



Covalent organic framework in situ grown on Fe₃O₄ hollow microspheres for stir bar sorptive-dispersive microextraction of triazole pesticides

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Received: 23 September 2022 / Accepted: 3 December 2022 / Published online: 20 December 2022
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Abstract

Based on covalent organic framework (COF) 1,3,5-tris-(4-formylphenyl)benzene-benzidine (TFPB-BD) in situ grown on Fe₃O₄ hollow microspheres and combined with gas chromatography-flame thermionic detector, a rapid and simple stir bar sorptive-dispersive microextraction method was developed for the determination of five triazole pesticides (paclobutrazol, hexaconazole, flusilazole, propiconazole, and tebuconazole). The synthesized TFPB-BD/Fe₃O₄ microspheres were characterized by transmission electron microscope, vibrating sample magnetometer, and thermogravimetric analysis, which showed that the material has strong magnetism and higher load capacity of COF. Under optimal conditions, the extraction equilibrium could be achieved within 9 min with detection limits of 0.17–1.48 μg L⁻¹ (S/N=3) and a linear range of 5–1000 μg L⁻¹. The developed method was applied to the determination of trace triazole pesticides in apples, pears, and cabbages with recoveries from 81 to 117%.

Keywords Triazole pesticides · Covalent organic framework · Stir bar sorptive-dispersive microextraction · Fruits and vegetables analysis · Magnetic hollow microspheres

Introduction

Triazole pesticides, a series of organic heterocyclic compounds, are easy to residue in fruits and vegetables because of their stable structure and rarely photodegradation under environmental conditions [1–4]. Long-term exposure will cause reproductive toxicity, hepatotoxicity, and developmental toxicity [5–7]. Therefore, a simple, rapid, and efficient method for determination of triazole pesticides in fruits and vegetables is critical to control food safety and protect human health.

There are several analytical methods used for the detection of triazole pesticides such as colorimetric sensing [8, 9], fluorescence sensing [6], and chromatography

[10]. Among them, chromatography is widely used for the analysis of various triazole pesticides, and the sensitivity and accuracy of determination are depend on efficient sample pretreatment [11]. Common pretreatment methods include liquid–liquid extraction (LLE) [12], liquid–liquid microextraction (LLME) [13], solid-phase microextraction (SPME) [1], magnetic solid-phase extraction (MSPE) [14], and stir bar sorptive extraction (SBSE) [15]. LLE needs to consume a large amount of organic solvents [16, 17]. Although LLME consumes less organic solvent, phase separation by centrifugation is still complicated to realize [18, 19]. SPME and SBSE use solid adsorbents that are easy to separate, but the contact area between adsorbents and samples is limited, which leads to longer extraction time [15, 20]. With the development of nanotechnology, MSPE has become a hot technology due to its low organic solvent consumption, fully contact with samples, and short extraction time [21, 22]. Nevertheless, in the process of MSPE extraction, the additional magnetic field is needed to collect the adsorbents in the both extraction and desorption process [23], which makes the operation a little complicated and may cause operation error.

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Stir bar sorptive-dispersive microextraction (SBSDME) combines the advantages of SBSE and MSPE [24–26]. With the vigorous stirring of the magnetic stir bar, the mass transfer rate is faster than that of the conventional MSPE, and the adsorbents are adsorbed on the stirring bar without external magnetic field [27]. Furthermore, the magnetic adsorbent is easy to recycle and has strong reusability, and it can adsorb different substances by adjusting its properties under different synthesis conditions. Benedé et al. [28] used CoFe_2O_4 @oleic as an adsorbent in SBSDMI to realize sensitive detection of eight lipophilic UV filters in water samples with the detection limits (LODs) in the low ng L^{-1} range. Grau et al. [29] used CoFe_2O_4 @Strata-XTM-AW in SBSDMI to selectively determine triphenyl and diphenyl phosphate in urine of nail polish users, and the method showed enrichment factors of 17 and 30. Madej et al. [30] synthesized magnetically modified graphene (G- Fe_3O_4) for the effective extraction of seven pesticides in aqueous solution by SBSDMI, and the LODs were below 14 ng mL^{-1} .

Magnetic covalent organic frameworks (MCOFs) not only have high saturation magnetization, but also have the advantages of COF, such as ordered crystal structure, large specific surface area and chemical stability, which make them potential magnetic adsorbents [31, 32]. Gao et al. [33] used in situ growth method to synthesize the stable core-shell structured MCOF Fe_3O_4 @TbBd for selective enrichment of peptides. Our group synthesized MCOF of 1,3,5-tris-(4-formylphenyl) benzene-Benzidine/ Fe_3O_4 (TpBD/ Fe_3O_4) by a facile coprecipitation method and used it for MSPE of 15 phthalate esters in beverages [34].

At present, most in situ growth methods of MCOFs are based on Fe_3O_4 solid microspheres/nanoparticles, so the COF layer was only limited to the surface [35]. Fe_3O_4 hollow microspheres have unsealed and loose structure, its strong magnetism is conducive to rapid magnetic separation, and its hollow structure improves the load capacity. Fe_3O_4 hollow microspheres can grow more COF than Fe_3O_4 solid microspheres, thus providing more adsorption sites [36].

Herein, COF TFPB-BD was in situ grown on Fe_3O_4 hollow microspheres (TFPB-BD/ Fe_3O_4) as the adsorbent of SBSDMI for rapid extraction of triazole pesticides. Combined with gas chromatography-flame thermionic detector (GC-FTD), triazole pesticides in fruits and vegetables (apples, pears, and cabbages) were conveniently extracted and determined.

Materials and methods

Materials and reagents

All the reagents used were at least analytical grade. 1,3,5-tris-(4-formylphenyl) benzene (TFPB) was purchased

from Tongchuangyuan Pharmaceutical Technology Co., Ltd. (Sichuan, China). Benzidine (BD) and mesitylene were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). Iron chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), 1,6-hexanediamine, anhydrous sodium acetate, glycol, methanol (MeOH), N,N-dimethylformamide (DMF), 1,4-dioxane, and glacial acetic acid were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Five triazole pesticides standard solutions with a concentration of 1000 mg L^{-1} were obtained from Tanmo Quality Inspection Technology Co., Ltd. (Jiangsu, China), including paclobutrazol, hexaconazole, flusilazole, propiconazole, and tebuconazole. The standard solutions were diluted with HPLC grade methanol to prepare stock solution and intermediate solution, and were stored at $-20 \text{ }^\circ\text{C}$ and $4 \text{ }^\circ\text{C}$ respectively. Fruits and vegetable samples (apples, pears, and cabbages) were randomly obtained from local supermarkets (Wuxi, China) and stored at $4 \text{ }^\circ\text{C}$ before analysis.

Instrumentation and analytical conditions

The morphology and element distribution of the TFPB-BD/ Fe_3O_4 were obtained by JEM 2100F transmission electron microscope (TEM, JEOL, Japan), high angle annular dark field scanning transmission electron microscopy (HAADF-STEM), and energy dispersive X-ray spectroscopy (EDX) (FEI, USA). Fourier transform infrared spectroscopy (FT-IR) was obtained on Nicolet IS10 spectrometer (Nicolet, USA). The magnetic hysteresis loops of the Fe_3O_4 and TFPB-BD/ Fe_3O_4 were measured by LakeShore7404 vibrating sample magnetometer (VSM, LakeShore, USA). The N_2 adsorption experiment was carried out on Autosorb-iQ analyzer (Quantachrome, USA). The thermogravimetric analysis (TGA) was conducted on STA 449 F5 Jupiter thermal gravimetric analyzer (NETZSCH, Germany). The SBSDMI experiment was carried out on KX-85-2AS intelligent constant temperature magnetic stirrer (Zhida Shengtong Scientific Instrument Co., Ltd., China). The magnetic bar was used as the stir bar (20 mm in length and 3 mm in diameter, Shenzhen Lala Magnetic Materials Co., Ltd., China).

Data collection and analysis were carried out on Shimadzu GC system (2030, Shimadzu, Japan). Capillary column HP-5 (30 m \times 0.25 mm \times 0.25 μm , Agilent, USA) was used for quantitative determination in the experiment. The injection was accomplished in splitless mode, the inlet temperature was $280 \text{ }^\circ\text{C}$, and the injection volume was $1 \mu\text{L}$. The air flow rate was 145 mL min^{-1} , the H_2 flow rate was 2 mL min^{-1} , and the carrier gas (N_2) flow rate was 30 mL min^{-1} . The column temperature program used for the separation was as follows: the initial temperature maintained at $80 \text{ }^\circ\text{C}$ (held for 2 min), then $20 \text{ }^\circ\text{C min}^{-1}$ to $260 \text{ }^\circ\text{C}$, and finally $10 \text{ }^\circ\text{C min}^{-1}$ to $280 \text{ }^\circ\text{C}$ (held for 1 min). The temperature of flame ionization detector (FTD) was $300 \text{ }^\circ\text{C}$.

Synthesis of the TFPB-BD/Fe₃O₄

Amine-functionalized Fe₃O₄ hollow microspheres (Fe₃O₄-NH₂) were synthesized by one-pot method (Text S1) according to the reported method [36]. The synthesis of the TFPB-BD/Fe₃O₄ (Optimization was provided in Text S2) was carried out as follows: 150 mg Fe₃O₄-NH₂ was dispersed in 10 mL 1,4-dioxane, then 10 mg TFPB and 150 μL acetic acid were added. The product TFPB/Fe₃O₄ was washed with DMF and 1,4-dioxane and then dried under vacuum. Then, 50 mg TFPB/Fe₃O₄ was dissolved in 4.5 mL mesitylene/1,4-dioxane (1:1, V:V) solution; 39.06 mg TFPB, 27.63 mg BD, and 0.5 mL 9 mol L⁻¹ acetic acid solution were added, and the reaction was carried out at room temperature for 48 h. The TFPB-BD/Fe₃O₄ was separated by a magnet, washed with DMF and ethanol, and dried under vacuum overnight.

SBSDME procedure

Sixteen milligrams of TFPB-BD/Fe₃O₄ composite was added in 10 mL spiked solution or sample solution. A magnetic bar (20 mm in length and 3 mm in diameter) was placed in the beaker and the SBSDME procedure was carried out. At the stirring rate of 600 rpm, the TFPB-BD/Fe₃O₄ was dispersed in the solution for extraction for 9 min, and then the stirring stopped; the TFPB-BD/Fe₃O₄ was adsorbed back to the stirring bar. After extraction, the magnetic bar was taken out and washed twice with water, then 500 μL MeOH was used for ultrasonic-assisted elution for 6 min. The eluent was filtered with a 0.22-μm filter for GC-FTD analysis.

Analysis of real samples

In order to evaluate the feasibility of SBSDME method in real samples, the quantitative determination of triazole pesticides was carried out in apples, pears, and cabbages. The sample preparation process was as follows: the fruit and vegetable samples were washed and used for homogenizing treatment. Then, 1.0-g sample was diluted with 10 mL pure water, added 0.1 g NaCl, and adjusted pH to 7 with 0.1 M HCl and 0.1 M NaOH solution. The SBSDME procedure was performed according to the method described in the “SBSDME procedure” section.

Results and discussion

The design of TFPB-BD/Fe₃O₄ for SBSDME of triazole pesticides

Triazole pesticides are nitrogenous heterocyclic compounds containing phenyl and triazolyl groups with the molecular

sizes between 10.1 and 13.0 Å (Fig. S4). And COF TFPB-BD has a large π conjugated system with the pore size of 32 Å, which is larger than the molecular sizes of triazole pesticides [37]. Triazole pesticides may be extracted from the sample solution onto COF TFPB-BD due to the action of the pore size, π-π interaction, or hydrogen bond, etc. Therefore, we used COF TFPB-BD as an adsorbent to be magnetized. Firstly, the monomer TFPB was bonded to the amine-functionalized Fe₃O₄ hollow microspheres by the aldehyde group of TFPB reacted with free -NH₂ groups. The TFPB-BD/Fe₃O₄ was synthesized by the condensation with the other monomer BD on TFPB/Fe₃O₄ via Schiff base reaction (Fig. 1a). Then, the prepared TFPB-BD/Fe₃O₄ composite was added to the sample solution, and SBSDME process was carried out with a magnetic bar (Fig. 1b). At a high stirring rate, the TFPB-BD/Fe₃O₄ was dispersed in the solution for extraction, and when the stirring stopped, the magnetic material was attracted back to the stirring bar. In this way, triazole pesticides were adsorbed to the TFPB-BD/Fe₃O₄ composite. After extraction, the stirring bar with TFPB-BD/Fe₃O₄ was taken out and eluted with MeOH. The eluent was filtered and quantitatively analyzed by GC-FTD.

Characterization of the TFPB-BD/Fe₃O₄

The HAADF-STEM and EDX elemental mapping data (Fig. 2a) show that the TFPB-BD (containing elements C, N, O) are uniformly bonded on the Fe₃O₄ hollow microspheres (containing elements Fe, O), and the thickness of COF TFPB-BD is about 1 μm. The distribution of element Fe is a hollow ring, and the elements C, N, and O are uniformly distributed in the whole sphere.

Thermogravimetric analysis (TGA) was used to compare the proportion of COF in MCOF grown in situ on Fe₃O₄ solid microspheres (Fe₃O₄@TFPB-BD) (Fe₃O₄@TFPB-BD was synthesized according to the reported method) [38] and hollow microspheres (TFPB-BD/Fe₃O₄) (Fig. 2b). For the two materials, there are obvious weight reduction curves in the range of 500–680 °C, indicating the weight reduction of COF shell. The residual mass of TFPB-BD/Fe₃O₄ was 54.4%, while the residual mass of Fe₃O₄@TFPB-BD was 75.6%, indicating that the proportion of COF in TFPB-BD/Fe₃O₄ is higher. Thus, the synthesis of MCOF with Fe₃O₄ hollow microspheres can increase the load capacity of COF. Other characterizations of TFPB-BD/Fe₃O₄ were provided in the Electronic Supplementary Material Text S3.

Optimization of the SBSDME parameters

In order to enhance the SBSDME extraction effect, the extraction and elution conditions were optimized. For extraction conditions, we investigated the effects of the amount of adsorbent, stirring rate, pH, salt

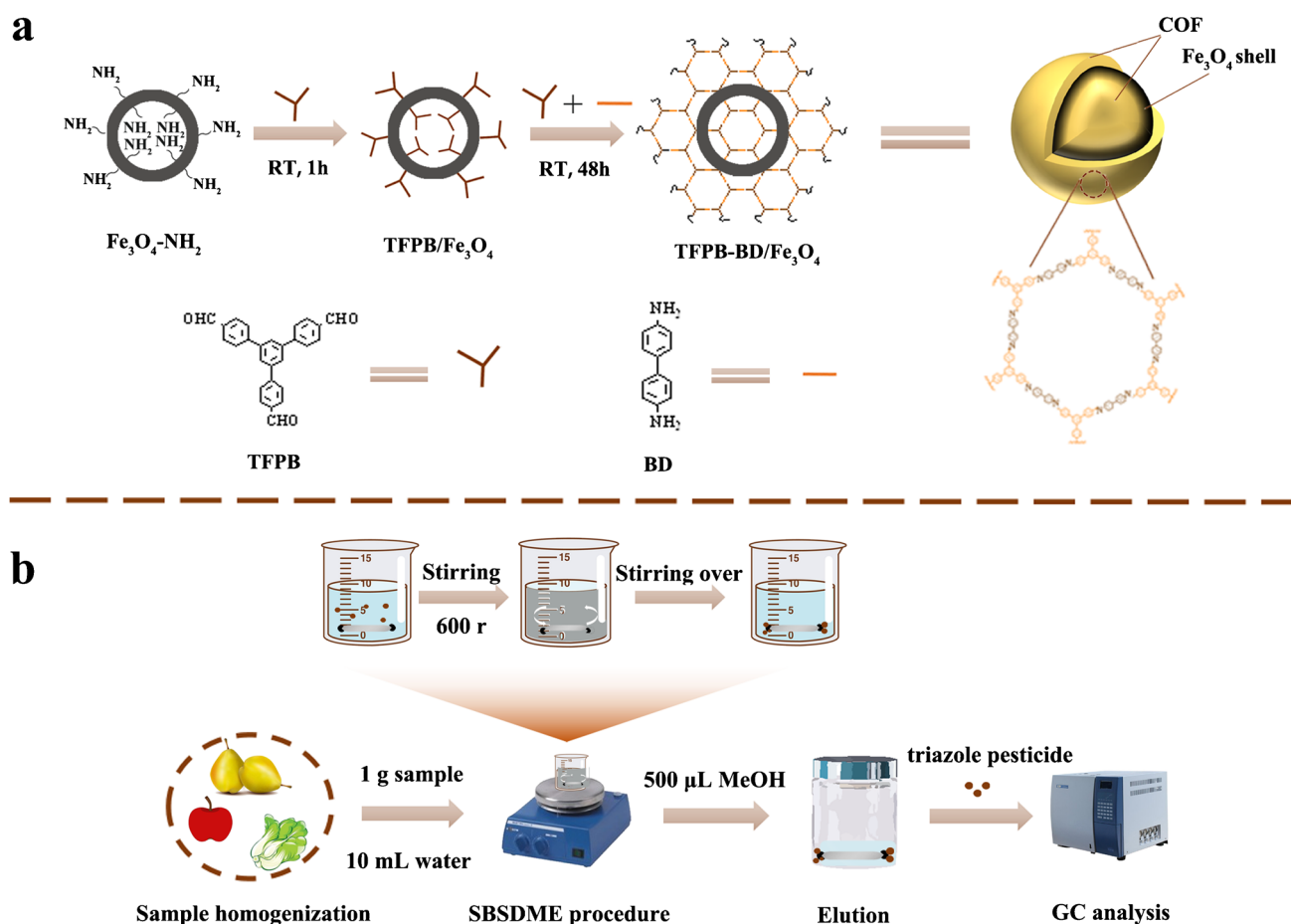


Fig. 1 Schematic diagram for (a) synthesis of the TFPB-BD/Fe₃O₄ and (b) application of the TFPB-BD/Fe₃O₄ as adsorbent for SBS-DME and the determination of triazole pesticides

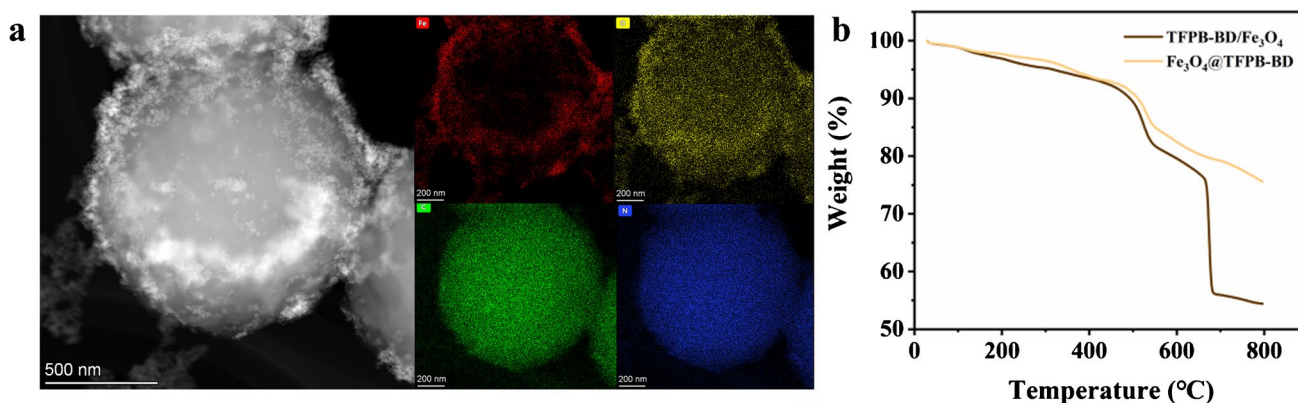
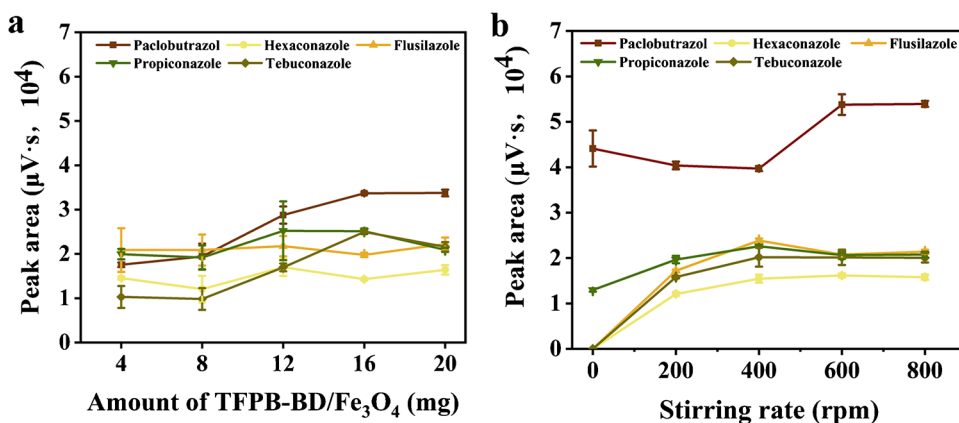


Fig. 2 The characterization of the TFPB-BD/Fe₃O₄. (a) HAADF-STEM image and EDX elemental mapping of the TFPB-BD/Fe₃O₄. (b) TGA curves of Fe₃O₄@TFPB-BD and TFPB-BD/Fe₃O₄

concentration, and extraction time. The amount of the TFPB-BD/Fe₃O₄ was optimized in the range of 4–20 mg (Fig. 3a), and the quantitative extraction has been reached at 16 mg. Stirring during the extraction process can disperse the magnetic adsorbent and accelerate the

diffusion of the target analyte from the sample to the adsorbents (Fig. 3b). The adsorption was balanced when the stirring rate reaches 600 rpm. Other optimizations of the SBS-DME parameters were provided in the Electronic supplementary material Text S4.

Fig. 3 Effect of (a) amount of adsorbent and (b) stirring rate on the TFPB-BD/Fe₃O₄ extraction efficiency



Method validation and adsorption mechanism exploration

The analytical performance of the TFPB-BD/Fe₃O₄-SBSDME-GC-FTD method for triazole pesticides was studied under optimized conditions (Table S1). The linear range of five triazole pesticides was 5–1000 μg L⁻¹ with $R^2 > 0.9949$. The LODs ($S/N=3$) and the quantification limits (LOQs) ($S/N=10$) were 0.17–1.48 μg L⁻¹ and 0.57–4.93 μg L⁻¹, respectively. Additionally, the intra-day and inter-day precision were evaluated by measuring the standard solution of 50 μg L⁻¹. As shown in Table S1, the intra-day RSDs ($n=6$) and inter-day RSDs ($n=6$) of five triazole pesticides were less than 9.9% and 11.5%, respectively. In order to evaluate the properties of the adsorbent materials, the reusability of the TFPB-BD/Fe₃O₄ was investigated (Fig. 4). After 20 adsorption/desorption cycles, the extraction efficiency of the TFPB-BD/Fe₃O₄ can maintain above 84.5%. These results show that the TFPB-BD/Fe₃O₄-SBSDME-GC-FTD method has good performance in the extraction of triazole pesticides. In order to further study the adsorption mechanism, XPS experiments of TFPB-BD/Fe₃O₄ before and after adsorption of triazole pesticides were observed (Fig. S5). The peak value of C=C at 284.43 eV before adsorption shifts to 284.51 eV after adsorption, which indicates the π - π interaction between TFPB-BD/Fe₃O₄ and triazole pesticides [39].

Compared with other triazole pesticides extraction methods reported in the literature (Table 1), this method has a shorter extraction time (9 min), and its linear range, LODs, and RSDs are similar to or better than other work. Most of the methods to detect triazole pesticides in fruits and vegetables need to consume a large amount of organic solvents (10–20 mL) to extract and purify [40–44]. The sample preparation of the TFPB-BD/Fe₃O₄-SBSDME-GC-FTD method for fruits and vegetables only needs homogenization and dilution. The extraction process does not require organic solvent consumption, and only 0.5 mL organic solvent is needed in the elution process, which is more environmentally friendly.

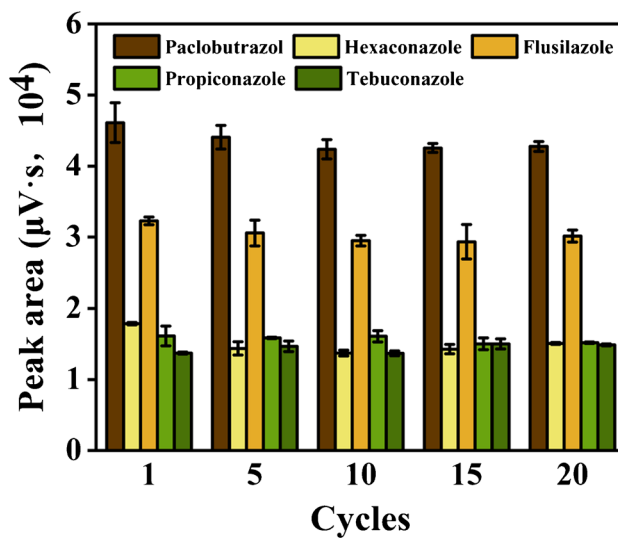


Fig. 4 Effect of number of cycles on the TFPB-BD/Fe₃O₄ extraction efficiency

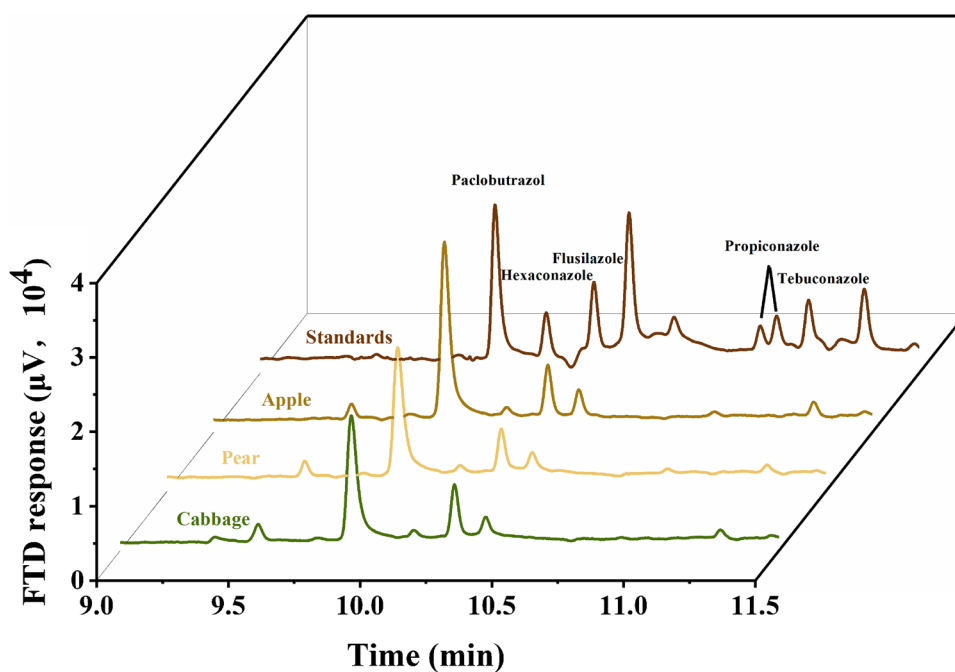
Application in real samples

In order to evaluate the accuracy and practicability of the TFPB-BD/Fe₃O₄-SBSDME-GC-FTD method, the triazole pesticides in fruits and vegetables (apples, pears, and cabbages) were detected. As shown in Fig. 5, paclobutrazol and flusilazole were detected in apple, pear, and cabbage samples (Table 2). And the contents of paclobutrazol in apples, pears, and cabbages were 0.42 mg kg⁻¹, 0.39 mg kg⁻¹, and 0.22 mg kg⁻¹. The contents of flusilazole were all below the LOQ.

The accuracy of the developed method was verified by a recovery study with spiking triazole pesticides at three concentration levels (0.1 mg kg⁻¹, 0.5 mg kg L⁻¹, and 1.0 mg kg L⁻¹). The calculation of recoveries showed that the sample matrix has little effect on the extraction efficiency of the method. As shown in Table 2, the recoveries of five triazole

Table 1 Comparison with the previously reported methods for the determination of triazole pesticides

Method	Materials	Sample	Linear range ($\mu\text{g L}^{-1}$)	LOD ($\mu\text{g L}^{-1}$)	RSD (%)	Extraction time	Ref
SEV-DLLME-GC-FID	-	Environmental water sample and juice	5–20,000	0.09–1.04	3.1–7.3	25	[45]
MSPE-HPLC-MS-MS	M-MOF-199	Environmental water sample	0.25–1000	0.05–0.1	1.5–9.1	15	[14]
MSPE-HPLC-MS-MS	Fe_3O_4 -MWCNT	Fruits and vegetables	5–500	0.52–1.83	1.2–2.8	20	[11]
SBSDME-GC-FTD	TFPB-BD/ Fe_3O_4	Fruits and vegetables	5–1000	0.17–1.48	2.1–9.9	9	This method

Fig. 5 Chromatogram of paclobutrazol, hexaconazole, flusilazole, propiconazole, and tebuconazole in fruits, vegetables, and standard solution by SBSDMI**Table 2** The concentrations (mg kg^{-1}) and recoveries (%) of five triazole pesticides in really samples ($n=3$)

Sample	Spiked concentration (mg kg^{-1})	Concentration (\pm SD, mg kg^{-1})/recovery (\pm SD, %)				
		Paclobutrazol	Hexaconazole	Flusilazole	Propiconazole	Tebuconazole
Apple	0	0.42 ± 0.01	ND	<LOQ	ND	ND
	0.1	111 ± 1	107 ± 3	91 ± 1	81 ± 2	87 ± 1
	0.5	99 ± 1	85 ± 3	92 ± 4	93 ± 6	93 ± 1
	1.0	115 ± 2	83 ± 3	111 ± 5	96 ± 5	87 ± 3
Pear	0	0.39 ± 0.01	ND	<LOQ	ND	ND
	0.1	95 ± 1	117 ± 5	116 ± 2	88 ± 2	81 ± 2
	0.5	100 ± 4	90 ± 2	114 ± 5	87 ± 5	92 ± 2
	1.0	110 ± 2	102 ± 6	95 ± 4	89 ± 2	93 ± 10
Cabbage	0	0.22 ± 0.01	ND	<LOQ	ND	ND
	0.1	102 ± 2	86 ± 2	86 ± 1	81 ± 4	86 ± 4
	0.5	110 ± 1	94 ± 5	104 ± 6	96 ± 1	98 ± 3
	1.0	94 ± 2	101 ± 4	109 ± 6	98 ± 3	103 ± 6

pesticides were 81–117%, and the RSDs < 11.3%, which showed that the method could be applied to the analysis of triazole pesticides in fruits and vegetables.

Conclusion

We explored a COF magnetization method based on Fe₃O₄ hollow microspheres to synthesize the TFPB-BD/Fe₃O₄, which was used as the adsorbent of SBSDME to extract triazole pesticides from fruits and vegetables. This method had the advantages of simple pretreatment, less organic solvent consumption, and short treatment time. Overall, it provided an example for the application of magnetic COFs combined with SBSDME method in the separation and enrichment of pesticides in complex matrix foods. Furthermore, other aromatic compounds close to the molecular sizes of triazole pesticides may cause interference. In future study, we will improve the selectivity of COF by functionalizing it (modifying functional groups, preparing molecular imprinting, etc.). And a small amount of organic solvent is still needed for desorption. In order to achieve environmentally friendly purposes, a step without solvent consumption also needs to be developed.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s00604-022-05613-x>.

Author contribution Yu-Xin Wang: conceptualization, methodology, formal analysis, investigation, writing original draft. Xiao-Fang Shen: conceptualization, resources, writing review and editing, funding acquisition. Yong-Wei Feng: conceptualization, methodology, investigation. Yue-Hong Pang: methodology, formal analysis, validation, investigation, project administration, funding acquisition.

Funding This work was supported by the National Natural Science Foundation of China (22276077, 21976070, 22076067) and the Fundamental Research Funds for the Central Universities (JUSRP22003).

Data availability The datasets during and/or analysed during the current study available from the corresponding author on reasonable request.

Declarations

Conflict of interest The authors declare no competing interests.

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