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Synthesis of MIL-53(Al) /Al thin film as a novel thin film for microextraction of pesticides in water, juice fruit and vegetable samples

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ABSTRACT

Traditional microextraction methods, such as micro-solid-phase extraction (μSPE) and conventional fiber-based SPME, suffer from complexity, long extraction times, and insufficient surface area, resulting in poor sensitivity for trace-level pesticide analysis. To address these limitations, for the first time, MIL-53(Al) metal-organic framework as a thin-film (TF) was synthesized directly on an aluminum thin sheet for the determination of three insecticides (thiacloprid, imidacloprid, and acetamiprid). To enhance the adsorbent amount, a 25*35 mm of MIL-53(Al)/Al thin sheet was rolled and placed in a pipette tip. The present approach offers significant advantages: enhanced surface area and rapid extraction in 15 min, and ease of use without the risk of clogging and back-pressure in pipette tip-μSPE. Response surface methodology optimization established optimal conditions at pH 6.5 and 50.0 mL sample volume. The TF-MOF-HPLC method achieved superior analytical performance with detection limits of 0.3–1.5 μg/L and quantification limits of 1.0–5.0 μg/L. Linear ranges of 1.0–300.0, 3.0–350.0, and 5.0–450.0 μg/L were obtained for acetamiprid, thiacloprid, and imidacloprid, respectively ($R^2 > 0.95$). The target insecticides were subsequently extracted from cucumber samples by ultrasonic extraction using only 1.4 mL of acetonitrile and pre-concentrated using the TF-MOF microextraction method. Method validation in water, cucumber, and juice samples demonstrated excellent recovery rates (86.0–100.7%) with good precision (relative standard deviation) ≤ 3.3%. These results indicate that the developed TF-MIL-53(Al) method is a simple, rapid, and highly sensitive alternative to conventional microextraction methods for environmental and food safety monitoring.

1. Introduction

Pesticides are chemical substances used to protect crops from harmful organisms and diseases, with their classification based on chemical composition and functional role [1,2]. On the other hand, the excessive or unregulated use of these chemicals heightens the dangers of overexposure and raises serious concerns regarding their potential impact on both human health and the surrounding environment [2]. They pose a significant threat to the nervous system [3]. Exposure of humans to pesticides is related to acute and long-term health problems [4]. Their extensive misuse has contributed to a concerning accumulation of residues in vegetables, fruits, water, and soil [3]. Pesticides include herbicides (e.g., glyphosate), fungicides (e.g., chlorothalonil), and insecticides (e.g., neonicotinoids) [5].

Among these categories, insecticides require particular attention due to their widespread use. Neonicotinoids represent a major insecticide class widely used in crop protection and seed treatments [6]. The extensive global use of neonicotinoid insecticides has generated significant ecological concerns due to their adverse effects on pollinators, aquatic ecosystems, and soil health, leading to regulatory scrutiny and demands for sustainable alternatives [7]. The increasing number of studies showing the harmful effects of pesticides emphasizes the need to develop more sensitive and reliable preparation methods that can detect multiple pesticide residues simultaneously. For pesticide detection, a variety of techniques such as gas chromatography (GC), high-performance liquid chromatography (HPLC), and liquid chromatography-mass spectrometry (LC-MS) are recognized for their high precision and sensitivity [8]. However, the efficiency of these analytical instruments depends fundamentally on the quality of sample preparation methods from their introduction into the instrument, which

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necessitates efficient extraction and preconcentration procedures. Solid-phase microextraction (SPME) is an analytical technique wherein target analytes undergo partitioning between the sample matrix and a thin polymeric film coating that functions as the adsorbent [9].

Among the numerous variants of the SPME technique, thin film - microextraction (TFME) deserves particular consideration due to its distinctive geometric configuration that differentiates it from conventional SPME approaches. [10]. Unlike traditional SPME methodology that employs cylindrical fiber geometry, TFME utilizes a flat support structure with a significantly more extensive surface area, thereby providing a substantially larger sorbent contact area in the form of a thin film coating on the support material. This enhanced surface area geometry results in improved extraction efficiency and capacity compared to conventional fiber-based SPME [10]. The initial TFME device was introduced in 2003 [11] subsequent developments have led to numerous modifications and improvements in both the physical configuration of the adsorbent and the underlying support materials, expanding the versatility and applicability of this microextraction approach [12]. To address these analytical challenges and improve detection limits, thin-film microextraction has emerged as a promising preconcentration technique. Thin films have been employed as an extraction phase for separating a wide variety of compounds [13]. Thin-film microextraction has garnered significant interest due to its rapid extraction kinetics, strong adsorption capacity, low solvent requirements, and ability to effectively eliminate the saturation problem [14]. In addition to effectively addressing and overcoming the saturation limitations commonly encountered in traditional extraction methodologies [15], TFME characterized by an exceptionally high surface area-to-volume ratio, is employed as an efficient adsorbent. To enhance the performance of thin film microextraction, researchers have undertaken diverse approaches to develop and implement novel sorbent materials [16]. Sorbent materials play a critical role in determining the extraction process's performance, including its efficiency, capacity, selectivity, sensitivity, and adaptability [14], such as polymers, polymeric ionic liquids, nanoparticles, covalent organic frameworks (COFs), and metal-organic frameworks (MOFs). Of these, MOFs are especially noteworthy because of their remarkable characteristics [17].

MOFs represent a rapidly advancing class of porous, crystalline materials constructed through the coordination-driven assembly of metal nodes (clusters or ions) and multidentate organic linkers [18]. The remarkable intrinsic properties of these materials, including ultrahigh porosity, substantial thermal stability [19], easy chemical modification [20], and structural robustness, have significantly expanded their potential technological applications, consequently stimulating extensive scientific and technological interest across multiple disciplines [19]. Aluminum-based metal-organic frameworks (Al-MOFs) offer several benefits, including exceptional physicochemical stability, which is attributed to the high bond strength of aluminum-oxygen (Al—O) linkages. Advances in synthetic methodologies have enabled the production of Al-MOF materials through more cost-effective and sustainable approaches. Al-MOFs have demonstrated significant potential in insecticide extraction applications, with MIL-53 (Al) mixed matrix membranes successfully applied for enrichment of neonicotinoid insecticides from environmental water samples, achieving satisfactory detection limits and good reusability [21]. MIL-68(Al) has been successfully applied for extracting various pesticides from fruit beverages, achieving high enrichment factors and satisfactory extraction recoveries [22]. Additionally, magnetic aluminum-based MOF composites have been developed for the efficient extraction of carbamate insecticides from agricultural products, demonstrating excellent reusability and high adsorption capacities [23].

Although the pipette tip-μSPE (PT-μSPE) technique has been considered due to its simplicity in packing the pipette tip with the adsorbent and low consumption of desorption solvent, the presence of backpressure inside the MOF-filled tip reduces the reproducibility and speed of the method [24]. It should also be noted that the tip packed with MOF quickly clogs when analyzing real samples such as fruit and vegetable juices [24]. In several previous studies, in order to overcome the problem of clogging and back pressure of the packed pipette tip, MOFs were spread on a polymer substrate in the form of small spherical beads and thin polymer sheets, and then were placed inside the tip [24,25]. This approach was successfully used for the extraction and determination of insecticides in real samples such as honey, fruit and vegetable juices. However, due to the entrapment of a large part of the MOF by the support polymers, the contact surface and extraction efficiency of the MOF with the sample solution were reduced compared to the case without polymer substance.

In this study, for the first time, the MIL-53(Al) was directly synthesized on thin aluminum sheets using solvothermal methods and used as an adsorbent in the thin-film microextraction technique. In order to further increase the amount of adsorbent, the thin aluminum sheets containing MOF were rolled and placed inside the pipette tip. The present approach, in addition to being simple, does not have the back-pressure and clogging problems of the PT-μSPE method, and at the same time, the extraction efficiency is increased due to the placement of the MOF on the surface of the substrate.

This represents the first application of synthesized MIL-53(Al) / aluminum thin film (MIL-53(Al)/Al-TF) for neonicotinoid microextraction in water, juice and cucumber samples. The novel MIL-53(Al)/Al-TF incorporated within a pipette tip was systematically optimized for factors affecting, including: sample solution pH, sample volume, desorption solvent type and volume, with extracted analytes quantified by HPLC-PDA. Response surface methodology (RSM) was employed to systematically assess and optimize the principal factors influencing pesticide adsorption in order to identify optimal conditions. After optimization, the MIL-53(Al)/Al-TF method was coupled with ultrasonic extraction to evaluate the analytical method for pesticide extraction and determination in food samples such as cucumber. Using ultrasonic extraction, pesticides were extracted from the cucumber matrix using the minimum amount of organic solvent, and in the second step, they were preconcentrated with high efficiency using MIL-53(Al)/Al-TF inside the pipette tip without clogging or interference. The adsorption capability and extraction performance were comprehensively evaluated against conventional methods. Results confirmed that the rolled thin-film configuration enhanced extraction efficiency while eliminating additional support materials, establishing a practical platform for routine environmental and food safety monitoring.

2. Materials and methods

2.1. Materials

Aluminum nitrate nonahydrate (Al $(NO_3)_3 \cdot 9H_2O$, 98%) and Terephthalic acid (C_6H_4 $(CO_2H)_2$) were purchased from Biochem Chemopharma (Cosnesur Loire,France). Methanol (99.5%) and NaOH (97%) were purchased from *Thomas Baker* (Mumbai, India). *N, N*-Dimethylformamide (DMF, 99.5%) was purchased from CARLO ERBA (France). Acetonitrile (99.9%) and HCl (37%) were purchased from Merck KGaA (Darmstadt, Germany). Aluminum foil was purchased from a local market. Analytical grade pesticides, including imidacloprid, thiacloprid, and acetamiprid, were obtained from Sigma-Aldrich (Seelze, Germany).

2.2. Apparatus

Scanning electron microscopy (SEM) analysis was performed using a LEO 1430VP electron microscope (Germany) operated at 15.0 kV. The particles were covered by a thin gold film, and the image was obtained using the backscattered electron detector under high vacuum conditions (5×10^{-10} Torr). Fourier-transform infrared spectroscopy (FT-IR) was performed using a PerkinElmer Spectrum RXI FTIR spectrometer (USA) in 2 *w*/w% KBr pellets at the wavelength range of 400–4000 cm^{-1} and

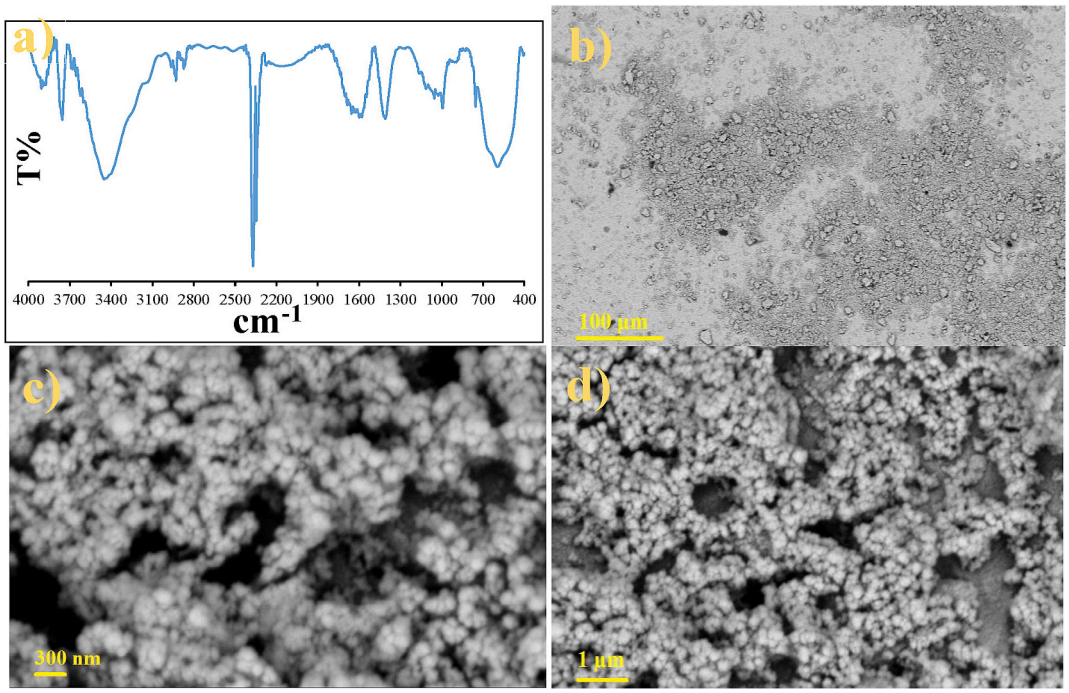


Fig. 1. (a) FTIR spectra of MIL-53 Al/Al in the range of 400–4000 cm^{-1}. (b, c and d) SEM images of MIL-53 Al/Al showing morphology at different magnifications.

resolution of 4 cm^{-1}. The extraction was controlled using a Watson-Marlow peristaltic pump (UK). pH measurements were conducted using an Eutech Instruments pH 510 pH/mV meter (USA) equipped with a CyberScan pH electrode.The oven (Binder) was used for drying and heating. The Teflon steel (100 mL) autoclave was used for performing a solvothermal reaction of the MOF synthesis. Energy Dispersive X-ray Spectroscopy (EDX) was conducted using (4500-Quanta, FEI, USA) with an accelerating voltage of 30 kV.

2.3. HPLC conditions

A high-performance liquid chromatography system equipped with an ultra C18, 150 × 4.6 mm, 5 µm (Restek, USA) column and a photodiode array detector (PerkinElmer, Flexar 15, USA) was used for the separation and quantification of extracted insecticides. The final HPLC parameters were established as described below: Chromatographic separation was achieved using a gradient elution system with ultrapure water (mobile phase A) and acetonitrile (mobile phase B). Based on the optimized method parameters, the gradient program was as follows: initial condition 23% B; 0–1.0 min, 23% to 30% B in 1.0 min (hold for 2.5 min), 30% to 40% B in 3.0 min; 40% to 62% B in 2.0 min (hold for 1.5 min); 62% to 23% B in 1.0 min followed by a return to initial conditions and column equilibration. The flow rate was maintained at 1.0 mL/min throughout the analysis with an injection volume of 15.0 µL. The column temperature was maintained at 35 °C, and detection was performed at 244 nm using the PDA detector.

2.4. Synthesis of MIL-53(Al)/Al thin film

To synthesize the MIL-53(Al)/Al thin film composite, ordinary cooker aluminum foil was used. First, 0.91 g (5 pieces) of rolled aluminum foil were washed with a small amount of methanol and ultrasonicated for 10 min to remove impurities. Subsequently, the aluminum foils were oxidized by immersion in a 2% NaOH solution, followed by ultrasonication for 10 min and manual agitation for an additional 7 min [26]. Next, the treated aluminum foils were placed in a solution comprising 0.75 g (2 mmol) of terephthalic acid and 50 mL of DMF, then subjected to ultrasonication without heating for 1 h. The reaction mixture was transferred into a Teflon-lined reactor and placed in an oven at 120 °C for 48 h.Following the cooling step, purification was performed by immersing the rolled aluminum foils in 50 mL of DMF overnight, followed by 25 mL of methanol twice for 30 min each, and finally in 25 mL of methanol for 1 h. The Al foils were subsequently dried in an oven at 200 °C for 2 h to eliminate any unreacted terephthalic acid residue.

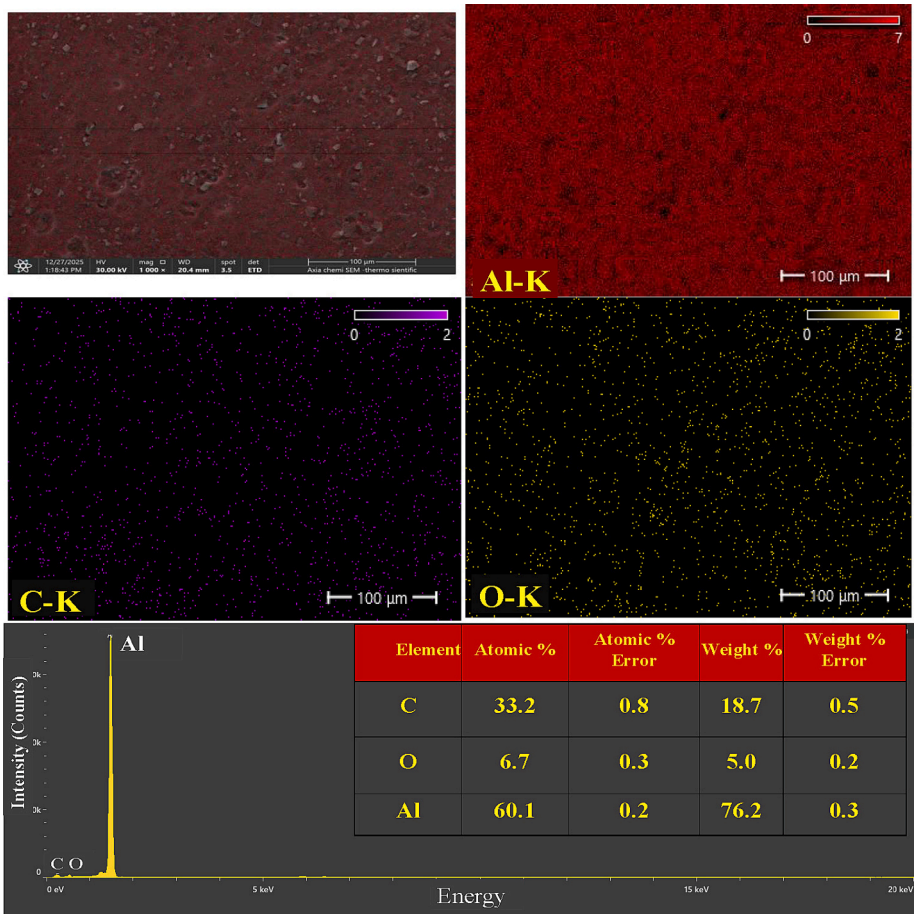
2.5. Preparation of micropipette tip extraction device

The roll of MIL-53(Al)/Al thin film prepared in section 2.3 (12 µm thick, 2.4 × 35 mm long) was placed in a 1000 µL-pipette tip. Subsequently, the prepared devices were washed sequentially with0.5 mL of acetonitrile and 1 mL of ultrapure water using a 3-mL syringe. The prepared devices were used for extracting neonicotinoid insecticides from the samples.

2.6. Preparation of samples

The collected Zakho river water sample was spiked with a certain amount of a neonicotinoid insecticide mixture. The canned orange juice was purchased from the local market. After spiking, the orange juice was diluted 1:3.33 (*v*/v) by adding 35 mL of ultrapure water to 15 mL of orange juice, resulting in a final dilution factor of 3.33. After that, it was determined according to section 2.7.

The preparation of the cucumber-spiked sample followed the protocol outlined by [27]. A cucumber was purchased from the local market. After washing it with ultra-pure water, the fruit was cut into pieces and transferred to an electric fruit mixer to blend thoroughly. 2.0 g of the prepared mix was placed into three separate plastic tubes, one of which was spiked with 75.0 µg/Kg of the insecticide mixture, and another with 150.0 µg/Kg. Next, 1.4 mL of ACN was added to each tube, followed by ultrasonication for 20 min. Then, 50.0 mL of ultrapure water was added to the tubes, and the samples were filtered through paper. The pH levels of resulted aqueous solutions were measured before analysis and adjusted to around 6.5. Finally, extraction was performed as described in Section 2.7.



Element	Atomic %	Atomic % Error	Weight %	Weight % Error
C	33.2	0.8	18.7	0.5
O	6.7	0.3	5.0	0.2
Al	60.1	0.2	76.2	0.3

Fig. 2. EDX elemental mapping images of MIL-53 Al/Al displaying the spatial distribution of Al, C, O.

2.7. Extraction procedure

The pH of the sample was adjusted to 6.5 through the controlled addition of 0.1 M HCl and 0.1 M NaOH solutions. Subsequently, 50.0 mL of the spiked sample was passed through a pipette tip containing the MIL-53(Al)/Al thin film (rolled), maintaining a flow rate of 3.0 mL/min. The adsorbed insecticides were then desorbed using 250.0 µL of methanol using a 1000 µL pipette. The 15.0 µL of collected desorption solvent was analyzed by HPLC-PDA.

2.8. Influencing factors

Four parameters were chosen for subsequent optimization: three continuous factors (sample solution volume, desorption solvent volume, and pH) and one categorical factor (desorption solvent type). Design-Expert software (version 13.0.5) was utilized to systematically design experiments aimed at investigating these parameters and their interactions. Central Composite Design (CCD) was applied to optimize the selected variables and enhance the extraction efficiency of the target neonicotinoid insecticides. For response evaluation, the combined peak areas of the three target insecticide compounds (imidacloprid, acetamiprid, and thiacloprid), as determined by HPLC, were used as the experimental response.

3. Results and discussion

3.1. FT-IR analysis

FTIR spectroscopy confirmed the successful synthesis of the metal-organic framework on the aluminum thin film substrate after it was transferred using a specialized knife. As shown in Fig. 1a the spectrum presents several characteristic absorption bands indicative of MOF formation:

The spectrum exhibits characteristic absorption bands at 1598 and 1411 cm^{-1}, corresponding to the asymmetric and symmetric COO^- stretching vibrations of the coordinated terephthalate linkers within the MIL-53 (Al) framework structure. The promotional effect of DMF in MIL-53(Al) formation has been well documented, where DMF facilitates aluminum coordination [28]. The absorption at 594 cm^{-1} corresponds to Al—O stretching vibrations, confirming the formation of the MIL-53 (Al) framework. The broad peak around 3450 cm^{-1} suggests minimal residual water content following the rigorous methanol washing and thermal activation. An additional strong band at 1384 cm^{-1} is observed, which can be assigned to C—O stretching vibrations or contributions from symmetric carboxylate stretching modes. The prominent absorption at 744 cm^{-1} corresponds to aromatic C—H out-of-plane bending vibrations, which are characteristic of the para-substitution pattern in the 1,4-benzenedicarboxylate (terephthalate) linker.

3.2. SEM analysis

Figs. 1b-d presents the surface morphology of MIL-53(Al) on Al sheet, which was examined by SEM at different magnifications, revealing a hierarchically structured material. At low magnification (100 µm) Fig. 1b shows the material as irregularly distributed micron-sized aggregates without the presence of large, well-defined single crystals, indicating that the material is composed of fine crystallites assembled into compact clusters.Fig. 1d at intermediate magnification (1 µm) exhibits aggregates that consist of densely packed submicron particles with a rough and highly textured surface, forming

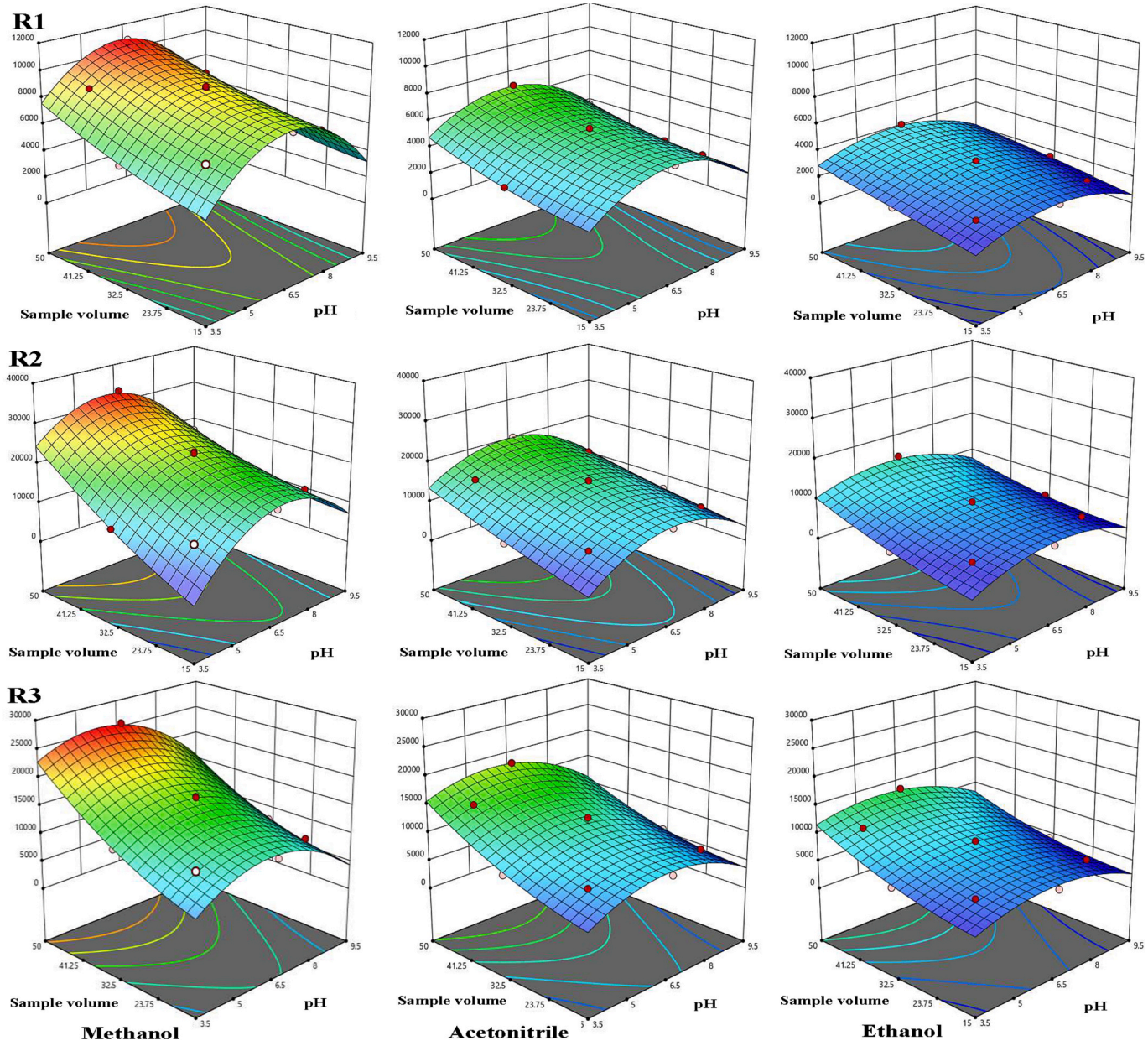


Fig. 3. Three-dimensional (3D) response surface for Imidacloprid (R1), Acetamiprid (R2), and Thiacloprid (R3).

interconnected interparticle voids. The synthesis of this MOF aligns well with the previously reported study [29]. Fig. 1c at higher magnification (300 nm) reveals densely packed nanocrystalline aggregates with distinct surface roughness, indicating multilevel porosity essential for enhanced mass transfer and adsorption capacity. The bright regions represent MOF particles, while darker areas correspond to void spaces, confirming the porous nature of the material. Moreover, individual particles exhibit sizes of 64.82–79.12 nm with morphologies ranging from spherical to irregular, typical of MIL-53 frameworks [30]. This morphology provides a high external surface area and abundant interparticle porosity in addition to the intrinsic microporosity of the MIL-53 framework.

3.3. EDX analysis and elemental mapping

Fig. 2 shows the EDX analysis, elemental quantification data, and elemental mapping of MIL-53 (Al). The EDX spectrum indicates the percentage composition of major elements in MIL-53(Al) (Al = 76.2 wt %), followed by carbon (C = 18.7 wt%) and oxygen (O = 5.0 wt%). The elemental mapping images in Fig. 2 display a uniform distribution of all elements throughout the MIL-53(Al) thin film. The aluminum mapping shows a strong and even distribution across the entire surface, while carbon and oxygen reveal consistent, evenly spread patterns that match the quantitative data. The uniform elemental distribution confirms the successful incorporation of terephthalic acid linkers into the framework and supports the formation of the characteristic MIL-53 (Al) structure, with aluminum functioning as the main metal node.

3.4. Optimization of the extraction method

The extraction parameters were systematically optimized using Response Surface Methodology (RSM) with a special design to achieve maximum analytical performance, similar to the approach employed by [31]. A central composite design (CCD) was implemented to optimize extraction parameters, incorporating three numerical variables and one categorical variable. The CCD approach offers distinct advantages: it

efficiently fits second-order polynomial models to model nonlinear relationships and curvature effects, provides adaptability in handling multiple factors, and delivers comprehensive insights into main effects, interactions, and quadratic terms with substantially fewer experimental runs compared to full factorial designs.

For the three quantitative factors (pH, sample volume, and desorption solvent volume), five levels were established (+1, −1, center point, +α, and − α), generating a comprehensive experimental design comprising 20 points. This design structure included 2^n (2^3 = 8) factorial points, 2n (2 × 3 = 6) axial points, and 6 center point replicates to refine factor optimization. The replicate center points were incorporated to minimize experimental noise and improve statistical precision Fig. 3.The categorical factor (solvent type) encompassed three different levels (methanol, acetonitrile, and ethanol), and the numerical factors levels of pH were (3.5, 5.0, 6.5, 8.0, 9.5), for those for sample volume were (15.0, 23.75, 32.5, 41.25 mL). Integration of this categorical variable expanded the experimental matrix, yielding a total of 36 randomized runs. All experiments were conducted in randomized order, with experimental configurations and corresponding responses systematically recorded. Analysis of variance (ANOVA) was performed on all response variables to assess the statistical significance of the developed models.

The ANOVA results for the formulated models are shown in tables S2-S10. For imidacloprid (R1), the model F-value of 1936.37 demonstrates exceptional model significance ($p < 0.0001$), table S2. In this case, desorption solvent volume, sample volume, pH, desorption solvent type, and their interactions represent significant factors. The Lack of Fit (LOF) F-value of 2.1 confirms that the LOF is not significant relative to pure error, validating model appropriateness (Table S2). The R^2 value of 0.9995, Adjusted R^2 of 0.9989, and Predicted R^2 of 0.9968 demonstrate outstanding model fit in Tables S3 and S4. For acetamiprid (R2), the variance analysis showed high significance with an F-value of 260.89. The LOF F-value of 1.38 shows a non-significant lack of fit in Table S5. The model achieved $R^2 = 0.9960$, Adjusted $R^2 = 0.9921$, and Predicted $R^2 = 0.9765$, indicating robust predictive capability Tables S6, S7. Nearly all input variables exert a substantial effect on the acetamiprid response predicted by the regression model. The ANOVA for thiacloprid (R3) demonstrated that the proposed model was significant with an F-statistic of 137.06, while the LOF remains non-significant, suggesting excellent data fit Table S8. The model achieved $R^2 = 0.9923$, Adjusted $R^2 = 0.9851$, and Predicted $R^2 = 0.9554$ Tables S9, S10. Extraction volume, sample volume, pH, and solvent type emerged as the most significant factors in the regression model for thiacloprid response, demonstrating their substantial impact on extraction efficiency. ANOVA results for all reduced models indicated that both R^2 and adjusted R^2 values surpassed 0.99 for each neonicotinoid compound, reflecting excellent model adequacy. The adequate precision parameter quantifies the ratio of signal to noise, with values exceeding 4 considered desirable. In this investigation, adequate precision values ranged from 50.52 to 167.17 across all analytes, indicating strong signals and confirming model significance for the extraction process. These values substantially exceed the minimum threshold, validating the models' predictive capabilities.

Solution pH emerged as a critical parameter influencing extraction performance. Optimal extraction occurred at pH 6.5, using methanol as desorption solvent. At pH values exceeding 8.0, extraction efficiency declined markedly due to surface deprotonation of the sorbent material, generating negatively charged surfaces that impede adsorption through electrostatic repulsion or competitive displacement by hydroxide ions.

Sample volume significantly influenced extraction outcomes, with responses improving progressively from 15 mL to 50 mL in accordance with mass transfer principles [31]. Using methanol as the desorption solvent, imidacloprid signals increased from 7400 units (15 mL) to 10,770 units (50 mL), acetamiprid from 15,500 to 33,045 units, and thiacloprid from 10,979 to 25,719 units. These results indicate that larger desorption volumes enhance analyte recovery by overcoming

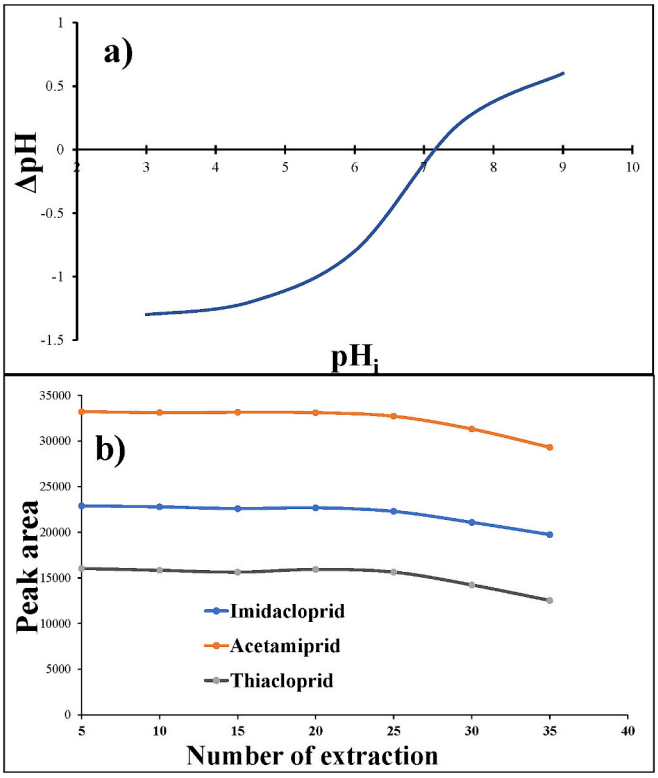


Fig. 4. (a) Point of zero charge (pH_{pzc}) determination for MIL-53 Al. (b) Effect of number of extractions on peak area for imidacloprid, acetamiprid, and thiacloprid using MIL-53 Al/Al.

analyte-sorbent interactions, with the differential recovery rates reflecting the varying hydrophobicity of the compounds. Similar trends have been reported for methanol desorption of neonicotinoids from MOF-based sorbents, where sufficient solvent volume is essential to achieve complete elution and quantitative recovery [32].

The three-dimensional response surface plots (Fig. 3) exhibited characteristic dome-shaped profiles consistent with second-order polynomial behavior. Maximum responses occurred at pH 6.5 and sample volumes of 50 mL for methanol-based desorption systems. Contour projections clearly delineated concentric zones of equivalent response, with optimal extraction windows positioned in the central-to-upper region of the design space, validating the appropriateness of the second-order polynomial model framework.

Solvent selection had a profound influence on extraction performance across all target analytes. Methanol provided optimal extraction efficiency through effective disruption of analyte-sorbent interaction, generating approximately 10,770 units for imidacloprid, 33,045 units for acetamiprid, and 25,719 units for thiacloprid under optimized conditions (pH 6.5, 50 mL sample volume). Response surfaces for methanol exhibited the highest peak intensities (red-orange zones) and broadest optimal regions. Acetonitrile demonstrated intermediate performance, producing 60–70% of methanol's response with moderate peak intensities (green-yellow zones) and narrower optimal regions. Ethanol showed the weakest extraction capability, characterized by predominantly blue-cyan zones and peak responses of 30,006,000 units across all analytes. These performance variations are attributed to differences in elution strength and intermolecular interactions at the sorbent interface. Methanol's superior performance derives from its optimal balance of polarity and hydrogen-bonding capability, facilitating efficient analyte desorption while maintaining excellent chromatographic compatibility [10].

Table 1
Analytical performance parameters for the determination of three neonicotinoid insecticides.

Neonicotinoid	RSD (%)	LOD (μg/L)	LOQ (μg/L)	Linear Range (μg/L)	r^2
Acetamiprid	2.4	0.3	1.0	1–300	0.9614
Imidacloprid	1.8	1.5	5.0	5–450	0.9679
Thiacloprid	3.3	1.0	3.0	3–350	0.9524

RSD based on 5 replicate experiments at 80.0 μg/L concentration.
LOD: Limit of Detection (S/N = 3).
LOQ: Limit of Quantification (S/N = 10).

3.5. Measuring the point of zero charge pH

The point of zero charge (pH_{pzc}) of the MIl-53(Al)/Al-TF was determined using the pH drift technique. Five separate 6.0 mL solutions of 0.01 M sodium nitrate were prepared with initial pH values of 3.0, 4.5, 6.0, 7.5, and 9.0. A piece of MIl-53(Al)/Al-TF (combined mass of 0.52 g) was immersed in each solution, and the mixtures were allowed to equilibrate for 24 h. Following equilibration, the final pH of each solution was recorded. The pH shift ($\Delta pH = pH_i - pH_f$) was calculated for each solution and plotted as a function of initial pH. The point where ΔpH equals zero, corresponding to pH 7.34, was identified as the pH_{pzc} of the MIL-53(Al)/Al thin film (Fig. 4 a). The pH_{pzc} is the pH where a material has equal amounts of positive and negative charges, creating a neutral surface. Below the pH_{pzc} (pH 3.0–6.0), the solution pH increased to 4.35, 5.7, and 6.8, respectively (ΔpH = +1.35, +1.2, +0.8), indicating proton consumption by the positively charged surface through protonation of aluminum hydroxyl and carboxylate groups. Near the pH_{pzc} at pH 7.5, minimal change occurred (ΔpH = −0.2), indicating charge neutrality. Above the pH_{pzc} at pH 9.0, deprotonation generated a negatively charged surface (ΔpH = −0.6) [33]. The pH_{pzc} of 7.34 is consistent with Al-based MOFs such as MIL-53(Al) and reflects the amphoteric nature of the framework [34].

3.6. Reusability

The prepared MIL-53(Al)/Al-TF was tested over 35 cycles of extraction performed in optimized conditions. To evaluate the reuse potential of this material, TF-μSPE performance tests were performed on a spiked aqueous sample with 100.0 μg/L of imidacloprid, acetamiprid, and thiacloprid. According to HPLC-PDA findings (Fig. 4 b), MIL-53(Al)/Al-TF maintained nearly consistent extraction efficiency throughout the first 25 cycles, after which a gradual decline in performance set in. Collectively, these findings indicate that the material withstands repeated use and retains its adsorption capability for a considerable number of cycles.

3.7. Figures of merit

Intra-day repeatability was assessed by performing five replicate analyses using samples spiked with 80 μg/L of each neonicotinoid (acetamiprid, imidacloprid, thiacloprid). The resulting relative standard deviations (RSD %) for the three compounds were ≤ 3.3%, demonstrating satisfactory precision for neonicotinoid analysis. Detection limits (LOD) calculated at S/N = 3 ranged from 0.3 to 1.5 μg/L, while quantification limits (LOQ) determined at S/N = 10 spanned 1.0 to 5.0 μg/L. Calibration curves exhibited linear responses between analytical signal and concentration for each neonicotinoid: 1.0–300.0 μg/L for acetamiprid ($r^2 = 0.9614$), 3.0–350.0 μg/L for thiacloprid ($r^2 = 0.9524$), and 5.0–450.0 μg/L for imidacloprid ($r^2 = 0.9679$), as presented in Table 1.

3.8. Real sample analysis

Following optimization of extraction parameters, the developed MIL-53(Al)/Al thin film microextraction method was applied to non-spiked and spiked real samples of fresh cucumber, water, and juice to assess its effectiveness for analyzing three insecticides in real samples (Table 2). The recovery experiments revealed excellent analytical performance across all spiked real samples, with relative recovery percentages ranging between 86.0% and 100.7%. Water matrices exhibited superior recovery rates (93.3–100.7%) due to low matrix effects Fig. 5. Orange juice matrices yielded acceptable recovery percentages (86.0–97.4%) even in the presence of interfering organic compounds (Fig. 5), whereas cucumber samples provided reliable relative recovery values (92.0–99.0%) despite their complex matrix Fig. 5. Non-spiked real samples showed no detectable residues of target insecticides in water and cucumber samples, while orange juice samples contained quantifiable levels of acetamiprid, presumably originating from pesticide application during cultivation. These findings validate the method's robustness and suitability for routine monitoring of neonicotinoid residues in environmental and food samples.

4. Comparison study

Table 3 presents a comparison of analytical performance parameters between the proposed TFME-HPLC method and previously reported extraction techniques for pesticide analysis. The developed method using MIL-53(Al) demonstrates superior repeatability (RSD ≤ 3.3%) and significantly reduced solvent consumption (0.25 mL) compared to conventional methods, while maintaining comparablelimits of detection and recovery rates across multiple matrices (water, cucumber, and juice samples). The method achieves a wide linear range (1.0–450.0 μg/L) suitable for regulatory monitoring, with competitive analysis time and reliable accuracy, positioning it as an environmentally friendly alternative for multi-residue pesticide determination.

Table 2
Recovery study results for neonicotinoid insecticides in spiked real samples using the TFME-HPLC method.

	Imidacloprid			Acetamiprid			Thiaclopride		
				Cucumber					
Added (μg/Kg)	0	75.0	150.0	0	75.0	150.0	0	75.0	150.0
Founded (μg/Kg)	n.d	69.0	144.0	< LOQ	73.0	148.5	n.d	71.0	147.0
RR%	–	92.0	96.0	–	97.3	99.0	–	94.6	98.0
				Orange juice					
Added (μg/L)	0	5.0	50.0	0	5.0	50.0	0	5.0	50.0
Founded (μg/L)	< LOQ	4.3	46.0	1.5	6.0	49.3	< LOQ	4.4	48.7
RR%	–	86.0	92.0	–	90.0	95.6	–	88.0	97.4
				Water					
Added (μg/L)	0	15.0	80.0	0	15.0	80.0	0	15.0	80.0
Founded (μg/L)	n.d	14.0	78.0	n.d	15.1	79.5	n.d	14.5	79.0
RR%	–	93.3	97.5	–	100.7	99.4	–	96.7	98.7

n.d: not detected.

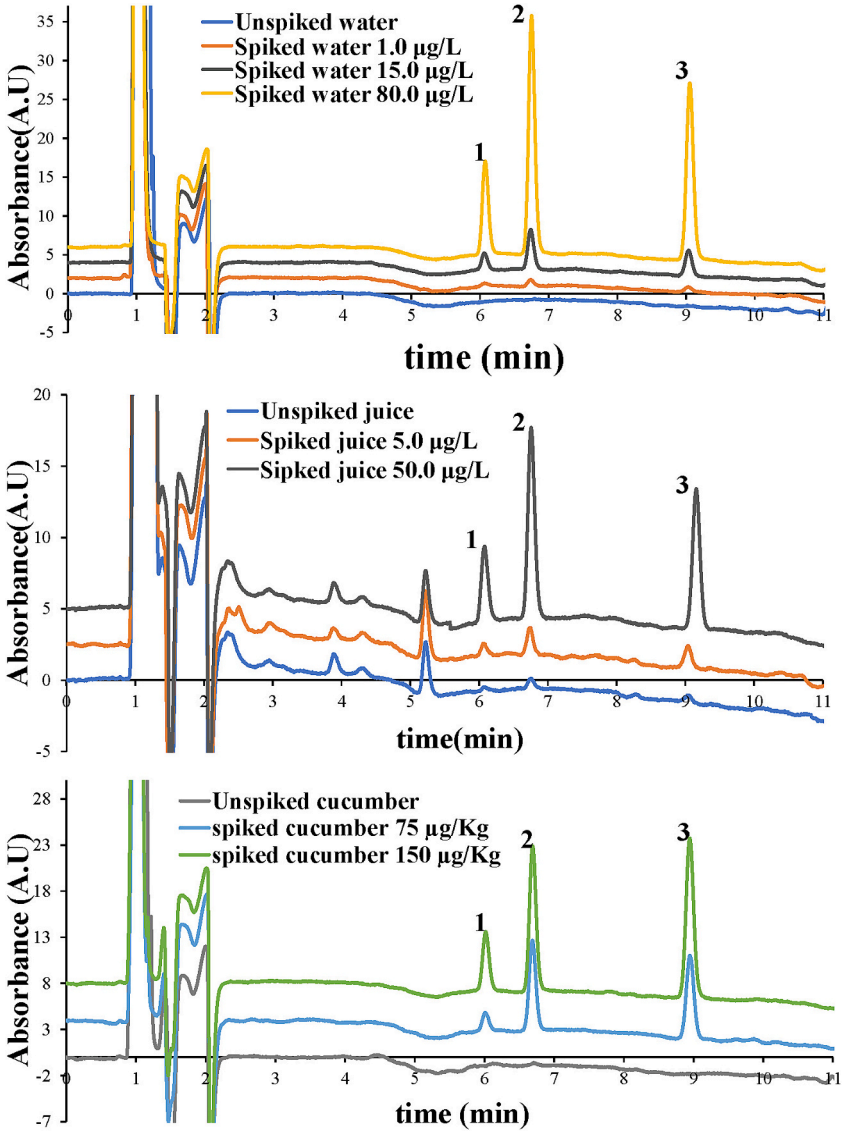


Fig. 5. HPLC-PDA chromatograms obtained at detection wavelength 270 nm in (A) water sample; unspiked, 1.0, 15.0, and 80.0 µg/L spiked concentrations, (B) orange juice sample; unspiked, 5.0, and 50.0 µg/L spiked concentrations, (C) cucumber sample; unspiked, 75.0, and 150.0 µg/Kg spiked concentrations. 1. Imidacloprid; 2. Acetamiprid; 3. Thiacloprid.

Table 3
Comparison of the proposed method against previously reported techniques for neonicotinoid insecticide analysis.

Method	Sample	LOD (µg/ kg)	R%	Linear range (µg/ kg)	Time (min)	RSD%	Solvent (mL)	Ref
QuEChERS-LC-MS/MS	Fruits and vegetables	0.5–2.0	70–120	2–500	30	≤15	10	[35]
QuEChERS-DLLME-LC-MS/MS	Grains	0.1–0.8	82–108	0.5–200	35	≤12	8	[36]
DLLME-LC-MS/MS	Honey	0.2–1.0	75–118	1–300	25	≤10	3	[37]
Magnetic SPE	Lemon juice, honey	0.03–0.2	92–108	0.1–200	35	≤7.5	3	[38]
QuEChERS-UPLC-Q-TOF/MS	Chili (fresh red, fresh green, dried)	0.1–50.0	86.9–105.2	0.3–16,000	8	≤9.5%	10	[39]
TFME-HPLC (MIL-53(Al)/Al)	Water, cucumber, juice	0.3–1.5	86–100.7	1–450	20	≤3.3	0.25	This study

5. Conclusion

Efficient trace-level pesticide determination requires sorbents with exceptional adsorption capacity and favorable chemical properties. Metal-organic frameworks provide unique advantages through their tunable porosity and selective interactions with target analytes. In this work, for the first time, MIL-53 (Al) was directly grown on aluminum foil substrates and configured as a rolled thin film within pipette tips, creating a practical microextraction device and eliminating time-intensive procedures. This approach addresses critical limitations in trace pesticide analysis through several key innovations. The thin-film preparation is straightforward and cost-effective, utilizing commercial

aluminum foil via a simple, reproducible protocol. The rolled configuration within the pipette tip eliminates the clogging and backpressure issues inherent to conventional SPE while enhancing extraction efficiency through increased surface area. The method requires minimal solvent (250 μL of methanol), completes extraction rapidly (20 min), and offers excellent portability for field applications. Importantly, the modular platform design enables future adaptation with different MOF architectures or alternative metal substrates, allowing systematic optimization for specific analyte classes. This flexibility, combined with scalability and low cost, positions the method as a versatile analytical tool. The successful integration of MOF materials with microextraction technology provides a practical, sustainable solution for pesticide monitoring in both well-equipped laboratories and resource-limited settings, advancing accessible environmental and food safety surveillance.

CRediT authorship contribution statement

Marwa Rafea Ismael: Writing – original draft, Resources, Methodology, Investigation, Formal analysis. **Soleyman Moinfar:** Writing – review & editing, Validation, Supervision, Project administration, Investigation, Data curation, 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.microc.2026.117692.

Data availability

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

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