by using which the optimal parameters are predicted through modeling and analysis study of independent variables on the response [46]. The BBD under RSM was chosen for it is efficient and requires fewer experimental units as compared to other RSM methods [47]. The design has three levels for each factor and requires fewer experiments for evaluating multiple variables with their interactions [48]. After the BBD optimization of extraction parameters to select the most optimal conditions, the system suitability parameters studied to derive that the HPLC system has been working optimally before the actual validation process. In this study, the BBD technique was employed in order to (i) find optimum values for the parameters; (ii) find variables that have a significant effect on peak area; (iii) optimize the peak area of the analytes, and (iv) study interactions. Several experimental parameters including pH (A), extraction solvent volume (B), and aqueous sample volume(C) were modified to perform the BBD. The response for each pesticide was calculated using the HPLC peak areas of two analytes as given in Table S2, for a three-factorial design with three levels (−1, 0, and +1) in the present study. The quadratic model was used to fit all pesticide responses. Tables S3 and S4 show the statistical analysis and mathematical model fitting of the experimental results about the adsorption of acetamiprid and thiacloprid. The quadratic model could significantly explain the responses of the variables and their interaction, according to ANOVA. The F-value for the model of the analyte acetamiprid (R1) was established at 29.55, whereas that of thiacloprid (R2) was 23.17. Hence, these values indicate the validity of the model statistically for the above two analytes. P-value less than 0.0500 indicates significant model terms [49]; R1 had a P-value of 0.0001, while R2 had a P-value of 0.0002. Hence, this confirmed the importance of the quadratic model terms. The non-significance of the Lack of Fit F-values is advantageous for better fitting of models. In number, Lack of Fit F for R1 was 1.29 while R2 had 0.66. It shows that the Lack of Fit is non-significant concerning pure error [50]. The parameters that assured all precision and accuracy of the model are C.V. %, standard deviation, and determination of coefficient (R^2); which could be referred in Table S5. R2 values of all determination coefficients are closer to 1. Therefore, the regression curve fits the data with less than 99 percent accuracy. The difference between adjusted R^2 and predicted R^2 is less than 0.2. The adjusted and predicted R^2 for R1 were 0.7777 and 0.9414, respectively. For R2, the adjusted and predicted R^2 were 0.7933 and 0.9258, respectively, thus, the difference is less than 0.2. Adequate accuracy is one of the parameters that serve to measure how well the selected quadratic model fits the data. The signal-to-noise ratio which is termed as "adequate precision" is more than 4 [50]. Calculated signal-to-noise ratios of the two analytes were found to be 20.5235 for R1 and 18.3528 for R2. This demonstrates the ability of the model to traverse the design space in an efficient manner and argues for the statistical significance of the generated model. The subsequent step in the design process involved the optimization of the factors deemed critical for the experiment and defining the response surface with their interactions in the BBD, as shown in Fig. 3; the generated response surfaces for the design are shown, illustrating the 3D response surface plots of the important variables. Three-dimensional surface response plots and contour plots comparing extraction efficiencies of the studied pesticides were drawn for the variables A (pH), B (extraction solvent volume), and C (aqueous solution volume) in a specific manipulated range while holding other variables constant and under ideal conditions; these results indicated the strong correlation existing between the independent parameters and their respective maximum response. Important to the elimination of R1 and R2 were pH

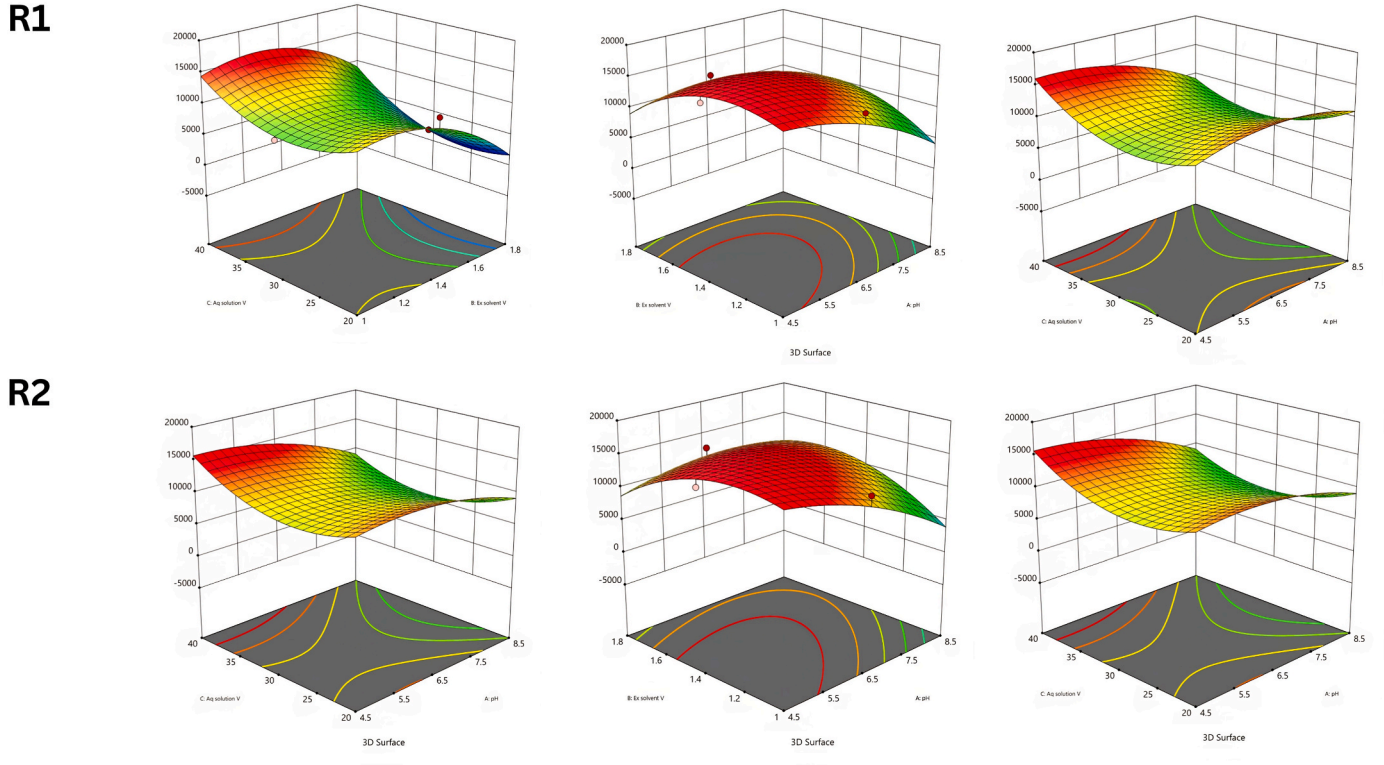

Fig. 3. The results obtained for the interaction between parameters using Design Expert software. (R1) for acetamiprid (R2) for thiacloprid. The 3D plot of pH, aqueous sample volume(mL), and extraction solvent volume(mL) interaction.

and aqueous sample volume. Sample solution pH has, in fact, heavily influenced extraction efficiency, playing a key role for analytes in MOFs' pore adsorption and consequently inducing MOF crystal shape change, charge species alteration, and change of analytes' existing forms [51]. Pesticides are dependent on pH, which in turn governs their hydrophobicity and hydrophilicity. In this research, the area of the elution peak correlating to sample pH values of 4.5-8.5 was investigated by using 0.1 M solutions of HCl and NaOH. The signals increased with increasing pH from 5.0 to 6.0. Then, extraction was maximized from pH 5.5 to 8.5, but thereafter decreased sharply, perhaps due to insecticide degradation or sorbent instability under highly alkaline conditions [52]. The major parameter in the UAE step is the volume of extraction solvent. The solvent volume should be enough to extract the pesticides from 6.0 g of the sample fruit and vegetable samples. In other words, the solvent should be able to completely interact with the sample surface and penetrate into it [33]. To ascertain the ideal solvent quantity giving maximum extraction efficiency, different volumes of MeCN (1.0, 1.4, and 1.8 mL) were added to 6.0 g of spiked samples. They were analyzed following the procedure outlined in section 2.8.a. As seen in Fig. 3, extraction efficiency was actually favored by using 1.4 mL of MeCN; thereafter 1.4 mL of MeCN was used for the subsequent experiments. Sample volume affects the peak area directly: the greater the sample volume, the more pesticides cause analytes to adsorb to the sorbent [53]. Different volumes of sample were used (20.0, 30.0, and 40.0 mL), the 40.0 mL sample volume was chosen for this study since a greater volume would permit greater recovery and enrichment during the extraction process.

3.4. Determination of the point of zero charge pH (pH_{pzc})

Point of zero charge (pH_{PZC}) tells us about pH at which net charge of solid surface particles becomes neutral. At the pH_{pzc}, the amounts of acidic functional groups and basic functional groups on the sorbent are equal. Below it, the sorbents are positively charged and prefer to adsorb anionic species. Above it, cationic species are preferred [54]. The immersion method was used to find the pH_{pzc} for (NH_2-MIL-101 (Cr)/PSF-TF). We prepared 10 solutions, each containing 7.0 mL of 0.1 M sodium nitrate. The pH of each solution was set at 2.0 to 11.0, the change of pH was done by the addition of 0.01 M NaOH and 0.01 M HCl. Then, 50.0 mg of the thin films was introduced to each of the solutions, and the mixtures were agitated for 24 h. Finally, the pH of each solution was checked again. The initial pH value (pH_i) and final pH value (pH_f) were determined, and the data plotted against the pH_i value showed in Fig. S5. The thin films produced have a pH_{pzc} of 4.8, yielding ΔpH values of 0.0. Thin films exhibit a positive net charge below pH 4.8, which helps in the adsorption of anionic pesticides; in contrast, the opposite holds for cationic pesticide adsorption above this value, where they are more negatively charged. The optimum pH thus determined was (5.0-6.0). Above 4.8, NH_2-MIL-101(Cr)/PSF-TF thin films carried a negative charge, promoting adsorption of cationic pesticides. Mildly acidic to neutral pH conditions (~6.0) should be maintained to ensure maximum adsorption of acetamiprid. The increase in pH leads to low extraction efficiency because the electrostatic repulsion force between acetamiprid molecules and adsorbent. The extraction efficacy of the as-synthesized frameworks decreased in a very acidic medium because of their possibly hydrolytic nature at a very low value of pH (pH = 2.0) [55]. The compound thiacloprid had a positive charge at pH < 4.0. In the present study, we found that adsorbent carries a positive charge at a pH of less than 4.8. Hence, the electrostatic repulsion leads to decreased extraction efficiencies. For the two analytes, the extraction efficiencies dropped when pH values ascended above 8.0 due to the increasing interaction that the anionic OH- species in the sample solution had with the thiacloprid cationic-π bonding [56]. Therefore, the two analytes exhibit the optimum pH of (5.0 to 6.0).

3.5. Comparison of the extraction efficiency of different amounts of MOFs in PSF-TF

Pesticide extraction using polysulfone thin films containing various loadings of NH_2-MIL-101(Cr) was studied. The films with 0 %, 16 %, 25 %, and 33 % of MOFs were synthesized, rolled, and placed into pipette tips for assessing the effect of MOF ratio on extraction efficiency. The pesticide peak area was measured after extraction under comparable conditions. Higher MOF content significantly improved extraction efficiency, confirming the MOFs were indeed related to the extraction process (Fig. 4 a); especially at 33.0 %, since this must correspond to more accessible active adsorption sites and further enhanced pore accessibility within the polysulfone matrix. As the percentage of MOF increases, the overall area exposed to the analyte increases, leading to more adsorption interactions (hydrophobic, π-π, or H-bonding) [57]. However, loading the MOF above 33% was not used due to inadequate homogenization of the composite. Higher MOF contents led to non-uniform dispersion and particle agglomeration, which could negatively affect the structural integrity of the composite and the reproducibility of the extraction performance.

3.6. Reusability

The synthesized NH_2-MIL-101(Cr)/PSF-TF was tested over 80 cycles of extraction performed in optimized conditions. To evaluate the stability and reuse potential of NH_2-MIL-101(Cr) without polymer preservative (PSF) and NH_2-MIL-101(Cr)/PSF-TF, their performance were tested on fruit and vegetable spiked with 100.0 μg kg^{-1} of acetamiprid and thiacloprid. According to HPLC-PDA findings (Fig. 4 b), NH_2-MIL-101(Cr)/PSF-TF maintained almost consistent extraction efficiency throughout the first 50 cycles, after which a gradual depreciation in

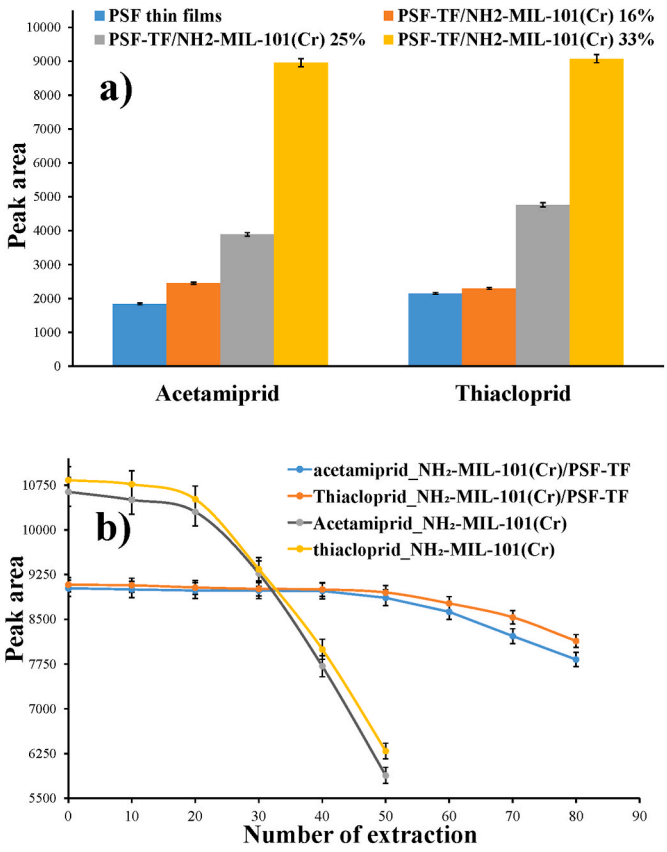

Fig. 4. (a) Comparison of the extraction efficiency of different amounts of Cr-MOF in PSF-TF. (b) Extraction performance and stability of the thin films adsorbed across 80 reuse recycle.

performance set in. However, in the case of 20 mg of NH_2-MIL-101(Cr) packed in the pipette tip, the results showed a higher extraction efficiency than when embedded in the polymer thin film. In contrast, after 20 reuses of NH_2-MIL-101(Cr) adsorbent, the extraction efficiency decreases significantly. Overall, these observations indicate that the stability of NH_2-MIL-101(Cr)/PSF-TF is increased compared to the case where NH_2-MIL-101(Cr) is used without polymer. It maintains its extraction efficiency for a significant number of cycles and is free from backpressure during extraction, which is much easier to use.

3.7. Figures of merit

The analytical performance of the developed UAE-TF-μ-SPE technique with NH_2-MIL-101(Cr)/PSF-TF as sorbent under optimal conditions was confirmed by evaluating relative recovery, the limit of detection (LOD), limit of quantification (LOQ), linearity range (L.R.), and relative standard deviation (RSD) [58,59] for the two target NEOs. The analytical performances of the improved technique are shown in Table 1. For the repeatability test, spiked cucumber samples were extracted at 40.0 μg kg^{-1} concentration for each of the analytes studied; the RSDs obtained from five results of replicated studies ranged from 2.7 % to 4.9 %. Thus, the inter-day precision was determined using three replicate experiments spread over three days without changing the sorbent, thereby suggesting the method has adequate precision for pesticide analysis. The method showed good L.R in the range of 1.0-200.0 μg kg^{-1} for acetamiprid and thiacloprid, while the respective R^2 values were 0.999 for acetamiprid and 0.996 for thiacloprid, indicating excellent linearity for the analyte of interest. The LOD was determined to be 0.2 μg kg^{-1} for both analytes, with the S/N at 3, while the LOQ established at S/N 10 was also 1.0 μg kg^{-1} for acetamiprid and thiacloprid.

3.8. Real samples analysis

The applicability and accuracy of the UAE-TF-μSPE method in various real samples ranging from cucumbers to tomatoes, plums, and apples was investigated by extracting NEOs under optimal conditions. HPLC-PDA typical chromatograms with 5.0, 30.0, 100.0 and 150.0 μg kg^{-1} spiked after the UAE-TF-μSPE method onto cucumber and tomato, respectively, are presented in Fig. 5. Plum is shown in Fig. S6. The results reveal that acetamiprid and thiacloprid in all the unspiked samples are below their limit of quantification. According to this, the proposed method was finally evaluated on grounds of the relative recovery rate of standard addition. In the recovery experiment, four concentrations of acetamiprid and thiacloprid, 5.0, 30.0100.0 and 150.0 μg kg^{-1}, were spiked into sample matrices. Table 2 summarizes these quantitative results and the relative recovery of target compounds. Average recovery rates in real samples for the two target compounds spiked were 82.0-102.0 %. This method, therefore, proved efficacious with terrific sensitivity towards pesticides.

Table 1
Analytical performance characteristics of the UAE-TF-μSPE-HPLC-PDA for the determination of neonicotinoids.

Analytes	LOD[a]	LOQ[b]	L.R[c]	RSD%[d]	RSD%[e]	R^2[f]
Acetamiprid	0.2	1.0	(1.0-200.0)	4.0	4.9	0.999
Thiacloprid	0.2	1.0	(1.0-200.0)	2.7	4.0	0.996

[a] Limit of detection (S/N = 3) (μg kg^{-1}).
[b] Limit of quantification(S/N = 10) (μg kg^{-1}).
[c] Linear Range (μg kg^{-1}).
[d] Relative standard deviation at a concentration of 40.0 μg kg^{-1} for each analyte for intra-day (n = 5).
[e] Relative standard deviation at a concentration of 40.0 μg kg^{-1} for each analyte for inter-day (n = 3).
[f] Coefficient of determination.

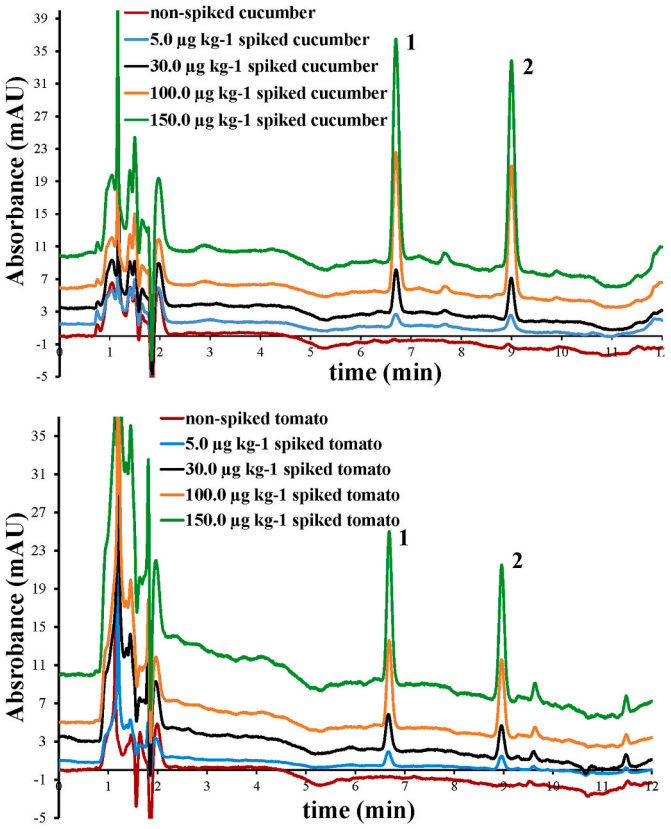

Fig. 5. The UAE-TF-μSPE-HPLC-PDA chromatograms of pesticides in unspiked and spiked cucumber and tomato were extracted by NH_2-MIL-101(Cr)/PSF-TF. 1: acetamiprid. 2: thiacloprid.

3.9. Matrix effect

The matrix effect percentage (ME %) was evaluated employing the below equations which are based on the analytical signals obtained in non-spiked and spiked samples [29,60].

$$ME\% = \frac{As - An}{Aw} \times 100$$

An, Aw, and As correspond to the peak response of the analyte from the non-spiked sample, spiked ultra-pure water and the spiked sample, respectively. In Table 2, the determination of target analyte in real sample cases is provided. The matrix effect for the analyte studied indicates that there is slight suppression of the signal. Values well within acceptable limits demonstrate the suitability of the method for analyzing the analytes in real samples without significant matrix interference.

3.10. Comparison of the proposed method with other methods

Over the years, several procedures have been explored for extracting pesticide residues from samples, and these include methods in Table 3 featuring this technique compared with some of the main alternative ones. The extraction efficiency of UAE-TF-μSPE-HPLC-PDA, using NH_2-MIL-101(Cr)/PSF-TF as a sorbent, was found to be comparable to that from other methods. Nevertheless, the extraction times and the requirement for organic solvents are lower than those of other methods. Consequently, this method is very applicable for quantifying pesticides in actual samples. In addition, we efficiently extract acetamiprid and thiacloprid in food sample via UAE and the sorbent is easily rolled and placed into the pipette tip through a simple process without the need for advanced laboratory equipment. The values of detection limit and linearity range obtained in our study, as provided in Table 3, are either

Table 2
Obtained cucumbers, tomatoes, plums, apples, and samples recoveries using a modified UAE-TF-μSPE-HPLC-PDA technique.

Cucumber										
Analytes	Acetamiprid					Thiacloprid				
Spiked(μg kg^{-1})	0	5.0	30.0	100.0	150.0	0	5.0	30.0	100.0	150.0
Founded(μg kg^{-1})	≤LOQ	4.2	25.8	100.0	147.0	≤LOQ	4.3	26.2	102.0	149.5
RR%	-	84.0	86.0	100.0	98.0	-	86.0	87.3	102.0	99.6
ME%			89.0					94.0		
Tomatoes										
Spiked(μg kg^{-1})	0	5.0	30.0	100.0	150.0	0	5.0	30.0	100.0	150.0
Founded(μg kg^{-1})	≤LOQ	4.1	25.5	92.4	143.5	n.d	4.5	27.6	96.2	148.3
RR%	-	82.0	85.0	92.4	95.6	-	90.0	92.0	96.2	98.8
ME%			84.0					87.0		
Plums										
Spiked(μg kg^{-1})	0	5.0	30.0	100.0	150.0	0	5.0	30.0	100.0	150.0
Founded(μg kg^{-1})	n.d	4.4	27.6	94.8	145.5	≤LOQ	4.2	27.0	94.3	143.4
RR%	-	88.0	92.0	94.8	97.0	-	84.0	90.0	94.3	95.6
ME%			81.0					85.0		
Apples										
Spiked(μg kg^{-1})	0	5.0	30.0	100.0	150.0	0	5.0	30.0	100.0	150.0
Founded(μg kg^{-1})	≤LOQ	4.3	27.0	96.4	149.0	≤LOQ	4.6	27.9	97.0	151.5
RR%	-	86.0	90.0	96.4	99.3	-	92.0	93.0	97.0	101.0
ME%			89.0					94.0		

n.d: not detected.
RR: related recovery.
ME: matrix effect.

Table 3
Comparison of the UAE-TF-μSPE-HPLC-PDA method with other related methods for the determination of pesticides.

methods	Samples (amount, g)	LOD (μg kg^{-1})	L.R (μg kg^{-1})	RSD %	Solvent volume (mL)	Time (min)	RR %	Ref.
QuEChERS-GC–MS/MS	vegetable and fruit (10.0)	0.21-9.6	(0.63-1000)	1.2-12.9	10.0	13.0	76.4-112.1	[61]
SPE-GC-MS	Vegetable and water (10.0)	294.0	-	1.6-4.1	200.0	1500.0	94.0-104.0	[62]
PT-μSPE-UHPLC-MS/MS	Vegetable (10.0)	0.03-10.0	0.1-200.0	5.3-19.0	0.2	22.0	64.0-133.0	[63]
MSPE-HPLC-MS-MS	Vegetables and fruits (10.0)	0.52–1.83	5.0–500.0	1.2-2.8	4.0	≥20.0	62.8-94.2	[64]
MSPE-HPLC–UV	Vegetables (10.0)	0.01-0.08	1.0–1000	5.9-9.1	300.0	30.0	88.4–112.0	[65]
UAE-TF-μSPE-HPLC-PDA	Vegetables and fruits (6.0)	0.2	(1.0-200.0)	2.7-4.0	1.55	35.0	85.0-102.0	This study

MSPD: matrix solid-phase dispersion.
SPE: solid phase extraction.

better or at least comparable to the ones previously reported. The present method possesses several advantages over those previously reported, including ease of loading of NH_2-MIL-101(Cr)/PSF-TF onto pipette tips, reusability of sorbent several times, reduced consuming organic solvent as well as desorption times, lowering backpressure, and preventing clogging formation in pipette tip. Moreover, the method under consideration displayed efficiency that is comparable or higher than the other previously reported approaches.

4. Conclusion

To this day, acetamiprid and thiacloprid analysis in food samples has remained a challenge primarily due to the complexity of the sample matrix. In this study, UAE and μSPE methods were combined for the first time to overcome these hurdles to food sample preparation before analysis. One of the main drawbacks of PT-μSPE method is the backpressure from the sample solution and clogging of the packed adsorbent even though the PT-μSPE methods are very efficient. In this study, to offset these setbacks, MOFs were incorporated into a rolled thin film of polysulfone polymer and mounted in pipette tips. In general, this technique provides a fast, cost-efficient method for extraction and preconcentration of residues of NEOs in food samples that is simple, less solvent-consuming, reproducible, and efficient. The results obtained confirm that the polysulfone thin films, in addition to serving as a support material for the MOFs, also enhanced the overall extraction performance by improving the surface adsorption of NEOs. Moreover, because of their enhanced stability, the polysulfone films containing MOFs could be reused many times. Overall, this strategy can lead to the achievement of a detection limit of 0.2 μg kg^{-1} in fruit and vegetable samples within about 40 min, consuming only 1.4 mL of acetonitrile solvent. Despite the significant strengths of this study, especially the simplicity of operation and the stability of the adsorbent, it can be noted that the extraction efficiency of NH_2-MIL-101(Cr) is relatively lower than that of NH_2-MIL-101(Cr)/PSF-TF, which is due to the partial embedding of the MOF in the polymer. In future studies, it may be possible to improve the extraction efficiency by using alternative polymers or by making the polymer films thinner. Thus, these promising results anticipate that these thin films can be used in future studies involving other MOFs and composites for the preconcentration of other pollutants in complex matrices.

CRediT authorship contribution statement

Soleen Burhan Ahmed: Writing – original draft, Resources, Methodology, Investigation, Formal analysis, Data curation. **Soleyman Moinfar:** Writing – review & editing, Validation, Supervision, Project administration, Formal analysis, Conceptualization.

Declaration of competing interest

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.aca.2026.345278.

Data availability

No data was used for the research described in the article.

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