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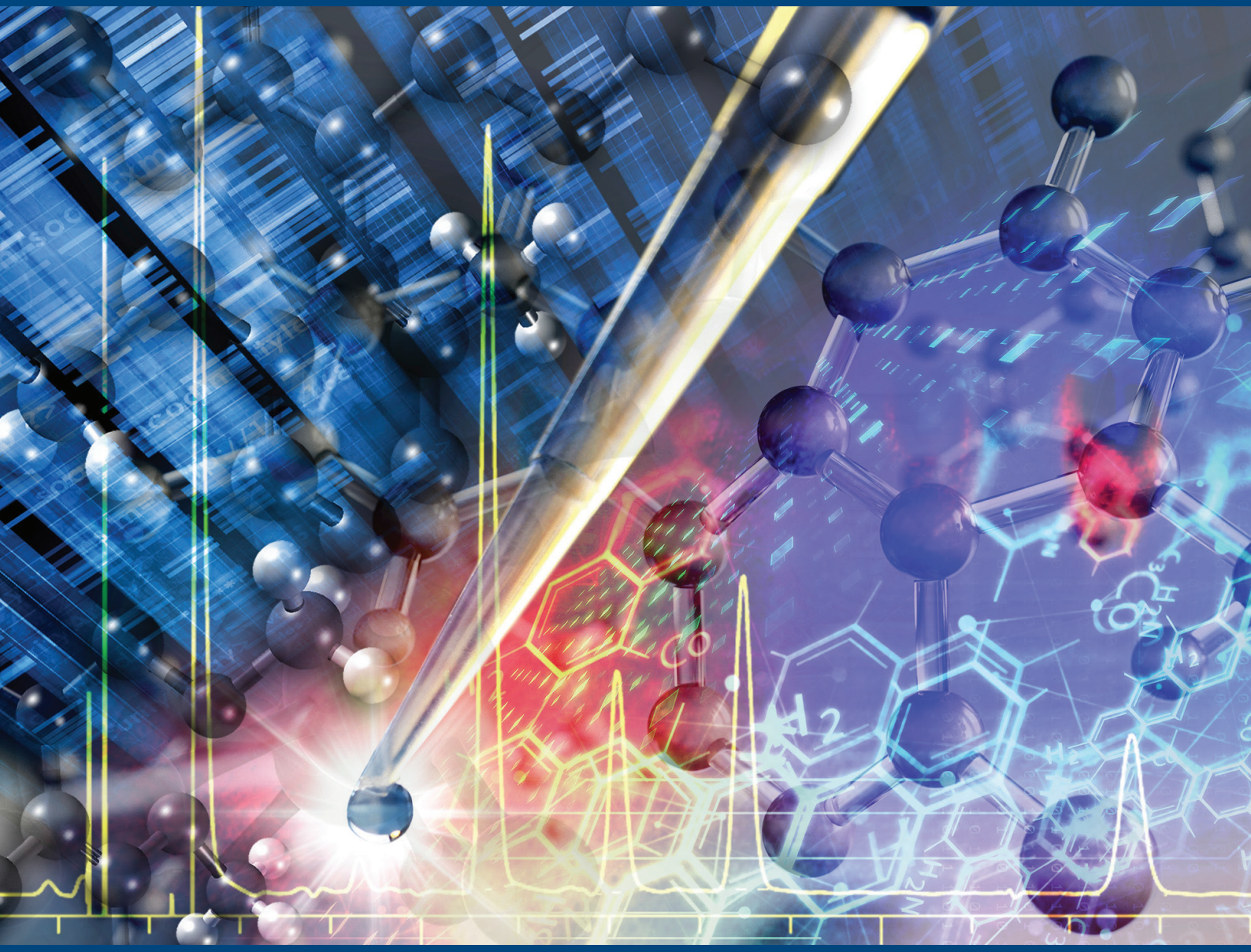

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RESEARCH ARTICLE

A semi-automatic solid phase extraction system based on MIL-101(Cr) foam-filled syringe for detection of triazines in vegetable oils

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In this study, several metal-organic framework-melamine foam columns were first developed and used as a laboratory-made semi-automatic solid phase extraction packed in syringe adsorber for the extraction of six triazine herbicides from vegetable oil samples coupled to high-performance liquid chromatography-tandem mass spectrometry. The metal-organic framework-foam columns were prepared using a simple approach by embedding the solid particles in melamine foam using polyvinylidene difluoride physical encapsulation. The method was applicable to a wide variety of metal-organic framework materials, and the incorporated materials retained their unique properties. Key factors that affect the extraction efficiency, including the MIL-101(Cr) amount, sample flow rate, type and volume of the eluting solvent, and flow rate of eluting solvent, were investigated. Under optimum conditions, the proposed method exhibited low limits of detection (0.017–0.096 ng/mL, S/N = 3) for six triazines. The relative standard deviations calculated for all herbicides ranged from 0.2 to 14.9%. This study demonstrated that the MIL-101(Cr)-foam column can be used as a high-quality adsorption material for the detection of triazines in vegetable oils.

KEYWORDS
melamine foam, metal-organic frameworks, polyvinylidene difluoride, semi-automated solid phase extraction, triazine herbicides

1 | INTRODUCTION

To satisfy the increasing daily requirement, herbicides have been widely used for the cultivation of oil crops to improve their quality and quantity. As a major group of herbicides, triazines are widely used for weed control [1, 2]. However, triazine residues can persist in the harvest stage; thus, the contamination of oil seeds or fruits may be transferred to oil products. The presence of herbicides in vegetable oils can affect the oil quality and pose human health risks [3–5]. The European Union has established maximum residue limits (MRLs) of some triazine herbicides from 0.05 to 0.1 mg/kg in oilseeds (Commission Directive 2008/149/EC). Therefore, it is crucial to develop a rapid and highly sensitive analytical method for monitoring triazine herbicides in complex oil samples.

However, the complex matrix interference of fat coextractives and low analyte concentrations [6] make the

Article Related Abbreviations: DMF, dimethylformamide; LTFP, low-temperature fat precipitation; MOF, metal-organic framework; MOF-FC, MOF foam column; MRL, maximum residue limit; MRM, multiple reaction monitoring mode; PVDF, polyvinylidene difluoride; SA-SPE, semi-automatic solid phase extraction

direct determination of herbicides more difficult by chromatographic methods. Therefore, for analyzing the oil sample matrix, additional steps aiming at clearing the presence of fat in the pretreatment process need to be added. In most cases, as the cleanup step, low-temperature fat precipitation (LTFP) [7], LLE [8], or a QuEChERS (quick, easy, cheap, effective, rugged, and safe)-based extraction method [9] was employed to remove fat. Compared to other common methods, SPE exhibits clear advantages of a lower organic solvent consumption, simplicity, and higher enrichment factor [10].

Metal-organic frameworks (MOFs) are typical hybrid inorganic-organic porous materials [11]. Due to their unique structure and excellent stability, MOFs are attractive materials for chromatographic separation [12, 13]. However, the high column resistance generated by the direct packing of MOF particles into SPE columns limits its application in SPE technology [14]. Melamine foam is a type of porous material, which can be used for the adsorption of environmental pollutants when properly coated. In addition, the unique structure (high porosity, >99%) of the foam allows it to be quickly separated from the sample matrix, which greatly simplifies the preprocessing steps [15]. Recently, functionalized foams have been reportedly prepared and used as adsorbents for the extraction of targeted analytes. However, they have only been used to analyze simple substrates such as fruit juice [16], water [17–19], and milk [20]. In addition, owing to the high fat content of the oil sample, a large amount of organic solvents is also required in the cleaning process before determination to remove the residual lipid from the foams. Recently, a drawdown coating process has been reported for the preparation of functional membranes by dispersing MOF crystals in a polyvinylidene difluoride (PVDF) matrix. The MOFs in the matrice retain their high specific surface areas, porous structures, as well as highly crystalline [21]. However, the reported preparation methods usually require an additional instrument and are difficult to prepare in batches. Still, these methods also provide theoretical support for the preparation of MOF functionalized melamine foam as an SPE-filled column adsorbent. To simplify the cleaning procedure of vegetable oil extraction, in this study, an assembling device comprising an injection pump, syringe, and MOF/PVDF-FCs was constructed, where the preparation of the MOF-filled column is simple, and the operation steps of traditional SPE are also considerably reduced.

In this study, for the first time, the injection-pump-assisted semi-automated SPE packed in syringe adsorber based on MOF/PVDF-FCs (MOF/PVDF-FCs-SA-SPE) was proposed for the extraction of trace triazine herbicides in vegetable oil samples prior to HPLC–MS/MS determination. Several representative MOFs, including MIL-101(Cr), MIL-101(Fe), ZIF-8(Zn), HKUST-1(Cu), and MIL-68(Al), were selected to prepare MOF/PVDF-FCs by a simple method, and their extraction abilities were investigated to select the optimum MOF/PVDF-FCs for the analysis of triazines. Then, the proposed method was applied for the analysis of six triazines from oil samples.

2 | MATERIALS AND METHODS

2.1 | Reagents and materials

Melamine foam is commercially available and was obtained from a local market (Changchun, China). Other chemicals needed during the synthesis of the selected MOFs are listed in the Supporting Information. PVDF was selected as a coupling agent and bought from Shijiazhuang Okaizhuote Instrument Technology (Hebei, China).

Standard triazine herbicides, including atraton, desmetryn, prometon, ametryn, prometryn, and dimethametryn, were bought from Dr. Ehrenstorfer (Augsburg, Germany) and their chemical structures can be found in Supporting information Table S1. Methanol (HPLC grade) and ultrapure water were selected as the mobile phase in this experiment and obtained from J&K Scientific (Pittsburgh, USA) and a Milli-Q water purification system (Millipore, USA). The standard working solutions (5 μg/mL) were prepared by mixing six individual stock solutions, which were made by dissolving individual triazine standard in HPLC grade methanol.

2.2 | Collection of oil samples

Five vegetable oil samples (denoted as samples 1, 2, 3, 4, and 5, respectively), including soybean oil, maize oils, edible vegetable blend oil, peanut oil, and sunflower seed oil, were provided by a local market (Changchun, China) and analyzed. Spiked samples (20 ng/mL) were freshly prepared by spiking the required volumes of the working solution into blank samples. After being well mixed (10 min vortex), the samples were stored in a 4°C refrigerator until analysis. All original samples were collected with the guidance of a EU standard (SANTE/11945/2015).

2.3 | Instrumentations

All chromatographic separations were performed on an Agilent 1260 HPLC system with the equalization mode

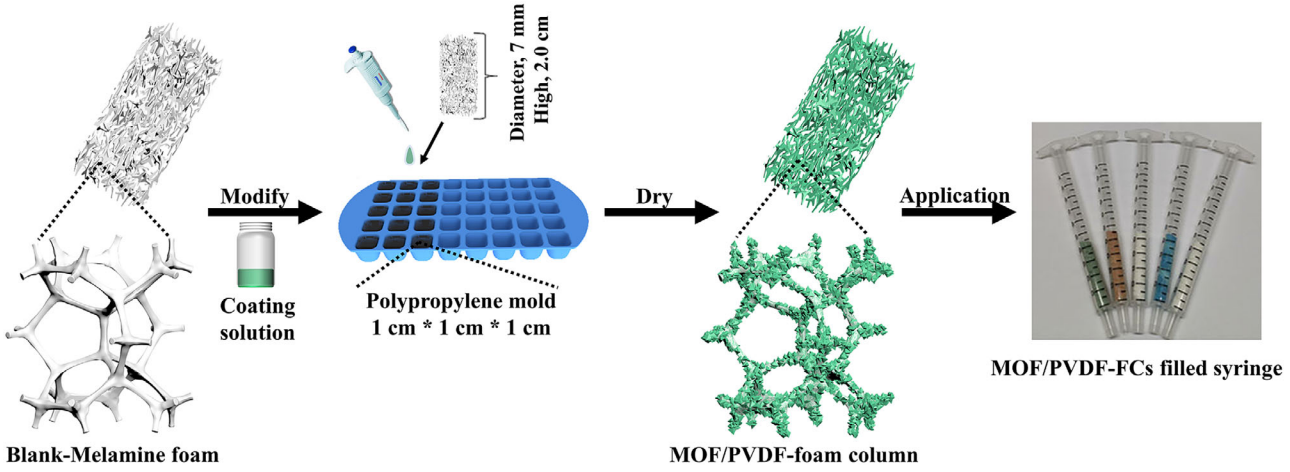

FIGURE 1 Preparation of MOF/PVDF-foam columns

consisting of methanol and ultrapure water (90:10, v/v), and delivered at a flow rate of 0.3 mL/min at 35 ± 0.8°C. Samples (5 μL) were injected into an eclipse XDB-C18 column (50 × 3.1 mm, 1.7 μm particle size) purchased from Thermofisher. A triple quadrupole mass spectrometer (TSQ Quantum AccessMAX, Thermofisher), which was used to identify and quantify target analytes, was operated in multiple reaction monitoring (MRM) mode. ESI was operated in a positive ionization mode. The MS/MS product ion parameter obtained following careful optimization and ESI parameters are summarized in Supporting information Table S1. A SEM (Hitachi SU-8020, Japan), an XRD (Rigaku Ultima IV, Japan), and a surface area and pore-size analyzer (Belsorp max, Microtrac BEL, Japan) were successively used to characterize the synthetic materials.

2.4 | Preparation of functionalized foam columns

The MOF/PVDF-FCs were prepared as follows: First, 7.5 wt% PVDF/ dimethylformamide (DMF) was prepared by the slow addition of PVDF into a beaker containing DMF under heating and stirring. Second, 150 mg of MIL-101(Cr) was dispersed in 5 mL of acetone for 20 min with ultrasonication, followed by the addition of 1.1 g of 7.5 wt% of PVDF/DMF into the above solution. A homogeneous solution was obtained in another 20 min. Next, the melamine foam column (FC, diameter = 0.7 cm, height = 2.0 cm) was pressed several times in a cube mold (1 × 1 × 1 cm) containing 600 μL of the coating solution until all the mixed solution was absorbed and dried in 85°C overnight. Figure 1 shows the synthetic route for the preparation of the porous MOF/PVDF-FC.

2.5 | Functionalized foam column-based semi-automated solid phase extraction procedure

The semi-automated SPE of triazines from vegetable sample is schematically depicted in the Fig. 2. First, 0.5 mL of vegetable oil was rapidly added into the syringe chamber containing two MIL-101(Cr)/PVDF-FCs, and then the piston mandrel was plugged. Then, the analytes were loaded in the FCs by syringe injection (flow rate = 300 mL/min) with the vegetable oil being discarded. The assembling device comprising an injection pump and a packed syringe was applied for the desorption of analytes adsorbed on the FC. Next, the MIL-101(Cr)/PVDF-FCs containing the analytes were washed with 1 mL of hexane (flow rate = 500 μL/min) to reduce the interferences from complex matrixes and avoid targets running away. The syringe plunger was pulled back and then injected to remove excess washing solvent from the FC. Then, 1 mL of the eluting solvent (ethyl acetate, flow rate = 300 μL/min) efficiently desorbed analytes from the FC. The eluates were volatilized to dryness under a mild nitrogen stream at 45°C and redissolved in 500 μL of methanol. The resulting solution was filtered using a 0.22-μm syringe filter, which was referred to as analytical solution. Then, 5 μL of the analytical solution was injected into the HPLC–MS/MS system.

3 | RESULTS AND DISCUSSION

3.1 | Synthesis and characterization of the selected metal-organic frameworks

Five MOFs, including MIL-101(Cr), MIL-101(Fe), ZIF-8(Zn), HKUST-1(Cu), and MIL-68(Al), respectively, were

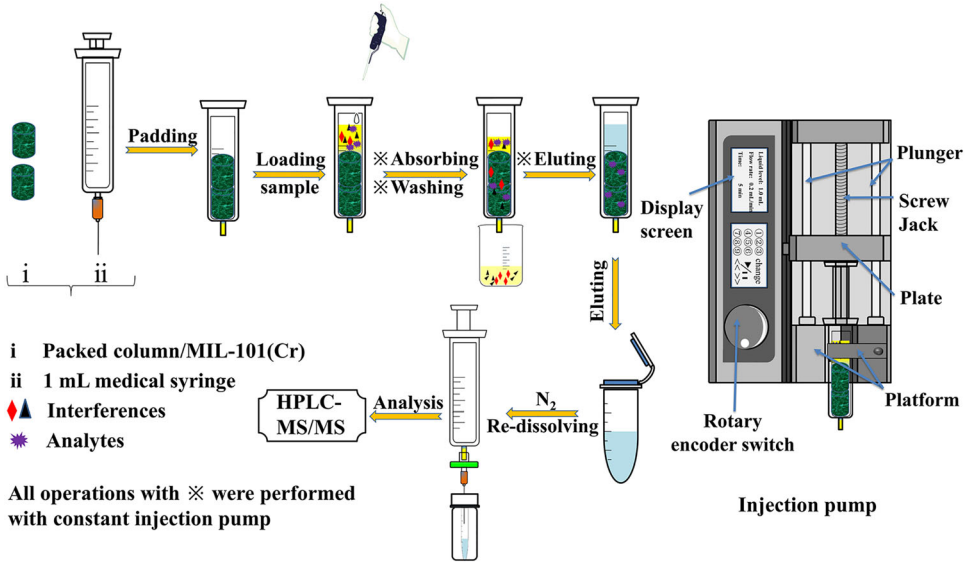

FIGURE 2 Schematic of MOF-foam-based semi-automated SPE extraction procedure

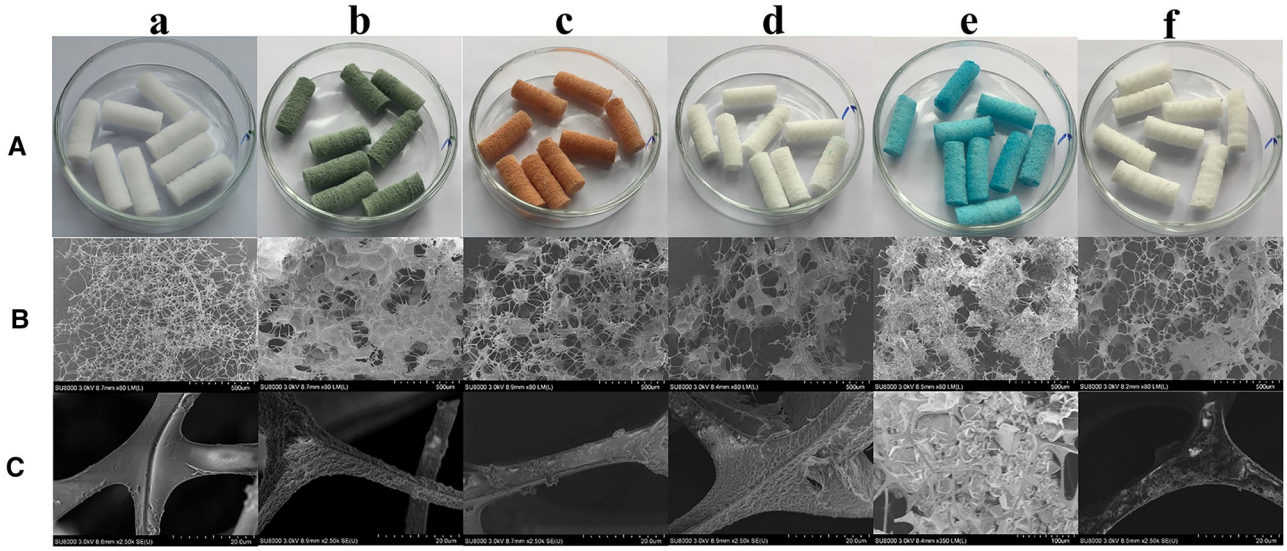

FIGURE 3 Physical images of foam column-modified MOFs; blank, MIL-101(Cr), MIL-101(Fe), ZIF-8(Zn), HKUST-1(Cu), and MIL-68(Al) (A, a–f) and SEM images at different magnifications (B, 80 ×; C 2.5k ×)

synthesized by a previous method [22–26]. The synthesis procedures can be found in the Supporting Information. Supporting information Fig. S1 shows the SEM images of the prepared MOF materials. The XRD patterns (Supporting information Fig. S2) of the synthesized MOFs were in good agreement with those reported previously [11, 24, 26–28]. The BET surface areas and some pore parameters of MOF materials were measured by N_2 adsorption isotherm experiments (Suppporting information Fig. S3) and summarized in Supporting information Table S2.

3.2 | Selection of functionalized foam columns

The selection of an appropriate MOF/PVDF-FC is crucial for extraction efficiency. In this study, several representative MOFs, such as MIL-101(Cr), MIL-101(Fe), ZIF-8(Zn), HKUST-1(Cu), and MIL-68(Al), were selected to prepare MOF/PVDF-FCs by the same experimental procedure. Figure 3 shows the SEM images at different magnifications (B, 80 ×; C 2.5k ×) and digital images of the porous foam materials. Bare melamine foam (without MOFs and

PVDF) (A-a) exhibited an interconnected 3D network with pores, the diameter of which ranged between 100 and 200 μm. The difference between the unmodified FC and MOF/PVDF-FCs was clearly observed (C, a–f), the smooth skeleton of melamine foam was modified with selected MOFs. In addition, the color of foam was also significantly different from the original white (A. a–f). The SEM image shown in Fig. 3 revealed that the MIL-101(Cr)- and ZIF-8(Zn)-modified FC coatings are more uniform than the other MOFs. The extraction performance of the resultant MOF/PVDF-FCs and "blank" FC was evaluated under the optimal conditions. Supporting information Fig. S4 shows the results. The "blank" FC adsorbed a marginal amount of target analytes, indicating that adsorption depends on the MOF of FCs. MIL-101(Cr) exhibited the best extraction performance for most triazines, probably related to the π-π interaction between triazines and terephthalic acid molecules loaded on MIL-101(Cr) surface [6]. In addition, the unsaturated metal sites on the skeleton of the MIL-101(Cr) may also covalently interact with the heteroatoms in triazines, and the large windows of MIL-101(Cr) allow the analytes to easily enter the cages [29].

FTIR spectra has been applied to further investigate the prepared MIL-101(Cr)/PVDF-FC material using a Fourier transform infrared spectrometer (Nicolet iS5, Thermo Scientific). The FTIR patterns of MIL-101(Cr) powder, PVDF powder, and MIL-101(Cr)/PVDF-FC are shown in Supporting information Fig. S5 by KBr pellet method. For single PVDF power, the peaks at 1412 and 1185 cm^{-1}, respectively correspond to the deformation and stretching vibration of $-CF_2$ [30]. The peaks at 1385 and 810 cm^{-1} correspond C–N stretching and bending of triazines ring in melamine, respectively. The C–H vibration peaks at 749 and 579 cm^{-1} are attributed to benzene ring of MIL-101(Cr) [31] indicate the MIL-101(Cr) was successfully modified on the foam.

In addition, SEM was employed to examine the morphologies of the MIL-101(Cr)/PVDF-FCs with different loads. Supporting information Fig. S6 shows the SEM images of MIL-101(Cr)/PVDF FCs (a–f) at different loads under different magnifications (B, 80 ×; C, 2.5k ×). Following the modification procedure detailed herein, the 3D network became filled with MOFs, and the density and thickness of the coating apparently increased with the mass of MIL-101(Cr) (Supporting information Fig. S6C, a–f).

3.3 | Optimization of solid phase extraction conditions

Various experimental parameters were optimized (spiked sample was 20 ng/mL). Respective data and figures can be found in the Supporting Information (Figs. S7–S10). The following experimental conditions were observed to give the best results: (a) amount of MIL-101(Cr): 150 mg; (b) sample flow rate: 300 μL/min; (c) type and volume of the eluting solvent: ethyl acetate, 1.0 mL; and (d) flow rate of the eluting solvent: 300 μL/min.

3.4 | Method validation

3.4.1 | Analytical performance

The proposed MIL-101(Cr)/PVDF-FCs-SA-SPE method was validated by the evaluation of the linearity, precision, LODs, LOQs, recovery, and matrix effect for the extraction and determination of the triazine herbicides in vegetable oil samples spiked under optimized conditions (Supporting information Table S3). The working curves were constructed by plotting the chromatographic corresponding signal (peak areas) versus the different spiked levels of the target triazines. Favorable linearities with high correlation coefficients ($r \geq 0.9937$) were obtained at a concentration range of 0.5 to 100.0 ng/mL for all analytical triazines. The intra- and interday relative standard deviations (RSDs, %, n = 5), used to measure the precision of the developed method, were obtained in recovery experiments at two different concentration levels (1 and 20 ng/mL) during the same day and five consecutive days. The results shown in Supporting information Table S3 demonstrate that the precisions of the developed method are acceptable, with the RSDs less than 15.8%. The LODs and LOQs were estimated as 3 and 10 times the signal-to-noise ratio (S/N) in the blank water sample, respectively. The LODs and LOQs of the method varied from 0.017 to 0.096 ng/mL and from 0.057 to 0.32 ng/mL, respectively. The matrix effect part can be found in the Supporting Information. The results shown in Supporting information Table S3 indicated that the matrix effects for all herbicides studied were observed to be less than 6.9%.

3.4.2 | Application to real samples

To validate whether the MOF/PVDF-FCs-SA-SPE method can be applied for the detection of trace herbicide residues in real oil samples, five oil samples were spiked with six triazines (analytes) at three different concentrations (0, 1.0, and 20.0 ng/mL, respectively). Analyzed by the current method under the optimal conditions, triazine herbicides were not observed for the unspiked real sample. Supporting information Table S4 summarizes the results obtained for samples spiked with 1.0 and 20.0 ng/mL of triazines obtained under the same conditions. The recoveries of all triazine herbicides were ranged from 77.0 to 118.3%,

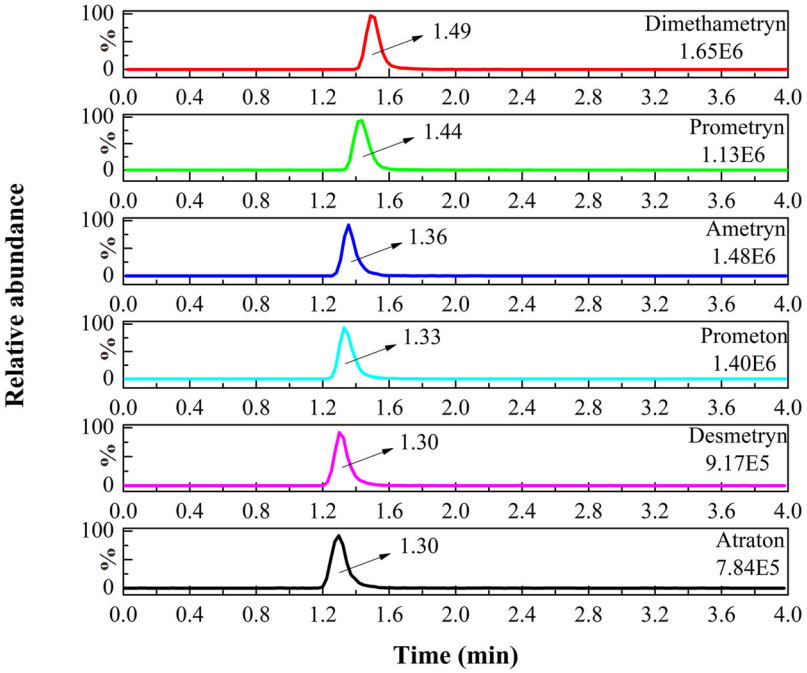

FIGURE 4 HPLC–MS/MS chromatograms obtained for a spiked blank sample 1 spiked with 20 ng/mL

with RSDs of less than 14.9%. Figure 4 shows the chromatograms of the spiked samples by the proposed method.

3.4.3 | Reusability of functionalized foam column materials

To assess the reusability of MIL-101(Cr)/PVDF-FCs, the MIL-101(Cr)/PVDF-FCs were repeatedly used four times in SPE. The packed syringe was washed with 1 mL of ethyl acetate at a flow rate of 500 μL/min and dried at 60°C for 3 h each time before reuse. The results illustrated in Supporting information Fig. S11 indicate that there is no significant reduction of the recoveries of the triazines studied after using the FC four times.

3.4.4 | Comparison to the other methods

This developed method was compared to the other relevant methods for the extraction of triazine herbicides in foods [6, 32-35]. Table 1 summarizes the detailed comparison. Notably, the volumes of organic solvents as well as the operating times for washing and eluting processes during the MIL-101(Cr)/PVDF-FC-semi-automated SPE were significantly reduced. The experimental procedure was also considerably simplified by employing the melamine FC, which eliminates the centrifugal separation of adsorbents in traditional solid phase extraction. The MIL-101(Cr)/PVDF-FC was used as a laboratory-made semi-automatic microextraction packed in syringe adsorber using a simple device; an advantage of the latter is that it can reduce the complex extraction procedure for an oil matrix. In addition, the current method exhibited good extraction efficiencies, and LODs obtained by the present method were similar to or less than those of most of the other methods reported previously.

Furthermore, performance comparison between the three typical commercial sorbents (activated carbon, Cleanert S C18, Cleanert PSA) functionalized FC and the MIL-101(Cr)/PVDF-FC for SPE is shown in Supporting information Fig. S12. Supporting information Fig. S13 shows the SEM images of the FC filled with commercial sorbents: clearly, the extraction performance of these sorbents was not satisfactory compared with that of the MIL-101(Cr)/PVDF-FC under similar extraction conditions, indicating that the MIL-101(Cr)/PVDF-FC-based semi-automated SPE method can be considered as a reliable and compatible chromatographic extraction technique.

4 | CONCLUSIONS

A novel analytical method of MOF-foam-based semi-automated SPE was proposed for the determination of triazines in vegetable oil samples. The main advantages of the proposed method included simplicity, suitable sensitivity, requirement of the least amount of organic solvents for analysis, and elimination of the centrifugation step in dispersive SPE. A level of 0.096 ng/mL of triazines studied in one sample was detectable. Although, the proposed MIL-101(Cr)/PVDF-FC-based semi-automated SPE can be used as a suitable pretreatment method of fatty samples for HPLC analyses. However, there is still a problem we need

TABLE 1 Comparison of the presented method with other reported methods

Extraction method	Analytes	Sample volume (mL)	Operation time (min)	Cleanup procedure	Analytical technique	RSD (%)	Recovery (%)	LOD (ng/mL)	Ref.
d-μ-SPE[a]	Triazine herbicides	2	29	0.5 mL *n*-hexane	HPLC-DAD	≤7.8	87.3-107	0.58-1.04	[6]
MIL-DLLME[b]	Triazine herbicides	1	13.3	1.5 mL deionized water + 1.5 mL ethyl acetate	HPLC-UV	≤7.7	81.8-114.2	1.31-1.49	[32]
LLE[c]	Pyrethroid insecticides	5 g		3 mL acetonitrile	GC-ECD	6-17	71-91	0.02-0.57 mg/kg	[33]
VA-RPLLME[d]	Triazine herbicides	4	6		HPLC-UV	≤8.4	60.1-107.2	0.60-1.50	[34]
LLE-dSPE[e]	Organophosphorus pesticides	5 g	17.5	0.50 g Na_2SO_4 +100 mg MWCNTs + 1.00 g neutral alumina	GC-MS	≤8.5	85.9-114.3	0.7-1.6	[35]
MIL-101(Cr)/PVDF-FCs-SA-SPE[f]	Triazine herbicides	0.5	8.4	1.0 mL *n*-hexane	HPLC-MS/MS	≤14.9	77.0-118.3	0.017-0.096	This work

[a]Dispersive micro-solid-phase extraction;
[b]magnetic ionic liquid-based dispersive liquid-liquid microextraction.
[c]Liquid-liquid microextraction.
[d]Vortex-assisted reversed-phase liquid-liquid microextraction.
[e]Liquid-liquid extraction-dispersive solid phase extraction.
[f]semi-automatic solid phase extraction.

to be improved. Due to the weak extraction performance of PVDF, the extraction performance of the prepared functional foam material mainly depends on the MOF material on the surface of melamine foam. Further looking for a bioadhesive with excellent extraction properties to replace PVDF is still underway in our group.

CONFLICT OF INTEREST

The authors have declared no conflict of interest.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

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