

Synthesis of a pyraclostrobin-imprinted ionic liquid- functionalized magnetic polymer for group-selective extraction and determination of strobilurin fungicides in fruit matrices

Meidi Wang

Chinese Academy of Quality and Inspection & Testing

Xiujuan Wang

Chinese Academy of Quality and Inspection & Testing

Xuesong Feng

China Medical University

Wei Guo

Chinese Academy of Quality and Inspection & Testing

Minli Yang

529513981@qq.com

Chinese Academy of Quality and Inspection & Testing

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Abstract

A pyraclostrobin-imprinted ionic-liquid-functionalized magnetic molecularly imprinted polymer ($\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@ \text{MIP}$) was developed as a group-selective adsorbent for magnetic solid-phase extraction (MSPE) of strobilurin fungicide residues from complex fruit matrices. The synthesized adsorbent exhibited a well-defined core-shell architecture and superparamagnetic behavior with a saturation magnetization of approximately 24 emu/g, enabling rapid magnetic separation within 15 s. Adsorption kinetics and isotherm studies demonstrated that $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@ \text{MIP}$ exhibited rapid adsorption (equilibrium time ≤ 30 min) and high adsorption capacities (19.02–22.85 mg/g) toward these compounds. Compared with the non-imprinted polymer, the material showed enhanced molecular recognition ability, with IF ranging from 1.474 to 2.949, indicating that the template-induced recognition sites contributed to the selective binding of target analytes. The enhanced adsorption performance was attributed to the synergistic effects of template-complementary cavities and multiple intermolecular interactions, including π -related interactions, hydrogen bonding, dipole-dipole interactions, and hydrophobic interactions. Furthermore, an MSPE-UPLC-MS/MS method was established. The developed method exhibited negligible matrix effects (-17.52 – 8.76%), high sensitivity (LODs of 0.015–0.333 $\mu\text{g/kg}$), satisfactory accuracy with recoveries of 82.40–99.09%, and good precision ($\text{RSDs} \leq 6.76\%$). Moreover, the adsorbent maintained satisfactory extraction performance after nine adsorption-desorption cycles and showed good batch-to-batch repeatability.

1. Introduction

The widespread use of strobilurin fungicides in modern agriculture has raised increasing concern regarding their residues in the food supply. Pyraclostrobin, a typical strobilurin fungicide, is extensively applied to control fungal diseases in fruits and vegetables because of its broad-spectrum activity and favorable field performance[1]. However, residues in fruits and vegetables may persist due to incomplete degradation and repeated application, leading to potential dietary exposure risks. According to National Standard of China(GB2763-2021) [2], maximum residue limits (MRLs) have been established for pyraclostrobin in various fruits, with limits of 0.05-2mg/kg in fruit matrices. Therefore, a reliable residue monitoring system needs to be established [3]. Accurate determination is further challenged because of the complex composition of fruit and vegetable matrices, including pigments, sugars, organic acids, lipids, and other endogenous components, which may cause substantial matrix interference during trace analysis[4]. Therefore, efficient and selective analytical methods are required for the determination of pyraclostrobin and related strobilurin fungicides in food samples.

At present, pyraclostrobin is mainly determined by chromatographic methods such as high-performance liquid chromatography (HPLC), liquid chromatography-tandem mass spectrometry (LC-MS/MS), and gas chromatography-tandem mass spectrometry (GC-MS/MS)[5]. These techniques provide high sensitivity and reliable quantification, and they are routinely combined with extraction procedures such as QuEChERS or other cleanup workflows for food analysis[6]. Nevertheless, the drawbacks of sample pretreatment such as cumbersome steps, instrument dependence, matrix-induced signal effects and time-consuming purification still limit analytical efficiency, especially when rapid and selective monitoring is required for complex fruit and vegetable samples[7].

Various sample-preparation techniques have been employed for the determination of pesticide residues in food matrices, including liquid-liquid extraction (LLE), solid-phase extraction (SPE), QuEChERS, and dispersive solid-phase extraction (d-SPE). Among these approaches, SPE remains widely used because of its relatively simple operation and compatibility with chromatographic analysis [8]. However, conventional sorbents often exhibit limited selectivity toward structurally related pesticides which may require relatively large solvent volumes or multistep cleanup procedures. Magnetic solid-phase extraction (MSPE) has therefore attracted increasing attention as an alternative strategy, because magnetic adsorbents can be directly dispersed in sample solutions and rapidly isolated by an external magnetic field, simplifying solid-liquid separation and improving extraction efficiency. Recent advances in MSPE have focused on functional magnetic sorbents such as molecularly imprinted polymers (MIPs), metal-organic frameworks (MOFs), and covalent organic frameworks (COFs). Among them, MIPs are particularly attractive for selective pesticide extraction because template-complementary cavities provide recognition sites matched in molecular size, shape, and functional-group distribution [9, 10]. Nevertheless, conventional MIPs may suffer from deeply buried and heterogeneously distributed binding sites, resulting in slow mass transfer and incomplete site accessibility [11, 12]. More importantly, previously reported pyraclostrobin-imprinted systems commonly relied on relatively hazardous organic porogens to maintain effective template-monomer interactions [13]. The introduction of a polymerizable imidazolium-based ionic liquid functional monomer may create a multifunctional recognition microenvironment within the imprinted cavities and provide an alternative strategy to overcome the limited recognition environment of conventional pyraclostrobin-imprinted systems [14]. Through multiple noncovalent interactions with pyraclostrobin, the ionic-liquid-containing polymer network strengthens template-monomer association during pre-polymerization and generates chemically diverse recognition sites after template removal. This design enables preferential recognition of pyraclostrobin while maintaining effective affinity toward structurally related strobilurin fungicides. In addition, the enhanced template-monomer interaction allows acetonitrile to serve as the porogenic solvent, providing a more compatible imprinting system. Meanwhile, the magnetic SiO_2 -supported surface-imprinting architecture shortens diffusion pathways, improves recognition-site accessibility, and enables rapid magnetic separation [15, 16]. On this basis, the present study developed a pyraclostrobin-imprinted ionic-liquid-functionalized magnetic MIP for the group-selective extraction of six strobilurin fungicides from banana and mango samples.

In this work, a pyraclostrobin-imprinted ionic-liquid-functionalized magnetic molecularly imprinted polymer was constructed on vinyl-modified $\text{Fe}_3\text{O}_4@\text{SiO}_2$ microspheres. Pyraclostrobin was used as the template molecule, 1-vinyl-3-ethylimidazolium bromide as the functional monomer, and ethylene glycol dimethacrylate as the cross-linker. The resulting $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@ \text{MIP}$ combined template-complementary cavities with an ionic-liquid-containing polymer environment and rapid magnetic separation. Its morphology, chemical composition, porosity, magnetic properties, adsorption behavior, selective recognition, and reusability were systematically investigated. Furthermore, a $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@ \text{MIP}$ -based MSPE method coupled with UPLC-MS/MS was developed for the determination of six strobilurin fungicides in banana and mango samples.

2. Experimental

2.1. Reagents and chemicals

Ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) and anhydrous sodium acetate were purchased from ANPEL Laboratory Technologies Inc. (Shanghai, China). Ethylene glycol, tetraethyl orthosilicate (TEOS), 3-(trimethoxysilyl) propyl methacrylate (MPS), acetic acid, formic acid, ammonium formate, and aqueous ammonia solution (25–28 wt%) were obtained from Aladdin Chemical Co., Ltd. (Shanghai, China). Ethylene glycol dimethacrylate (EGDMA), 2,2'-azobisisobutyronitrile (AIBN), and 1-vinyl-3-ethylimidazolium bromide were purchased from Adamas Reagent Co., Ltd. through Shanghai Titan Scientific Co., Ltd. (Shanghai, China). UPLC-grade acetonitrile, methanol, and ethanol were purchased from Thermo Fisher Scientific (Massachusetts, USA). Ultrapure water was produced using a Milli-Q water purification system (Millipore, Bedford, MA, USA).

Analytical standards of pyraclostrobin and trifloxystrobin were obtained from TMstandard and BePure, respectively, through Shanghai Titan Scientific Co., Ltd. (Shanghai, China). Analytical standards of azoxystrobin, picoxystrobin, fluoxastrobin, and enestroburin were purchased from Weiye Metrology (Beijing, China). Fluopyram, fluxapyroxad, and benzovindiflupyr, which were used as interfering compounds, were obtained from Tanmo Quality Testing Technology Co., Ltd. (Beijing, China). Fresh banana and mango samples were purchased from Qixian Supermarket (Beijing, China). The samples were transported to the laboratory and stored under appropriate conditions before sample preparation.

Individual stock solutions of the six target analytes and three interfering compounds were prepared at 100 mg/L in acetonitrile and stored at -20°C in amber glass bottles. Individual working solutions were prepared by diluting each stock solution with acetonitrile and ultrapure water to the desired concentrations for adsorption experiments. Mixed working solutions were obtained by mixing the individual working solutions and were used for MSPE extraction and method validation.

2.2 Preparation of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@\text{MIP}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@\text{NIP}$

2.2.1. Synthesis of Fe_3O_4 microspheres

Fe_3O_4 microspheres were synthesized using a solvothermal method adapted with minor modifications from Li et al. [17] $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (1.35 g) and sodium acetate (3.60 g) were dissolved in 50 mL of ethylene glycol under magnetic stirring. After homogeneous dispersion, the yellow solution was transferred into a Teflon-lined stainless-steel autoclave and heated at 200°C for 8 h. The autoclave was then cooled to room temperature. The resulting black magnetic particles were washed six times with ethanol and finally collected with a magnet, followed by vacuum drying at room temperature.

2.2.2. Synthesis of $\text{Fe}_3\text{O}_4@\text{SiO}_2$

$\text{Fe}_3\text{O}_4@\text{SiO}_2$ core-shell particles were prepared using a modified Stöber process based on the ammonia-catalyzed hydrolysis and condensation of tetraethyl orthosilicate (TEOS) [18]. Fe_3O_4 (1.0 g) was placed in a two-necked flask, followed by the addition of 100 mL of ethanol-water (15:4, v/v). After ultrasonic dispersion for 30 min, 3 mL of 25% ammonia solution and 4 mL of TEOS were added. The mixture was stirred at room temperature for 24 h. The magnetic particles were then separated by an external magnetic field, washed repeatedly with methanol, and vacuum-dried.

2.2.3. Synthesis of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-MPS}$

The vinyl-modification procedure was adapted from a reported MPS-grafting method for $\text{Fe}_3\text{O}_4@\text{SiO}_2$ magnetic carriers [19]. $\text{Fe}_3\text{O}_4@\text{SiO}_2$ (0.5 g) was transferred into 100 mL of acetic acid-water (1:9, v/v) in a 250 mL two-necked flask. Then, 150 μL of MPS was added, and the mixture was stirred at 60°C for 5 h. The resulting vinyl-modified $\text{Fe}_3\text{O}_4@\text{SiO}_2$ particles ($\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-MPS}$) were washed alternately with water and methanol three times and vacuum-dried.

2.2.4. Preparation of magnetic molecularly imprinted polymer ($\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@\text{MIP}$) for pyraclostrobin

Pyraclostrobin (78 mg) and 1-vinyl-3-ethylimidazolium bromide (164 mg) were dissolved in 40 mL of acetonitrile. The solution was stirred at room temperature for 3 h to facilitate pre-polymerization association between the template and the functional monomer. Subsequently, $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}$ (200 mg), EGDMA (0.7 mL), and AIBN (100 mg) were added to the mixture. After ultrasonic dispersion for 30 min, the mixture was purged with nitrogen for 30 min to remove dissolved oxygen, sealed, and polymerized at 60°C for 24 h under continuous stirring. The stepwise synthesis of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@\text{MIP}$ is schematically illustrated in Fig. 1(A).

The resulting $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@\text{MIP}$ was isolated using an external magnet and repeatedly washed with methanol/acetic acid (9:1, v/v) to remove the template molecule. Template removal was continued until pyraclostrobin was no longer detectable in the washing solution by UPLC-MS/MS. The material was subsequently washed with methanol until the washing solution approached neutrality and was then vacuum-dried at 50°C .

2.2.5 Preparation of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@\text{NIP}$

The corresponding non-imprinted polymer, $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@\text{NIP}$, was prepared following the same procedure used for $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@\text{MIP}$, except that pyraclostrobin was omitted during the pre-polymerization stage.

2.3 Characterization of the prepared adsorbents

The surface morphology and microstructure of the synthesized materials were characterized by scanning electron microscopy using a GeminiSEM 300 microscope (ZEISS, Germany). Transmission electron microscopy was performed using a Talos F200X microscope (Thermo Scientific, USA) to observe the particle morphology, core-shell structure, and thickness of the surface coating layer. Particle sizes and shell thicknesses were determined from representative electron microscopy images using ImageJ software. Fourier-transform infrared spectra were recorded using a Nicolet iS20 FTIR spectrometer (Thermo Scientific, USA) over the wavenumber range of $4000\text{--}400\text{ cm}^{-1}$ to identify changes in the characteristic functional groups during the stepwise

preparation of the magnetic imprinted polymer. X-ray diffraction patterns were obtained using a D8 Focus X-ray diffractometer (Bruker, Germany) equipped with Cu K α radiation. The diffraction data were collected over a 2θ range of $10\text{--}80^\circ$ at a scanning rate of $2^\circ/\text{min}$ to investigate the crystalline structure and phase stability of Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}$, and $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@ \text{MIP}$. Nitrogen adsorption–desorption measurements were performed at 77 K to comparatively determine the specific surface areas and pore characteristics of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@ \text{MIP}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@ \text{NIP}$. Before measurement, both powdered samples were degassed at 120°C for 8 h under identical conditions. The specific surface areas were calculated using the Brunauer–Emmett–Teller method, and the pore-size distributions in the range of 2–50 nm were determined using the Barrett–Joyner–Halenda method [20]. The surface elemental composition and chemical states of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@ \text{MIP}$ were analyzed by X-ray photoelectron spectroscopy using a K-Alpha spectrometer (Thermo Scientific, USA). Survey spectra and high-resolution spectra of the principal elements were recorded to verify the incorporation of the SiO_2 , MPS, and ionic-liquid-containing imprinted polymer layers. The magnetic properties of Fe_3O_4 and $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@ \text{MIP}$ were measured at room temperature using a Lake Shore 8604 vibrating sample magnetometer (Lake Shore Cryotronics, USA) over a magnetic-field range of -2 to $+2$ T. The saturation magnetization, coercivity, and remanent magnetization were evaluated to determine whether the synthesized materials retained sufficient magnetic responsiveness for rapid magnetic separation.

2.4 UPLC-MS/MS analysis

The target analytes were determined using a Waters Xevo TQ-XS UPLC–MS/MS system (Waters, Milford, MA, USA). Chromatographic separation was performed on a C18 column ($100\text{ mm} \times 2.1\text{ mm}$, $1.7\text{ }\mu\text{m}$) maintained at 40°C , with a constant flow rate of 0.3 mL/min and an injection volume of $2\text{ }\mu\text{L}$. The mobile phase consisted of water containing 0.1% formic acid and 2 mmol/L ammonium formate (A) and acetonitrile (B). The gradient elution program was as follows: $0\text{--}2.0\text{ min}$, $2\text{--}25\%$ B; $2.0\text{--}4.5\text{ min}$, $25\text{--}55\%$ B; $4.5\text{--}6.5\text{ min}$, $55\text{--}85\%$ B; $6.5\text{--}7.5\text{ min}$, $85\text{--}98\%$ B; $7.5\text{--}8.0\text{ min}$, 98% B; and $8.0\text{--}10.0\text{ min}$, $98\text{--}2\%$ B. Mass spectrometric detection was performed in positive electrospray ionization mode using multiple-reaction monitoring (MRM). The source and desolvation temperatures were set at 150 and 500°C , respectively. The cone-gas and desolvation-gas flow rates were maintained at 150 and 1000 L/h , respectively. Data acquisition and processing were performed using MassLynx V4.2 and TargetLynx XS software (Waters). The optimized MRM transitions and corresponding mass spectrometric parameters for the six strobilurin fungicides are summarized in Table S1.

2.5 Sample pretreatment

Fresh banana and mango samples were peeled, cut into small pieces, and homogenized using a laboratory blender. A 10.0 g portion of each homogenized sample was accurately weighed into a 50 mL polypropylene centrifuge tube, followed by the addition of 20 mL of acetonitrile/water/formic acid ($85:14:1$, v/v/v). The mixture was vortexed for 2 min , ultrasonicated at room temperature for 30 min , and centrifuged at $8,000\text{ rpm}$ at 4°C for 5 min . Approximately 10 mL of the supernatant was carefully transferred into a clean glass tube and evaporated to dryness under a gentle stream of nitrogen at 40°C . The residue was reconstituted in 10 mL of ultrapure water, and the solution pH was adjusted to 8.0 using dilute hydrochloric acid or sodium hydroxide solution. After filtration through a $0.22\text{ }\mu\text{m}$ nylon membrane, a 5 mL aliquot of the resulting solution was subjected to the MSPE procedure.

2.6 Magnetic solid-phase extraction procedures

For efficient extraction, 14 mg of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@ \text{MIP}$ was added to 5 mL of the pretreated sample solution adjusted to pH 8.0 . The mixture was shaken vigorously at 1800 rpm for 30 min to ensure sufficient interaction between the adsorbent and the target analytes. Following adsorption, the magnetic adsorbent was rapidly isolated from the solution using an external magnet for 15 s , and the supernatant was discarded. The retained analytes were subsequently desorbed using 8 mL of methanol/water ($1:1$, v/v) under ultrasonication for 30 min . After magnetic separation, the eluate was collected, filtered through a $0.22\text{ }\mu\text{m}$ nylon membrane, and subjected to UPLC-MS/MS analysis. The workflow of the MSPE procedure is schematically illustrated in Fig. 1(B).

3. Results and discussions

3.1. Characterization of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@ \text{MIP}$

The successful stepwise preparation of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@ \text{MIP}$ was verified by systematically comparing the morphological, structural, chemical, porous, and magnetic properties of Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{SiO}_2$, $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}$, and $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@ \text{MIP}$.

The surface morphology and microstructure of the magnetic particles during the stepwise preparation process were characterized by SEM and TEM. As shown in Fig. 2(A–C), Fe_3O_4 exhibited a nearly spherical morphology with a relatively rough surface, whereas the particle surfaces became smoother after SiO_2 coating. Following the formation of the molecularly imprinted polymer layer, $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@ \text{MIP}$ retained its approximately spherical morphology and exhibited an increased particle size. The corresponding TEM images in Fig. 2(D–F) further revealed the structural evolution of the particles. A continuous outer layer was observed around the magnetic core of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@ \text{MIP}$, with an average thickness of approximately 20 nm .

$\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@ \text{MIP}$ was further confirmed by FT-IR spectroscopy, as shown in Fig. 3(A). Bare Fe_3O_4 exhibited a characteristic absorption band at approximately 595 cm^{-1} , corresponding to Fe–O stretching vibration of the magnetic core. After SiO_2 coating, new absorption bands appeared at approximately 1095 , 951 , 801 , and 473 cm^{-1} , which were assigned to the asymmetric stretching, silanol bending, symmetric stretching, and bending vibrations of Si–O–Si or Si–OH groups, respectively, confirming the formation of the silica shell. Following MPS modification, a new band at approximately 1628 cm^{-1} was observed and attributed to the C = C stretching vibration of the methacrylate group, indicating the successful introduction of polymerizable vinyl groups. After imprinting polymerization, new aliphatic C–H stretching bands appeared at approximately 2927 and 2854 cm^{-1} , accompanied by obvious changes in the vinyl-related band around 1628 cm^{-1} , demonstrating the formation of the organic imprinted polymer layer. $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@ \text{MIP}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@ \text{NIP}$ exhibited similar polymer-backbone features, whereas differences in their peak positions and relative intensities reflected the different chemical microenvironments generated in the presence and absence of the template molecule. Meanwhile, the characteristic Fe–O and Si–O–Si bands remained detectable after polymerization, indicating that the Fe_3O_4 core and SiO_2 shell were preserved throughout the preparation process.

The crystalline structures of Fe_3O_4 and $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@ \text{MIP}$ were investigated by XRD. As shown in Fig. 3(B), Fe_3O_4 exhibited characteristic diffraction peaks at 2θ values of 30.1° , 35.5° , 43.2° , 53.5° , 57.0° and 62.6° , corresponding to the (220), (311), (400), (422), (511) and (440) crystal planes of spinel Fe_3O_4 , respectively [21]. After SiO_2 coating and MPS modification, the characteristic diffraction peaks of Fe_3O_4 remained detectable, although their intensities decreased because of the surrounding noncrystalline layers. $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@ \text{MIP}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@ \text{NIP}$ retained the same characteristic peak positions, indicating that the crystalline structure of the Fe_3O_4 core remained intact throughout the surface-modification and polymerization processes. In addition, broad diffraction features observed in the low-angle region were attributed to the amorphous SiO_2 and cross-linked polymer layers. The similar diffraction patterns of the imprinted and non-imprinted materials indicated that template introduction did not alter the crystalline phase of the magnetic core or the principal structure of the polymer matrix.

The pore characteristics of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@ \text{MIP}$ and $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@ \text{NIP}$ were comparatively investigated by nitrogen adsorption–desorption analysis. As shown in Fig. 3(C), both materials exhibited adsorption–desorption hysteresis loops at relatively high relative pressures, indicating the presence of mesopores and interparticle voids. The material exhibited an adsorption–desorption hysteresis loop at relatively high relative pressures, indicating the presence of mesopores and interparticle voids. The BET specific surface area of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@ \text{MIP}$ was $16.89 \text{ m}^2/\text{g}$, approximately 6.0 times higher than that of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@ \text{NIP}$ ($2.81 \text{ m}^2/\text{g}$). The total pore volume of the MIP was $0.0475 \text{ cm}^3/\text{g}$, which was approximately 2.9 times that of the NIP ($0.0163 \text{ cm}^3/\text{g}$). Moreover, the average adsorption pore diameters of the MIP and NIP were 11.25 and 23.23 nm, respectively. Although the NIP exhibited a larger average pore diameter, its substantially lower specific surface area and pore volume indicated a less-developed porous structure with fewer accessible adsorption sites. In contrast, template removal from the MIP generated additional cavities and interconnected pore channels, resulting in a higher accessible surface area and pore volume. These structural differences facilitated the diffusion of the strobilurin fungicides and increased their accessibility to the imprinted recognition sites, thereby supporting the higher adsorption performance of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@ \text{MIP}$.

The magnetic properties of Fe_3O_4 and $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@ \text{MIP}$ were investigated using vibrating sample magnetometry. As shown in Fig. 3(D), the saturation magnetization decreased from approximately 68 emu/g for bare Fe_3O_4 to approximately 24 emu/g after coating with the SiO_2 , MPS and MIP layers. This decrease was attributed to the increased proportion of nonmagnetic components surrounding the Fe_3O_4 core. Despite the reduction in saturation magnetization, $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@ \text{MIP}$ retained superparamagnetic behavior and exhibited a strong response to an external magnetic field [22]. Moreover, the material could be rapidly separated from the solution within 15 s using a magnet, demonstrating its suitability for efficient MSPE.

X-ray photoelectron spectroscopy (XPS) was performed to investigate the surface elemental composition and chemical states of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@ \text{MIP}$. As shown in Fig. 3(E), the survey spectrum displayed characteristic signals of C, O, N, Si, and Fe elements, confirming the successful integration of the Fe_3O_4 magnetic core, SiO_2 shell, MPS interfacial layer, and ionic-liquid-functionalized imprinted polymer. The high-resolution N 1s spectrum (Fig. 3(F)) was deconvoluted into three components at 398.84, 400.02, and 401.84 eV, which were assigned to C = N, C–N, and positively charged nitrogen species in the imidazolium groups, respectively. The presence of these nitrogen-containing species confirmed the successful incorporation of the ionic-liquid functional monomer into the imprinted polymer layer. [23]. In addition, the C 1s spectrum verified the formation of the organic cross-linked polymer network through the presence of carbon-containing functional groups, while the Si 2p spectrum confirmed the coexistence of Si–O species from the SiO_2 shell and silicon-containing groups introduced by MPS modification. The O 1s spectrum further demonstrated the presence of oxygen-containing bonds associated with SiO_2 , the polymer layer, and the Fe_3O_4 core, and the Fe 2p spectrum confirmed the coexistence of Fe^{2+} and Fe^{3+} characteristic of magnetite. Collectively, these XPS results verified the successful stepwise construction of the $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@ \text{MIP}$ composite.

3.2 Optimization of extraction conditions

To maximize the extraction performance of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@ \text{MIP}$ toward the six strobilurin fungicides, the critical parameters of the MSPE procedure, including adsorbent dosage, adsorption pH, adsorption time, desorption solvent selection, desorption solvent volume, and desorption time, were systematically optimized using 5 mL of mixed aqueous standard solution containing each analyte at $20 \mu\text{g}/\text{L}$. All experiments were performed in triplicate. The following conditions provided the best extraction performance: (a) adsorbent dosage, 14 mg; (b) adsorption pH, 8.0; (c) adsorption time, 25 min; (d) desorption solvent, methanol/water (1:1, v/v); and (e) desorption solvent volume, 8 mL. The detailed optimization results are shown in Fig. S1 and the Electronic Supporting Material (ESM)

3.3 Selectivity of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@ \text{MIP}$ and adsorption behavior of the prepared adsorbents

The selectivity of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@ \text{MIP}$ was first evaluated using fluopyram, fluxapyroxad, and benzovindiflupyr as interfering compounds at concentrations of 1, 10, and 50 ng/mL. The adsorption efficiencies of these three interfering compounds remained low at all three concentrations, ranging from 17.11% to 22.58%. In contrast, the six target strobilurin fungicides exhibited substantially higher adsorption efficiencies of 84.7–91.5%, 82.1–98.1%, and 82.8–99.6% at 1, 10, and 50 ng/mL, respectively. The consistently higher adsorption of the target compounds at each concentration demonstrates the preferential recognition of strobilurin fungicides by $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@ \text{MIP}$ over the selected non-target fungicides [24].

To further clarify the contribution of the imprinted layer to adsorption, different types of adsorbents were comparatively evaluated under identical conditions. As shown in Fig. 4, the recoveries obtained using Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{SiO}_2$, and $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}$ were 20.50–29.60%, 21.04–39.89%, and 26.38–43.83%, respectively. $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@ \text{NIP}$ provided recoveries of 31.12–68.07%, whereas $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@ \text{MIP}$ achieved markedly higher recoveries of 71.47–102.84%. The pronounced enhancement in adsorption after formation of the imprinted layer demonstrates that the template-derived recognition sites play a major role in the retention of the target strobilurin fungicides.

As summarized in Table 1, the IF of the six strobilurin fungicides ranged from 1.474 to 2.949. Pyraclostrobin showed the highest imprinting factor ($\alpha = 2.949$), whereas the other five fungicides exhibited values of 1.474–2.149. Among the non-template analytes, azoxystrobin exhibited the highest imprinting factor (α

= 2.149). This relatively high value may be related to its structural similarity to pyraclostrobin. The two compounds have comparable molecular weights (403.4 and 387.8, respectively) and both contain extended aromatic/heteroaromatic moieties together with multiple oxygen-containing functional groups. These similarities in molecular dimensions, hydrophobic character, and interaction-site distribution allow azoxystrobin to partially fit the pyraclostrobin-derived cavities and interact with the surrounding functional groups through π - π , dipolar, and hydrogen-bonding interactions. Nevertheless, its lower imprinting factor than that of pyraclostrobin indicates that the cavity complementarity remains more favorable for the template molecule. Overall, $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@ \text{MIP}$ exhibits broad recognition toward structurally related strobilurin fungicides while retaining a certain preference for pyraclostrobin.

Table 1

IF of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@ \text{MIP}$ for six strobilurin fungicides

Target analyte	MIP adsorption capacity (mg/g)	NIP adsorption capacity (mg/g)	IF
Pyraclostrobin	21.85	7.409	2.949
Enestroburin	19.53	13.250	1.474
Azoxystrobin	19.14	8.906	2.149
Trifloxystrobin	22.85	12.365	1.848
Picoxystrobin	21.25	14.064	1.511
Fluoxastrobin	19.02	8.976	2.119

3.4 Reusability and batch-to-batch repeatability of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@ \text{MIP}$

The reusability of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@ \text{MIP}$ was evaluated through nine consecutive adsorption–desorption cycles under the optimized extraction conditions. After each cycle, the recovered adsorbent was alternately washed with methanol and water to remove residual analytes and was subsequently reused. As shown in Figure S2, the recoveries of the six target analytes remained within 77.57–104.65% throughout the nine cycles, with RSDs ranging from 4.8% to 7.2%, demonstrating the good reusability and stability of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@ \text{MIP}$. No substantial deterioration in extraction performance was observed, indicating that the imprinted polymer layer retained its recognition ability during repeated adsorption, desorption, and regeneration processes. Batch-to-batch repeatability was further evaluated using independently synthesized batches of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@ \text{MIP}$. The resulting RSDs ranged from 5.0% to 7.8%, demonstrating satisfactory consistency of the material preparation procedure and supporting its potential application in routine sample pretreatment.

3.5 Adsorption performance

The adsorption behavior of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@ \text{MIP}$ toward six strobilurin fungicides was preliminarily investigated through adsorption isotherms and kinetics. The corresponding calculation equations are provided in the Supporting Information. The adsorption isotherm curves are presented in Fig. 5(A), and the fitted model parameters are summarized in Table S2. The Langmuir and Freundlich models were employed to evaluate the adsorption mechanism of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@ \text{MIP}$. The Langmuir model exhibited a superior fitting performance compared with the Freundlich model, with correlation coefficients of $R^2 > 0.995$ and $R^2 > 0.946$, respectively. These results indicated that the adsorption of strobilurin fungicides onto $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@ \text{MIP}$ mainly followed a monolayer adsorption mechanism on relatively homogeneous recognition sites. According to the Langmuir model, the theoretical maximum adsorption capacities (Q_{max}) were calculated to be 21.85, 19.14, 22.85, 21.25, 19.02, and 19.53 mg/g for pyraclostrobin, azoxystrobin, trifloxystrobin, picoxystrobin, fluoxastrobin, and enestroburin, respectively. The relatively high adsorption capacities could be attributed to the abundant specific recognition cavities formed by molecular imprinting, together with the multiple noncovalent interactions provided by the ionic-liquid functional monomer, which facilitated the selective binding of strobilurin molecules.

The adsorption kinetic curves of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@ \text{MIP}$ are shown in Fig. 5(B). The adsorption capacities increased rapidly during the initial stage and gradually approached equilibrium with prolonged adsorption time. For all six strobilurin fungicides, adsorption equilibrium was reached at approximately 30 min, after which the adsorption capacities remained nearly unchanged. This relatively short equilibrium time indicated the rapid accessibility of the imprinted recognition sites. The adsorption kinetic data were further analyzed using pseudo-first-order and pseudo-second-order models, and the fitting parameters are summarized in Table S3. The pseudo-second-order model exhibited superior fitting performance compared with the pseudo-first-order model, with correlation coefficients of $R^2 > 0.991$ and $R^2 > 0.959$, respectively. These results suggested that the adsorption process was mainly controlled by specific interactions between the strobilurin fungicides and the recognition sites within the imprinted cavities, including hydrogen bonding, π -related interactions, dipole interactions, and other noncovalent interactions.

Overall, the adsorption of the six strobilurin fungicides onto $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@ \text{MIP}$ was mainly dominated by homogeneous monolayer adsorption, and the adsorption process followed the pseudo-second-order kinetic model, demonstrating the important role of specific molecular recognition interactions in the adsorption process [25].

3.6 Possible adsorption mechanism

The adsorption mechanism of the six strobilurin fungicides on $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@ \text{MIP}$ involved molecular imprinting recognition combined with multiple noncovalent interactions. During pre-polymerization, pyraclostrobin interacted with 1-vinyl-3-ethylimidazolium bromide and other functional groups in the polymerization system. Subsequent crosslinking fixed these interactions within the polymer layer, and template removal generated recognition cavities complementary to pyraclostrobin in molecular size, spatial configuration, and functional-group distribution [26]. Owing to their similar aromatic and methoxyacrylate-related structures, the other five strobilurin fungicides could also enter these cavities, resulting in group-selective recognition. Within the

cavities, π -related interactions, hydrogen bonding, and dipole–dipole interactions further stabilized analyte binding, while the hydrophobic polymer microenvironment enhanced affinity toward the relatively nonpolar target molecules. The superior extraction performance of the MIP over the NIP and intermediate materials further supported the contribution of the imprinted cavities, whereas its larger surface area and pore volume facilitated access to the recognition sites.

3.7 Method validation

Matrix effects may influence the ionization efficiency of target analytes during UPLC–MS/MS analysis, which was evaluated using ME (%) = [(slope of the matrix calibration curve/slope of the solvent calibration curve) – 1] × 100. The ME values ranged from – 3.72% to 8.76% in banana and from – 17.52% to – 1.31% in mango. Although ion suppression was more pronounced in mango, all ME values remained within ± 20%, indicating that the matrix effects were acceptable and did not substantially affect quantitative analysis [27]. Therefore, matrix-matched calibration was not required, and solvent-based calibration curves were used for quantitative determination of the six strobilurin fungicides.

The analytical performance of the developed Fe₃O₄@SiO₂@MPS@MIP-based MSPE–UPLC–MS/MS method was further evaluated in banana and mango samples, and the validation parameters are summarized in Table 2. The lower limits of the linear ranges varied from 0.045 to 0.885 µg/L in banana and from 0.045 to 1.000 µg/L in mango, with a common upper limit of 100 µg/L. The coefficients of determination (R²) were 0.9919–0.9995 and 0.9909–0.9993 for banana and mango, respectively. The LODs and LOQs were 0.015–0.295 and 0.045–0.885 µg/kg in banana, and 0.015–0.333 and 0.045–1.000 µg/kg in mango, respectively. The intra-day and inter-day RSDs did not exceed 5.06% and 6.76%, respectively, demonstrating satisfactory precision.

Table 3 Determination results and spiked recovery of six strobilurin fungicides in real samples			
Analytes	Spiked (µg/kg)	Banana	Mango
		Averaged recovery (%)	Averaged recovery (%)
Pyraclostrobin	0	N.D.	N.D.
	1	85.20 ± 3.15	80.68 ± 5.84
	10	82.40 ± 3.17	82.79 ± 2.41
	50	89.27 ± 3.47	89.10 ± 3.19
Azoxystrobin	0	N.D.	N.D.
	1	75.81 ± 11.71	79.45 ± 1.76
	10	91.44 ± 2.91	91.51 ± 2.45
	50	92.33 ± 2.75	92.52 ± 2.92
Trifloxystrobin	0	N.D.	N.D.
	1	95.26 ± 3.45	96.28 ± 4.45
	10	95.32 ± 4.62	95.28 ± 4.47
	50	97.58 ± 3.28	97.96 ± 3.28
Picoxystrobin	0	N.D.	N.D.
	1	86.39 ± 4.76	87.60 ± 7.69
	10	99.09 ± 2.29	99.09 ± 1.98
	50	97.51 ± 2.24	96.88 ± 2.26
Fluoxastrobin	0	N.D.	N.D.
	1	88.31 ± 2.94	87.15 ± 3.92
	10	88.88 ± 5.71	90.74 ± 4.73
	50	89.58 ± 3.55	88.22 ± 4.06
Enestroburin	0	N.D.	N.D.
	1	88.55 ± 3.32	90.28 ± 3.00
	10	92.95 ± 3.35	93.98 ± 3.13
	50	92.50 ± 3.73	91.72 ± 2.50
N.D., not detected.			

Method accuracy and applicability to real samples were further evaluated by spiked-recovery experiments. These fortification levels were selected with consideration of both method sensitivity and regulatory residue monitoring. As shown in Table 3, the blank banana and mango samples showed no detectable levels of the target analytes. At the three spiking levels (1, 10, and 50 µg/kg), the recoveries ranged from 75.81% to 99.09% in banana and from

79.45% to 99.09% in mango, with RSD values of 2.24–11.71% and 1.76–7.69%, respectively. The relatively higher RSD values observed at the lowest spiking level (1 µg/kg) were mainly associated with the lower analyte concentration and increased influence of matrix background. Overall, these results demonstrate that the proposed method provides satisfactory sensitivity, precision, accuracy, and applicability for the determination of six strobilurin fungicides in banana and mango samples.

Table 2
Method validation parameters of the developed Fe₃O₄@SiO₂@MPS@MIP-based MSPE–UPLC–MS/MS method for six strobilurin fungicides in banana and mango samples

Matrix	Analytes	Linear range (µg/L)	R ²	LOD (µg/kg)	LOQ (µg/kg)	Intra-day RSD (% , n = 5)	Inter-day RSD (% , n = 5)	Matrix effect (%)
Banana	Pyraclostrobin	0.705–100	0.9975	0.235	0.705	5.06	6.76	1.26
	Enestroburin	0.660–100	0.9929	0.220	0.660	0.96	1.79	−3.72
	Azoxystrobin	0.045–100	0.9995	0.015	0.045	1.27	2.18	4.45
	Trifloxystrobin	0.405–100	0.9919	0.135	0.405	1.78	1.94	0.33
	Picoxystrobin	0.480–100	0.9970	0.160	0.480	1.86	2.52	2.06
	Fluoxastrobin	0.885–100	0.9982	0.295	0.885	5.01	4.69	8.76
Mango	Pyraclostrobin	0.735–100	0.9967	0.245	0.735	1.07	2.80	−1.31
	Enestroburin	0.750–100	0.9971	0.250	0.750	1.92	2.82	−14.34
	Azoxystrobin	0.045–100	0.9993	0.015	0.045	2.03	2.69	−2.65
	Trifloxystrobin	0.495–100	0.9909	0.165	0.495	2.15	3.88	−17.52
	Picoxystrobin	0.495–100	0.9991	0.165	0.495	1.84	2.12	−2.73
	Fluoxastrobin	1.000–100	0.9990	0.333	1.000	3.93	4.40	−7.81

3.8 Application of Fe₃O₄@SiO₂@MPS@MIP in real sample analysis

To evaluate the accuracy and applicability of the developed method in real food samples, spiked recovery experiments were performed over the concentration range of 0–50 µg/kg. No target analytes were detected in the unspiked samples. In the tested food matrices, the recoveries ranged from 75.81% to 99.09%, with RSDs of 1.76–11.71%. These results demonstrate that the developed Fe₃O₄@SiO₂@MPS@MIP-based MSPE–UPLC–MS/MS method provides acceptable accuracy and applicability for the determination of six strobilurin fungicides in real food samples.

3.9 Comparison with existing methods

The analytical performance of the developed Fe₃O₄@SiO₂@MPS@MIP-based MSPE–UPLC–MS/MS method was compared with previously reported methods for the determination of pyraclostrobin and other strobilurin fungicides, as summarized in Table 4. Among these methods, the pyraclostrobin-imprinted extraction method reported by Wang et al. required 100 mg of MIP adsorbent, with both adsorption and desorption times of 50 min, and exhibited an LOD of 10 µg/kg [13]. In comparison, the present method required only 14 mg of Fe₃O₄@SiO₂@MPS@MIP, with adsorption and desorption times of 30 min each, thereby reducing adsorbent consumption and shortening the overall sample pretreatment process.

In addition, the previously reported QuEChERS–UPLC–MS/MS method showed an LOQ of 5 µg/kg for strobilurin fungicides, with recoveries of 76.9–114.2% and RSD values below 13.6% [28]. For the determination of strobilurin fungicides in traditional Chinese medicinal materials using SPE–LC–MS/MS, the LOQ of pyraclostrobin was 4 µg/kg, while the overall recoveries ranged from 60.4 to 110% with RSD values of 1.2–17% [29]. Zhou et al. developed an SPE–UPLC–MS/MS method for the determination of strobilurin fungicides in fruit samples, achieving recoveries of 60.4–120% and RSD values of 2.15–15.1% [30]. Hu et al. reported a magnetic molecularly imprinted polymer-based MSPE method for the extraction of strobilurin fungicides from agricultural products, which achieved recoveries of 71.5–115.8%, with LODs and LOQs of 0.03–0.49 µg/kg and 0.09–1.64 µg/kg, respectively [14]. However, the extraction performance of the reported method was mainly evaluated based on individual analyte systems, whereas the present Fe₃O₄@SiO₂@MPS@MIP method enabled the simultaneous enrichment of six strobilurin fungicides under competitive adsorption conditions. By comparison, the present method provided LODs and LOQs of 0.015–0.333 µg/kg and 0.045–1.000 µg/kg, respectively, together with recoveries of 75.81–99.09% and RSD values of 0.96–6.76%, indicating good analytical sensitivity, accuracy, and precision.

Furthermore, owing to the magnetic Fe₃O₄ core, Fe₃O₄@SiO₂@MPS@MIP could be rapidly separated from the sample solution using an external magnetic field, with the magnetic separation process requiring only approximately 15 s, thereby simplifying the solid–liquid separation step compared with conventional SPE. In addition, the adsorbent maintained relatively stable extraction performance after nine consecutive adsorption–desorption cycles, demonstrating good reusability. Overall, compared with previously reported methods, the proposed method provides a favorable combination of low adsorbent consumption, satisfactory sensitivity, good recoveries and precision, convenient magnetic separation, and adsorbent reusability, highlighting its potential for the efficient determination of strobilurin fungicides in fruit samples.

Table 4
Comparison of the proposed method with previously reported methods for the determination of strobilurins

Samples	Pretreatment method	Analytical method	Adsorbent	Adsorbent amount	Extraction/desorption time	Solvent consumption	Linear range	LOD
Ginseng	MIDSPE	UPLC	Pyraclostrobin-MIP	100 mg	Adsorption: 50 min; desorption: 50 min	8.0 mL MeOH/AcOH (9:1, v/v)	Range not stated; $R^2 = 0.9987$	10 $\mu\text{g/kg}$
Maize, wheat, grape, apple, cucumber, and tomato	QuEChERS + d-SPE	UPLC–MS/MS	C18	C18 d-SPE; mass not stated	QuEChERS extraction + d-SPE cleanup; exact pretreatment time not stated	ACN extraction; exact volume not stated	Range not stated; $R^2 > 0.9929$	Not separately reported
Chinese herbs	SPE	LC–MS/MS	Amino SPE cartridge	500 mg/6 mL	Water soaking: 15 min; homogenization: 1 min; SPE cleanup	2 × 15 mL EtOAc extraction; 10 mL EtOAc/toluene (7:3, v/v) SPE elution	1–20, 2–40, or 5–100 $\mu\text{g/L}$, analyte-dependent	0.5–3 $\mu\text{g/kg}$
Orange, banana, apple, and pineapple	SPE	UPLC–MS/MS	SupelClean LC-NH ₂	SupelClean LC-NH ₂ cartridge; bed mass not stated	ACN extraction + SPE cleanup; exact times not stated	ACN extraction; exact volume not stated	1–20 $\mu\text{g/L}$ (Pyraclostrobin); 5–100 $\mu\text{g/L}$ (others)	Not reported
Agricultural products (winter jujube, pear, zucchini, and cucumber)	MSPE	HPLC–MS/MS	Fe ₃ O ₄ @SiO ₂ @NH ₂ @MMIP	30 mg	Adsorption: 5 min; desorption: 20 s	4 mL MeOH	5–200 ng/mL	0.03–0.1 ng/g
Banana and mango	MSPE	UPLC–MS/MS	Fe ₃ O ₄ @SiO ₂ @MPS@MIP	14 mg	Adsorption: 30 min; magnetic separation: 15 s	8 mL MeOH/H ₂ O (1:1, v/v)	Lower limit: 0.045–1.000 $\mu\text{g/kg}$; upper limit: 100 $\mu\text{g/kg}$	0.015–0.333 $\mu\text{g/kg}$

4. Conclusion

In this study, a pyraclostrobin-imprinted ionic-liquid-functionalized magnetic molecularly imprinted polymer, Fe₃O₄@SiO₂@MPS@MIP, was successfully prepared and applied to the selective MSPE of six strobilurin fungicides. The material exhibited a well-defined core–shell structure, a BET specific surface area of 16.89 m²/g, and a saturation magnetization of approximately 24 emu/g, allowing rapid magnetic separation from the sample solution. Compared with Fe₃O₄, Fe₃O₄@SiO₂, Fe₃O₄@SiO₂@MPS, and Fe₃O₄@SiO₂@MPS@NIP, the MIP exhibited substantially higher extraction performance, confirming the important contribution of template-generated recognition cavities to selective adsorption, with apparent maximum adsorption capacities of 19.02–22.85 mg/g for the six target analytes. Based on these favorable recognition and adsorption properties, an MSPE–UPLC–MS/MS method was established under the optimized conditions of 14 mg adsorbent, pH 8.0, an adsorption time of 30 min, and methanol/water (1:1, v/v) as the desorption solvent. The linear ranges varied from 0.045 to 100 $\mu\text{g/L}$, with coefficients of determination (R^2) ranging from 0.9909 to 0.9995. The LODs and LOQs were 0.015–0.333 $\mu\text{g/kg}$ and 0.045–1.000 $\mu\text{g/kg}$, respectively. Satisfactory recoveries of 75.81–99.09% were obtained in banana and mango samples, while the intra-day and inter-day RSDs did not exceed 5.06% and 6.76%, respectively. The adsorbent also maintained satisfactory extraction performance over nine adsorption–desorption cycles and showed acceptable batch-to-batch repeatability. These results demonstrate that Fe₃O₄@SiO₂@MPS@MIP is an effective magnetic sorbent for the selective extraction and determination of trace strobilurin fungicide residues in complex fruit matrices. Nevertheless, the relatively limited specific surface area of the current sorbent may restrict its adsorption performance. Therefore, future studies will focus on optimizing the surface architecture and pore characteristics of magnetic molecularly imprinted sorbents to increase accessible recognition sites, enhance adsorption capacity and practical performance, and extend their application to a broader range of complex food matrices.

Declarations

Declarations of AI-assisted Technologies

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Author Contribution

M.W. contributed to conceptualization, methodology, and writing – review & editing. X.W. contributed to validation and writing – review & editing. X.F. contributed to writing – review & editing. W.G. contributed to supervision and writing – review & editing. M.Y. contributed to conceptualization, validation, supervision, project administration, and funding acquisition. All authors reviewed and approved the final manuscript.

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Figures

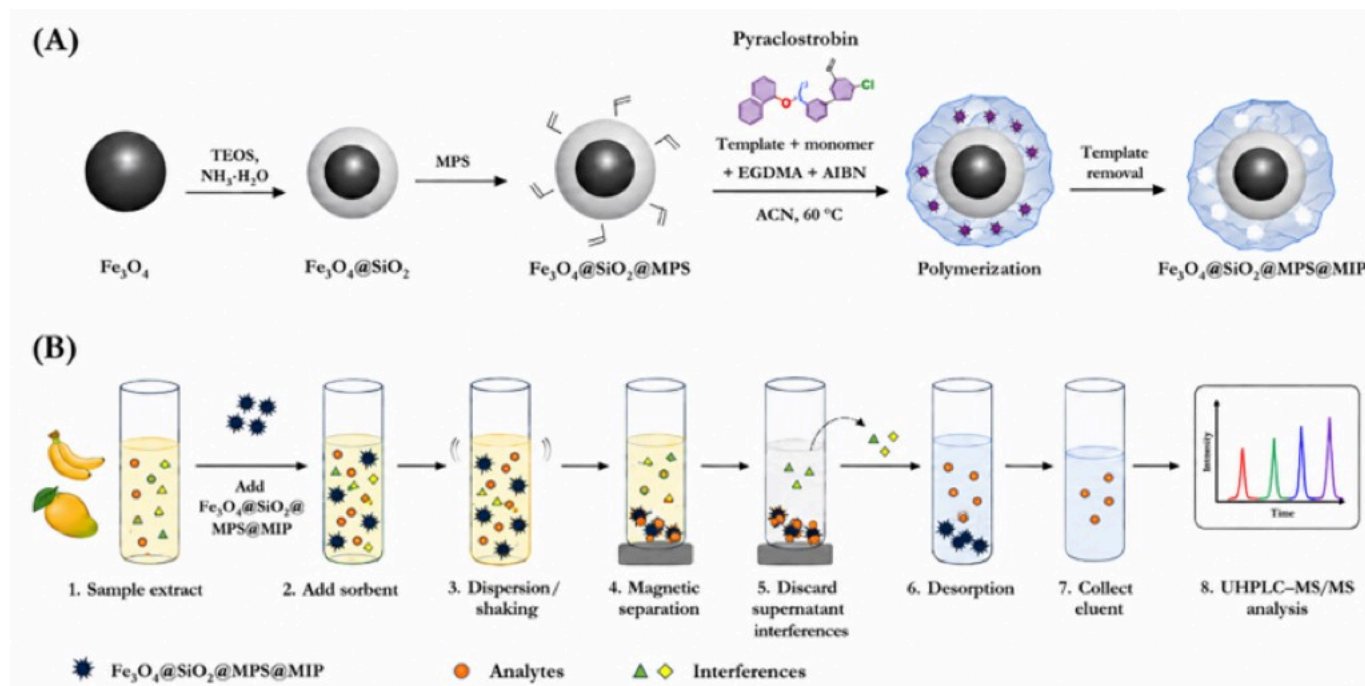


Figure 1

Schematic illustration of (A) the synthesis of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@ \text{MIP}$ using pyraclostrobin as the template molecule and (B) the magnetic solid-phase extraction procedure for the determination of six strobilurin fungicides in banana and mango samples followed by UPLC-MS/MS analysis.

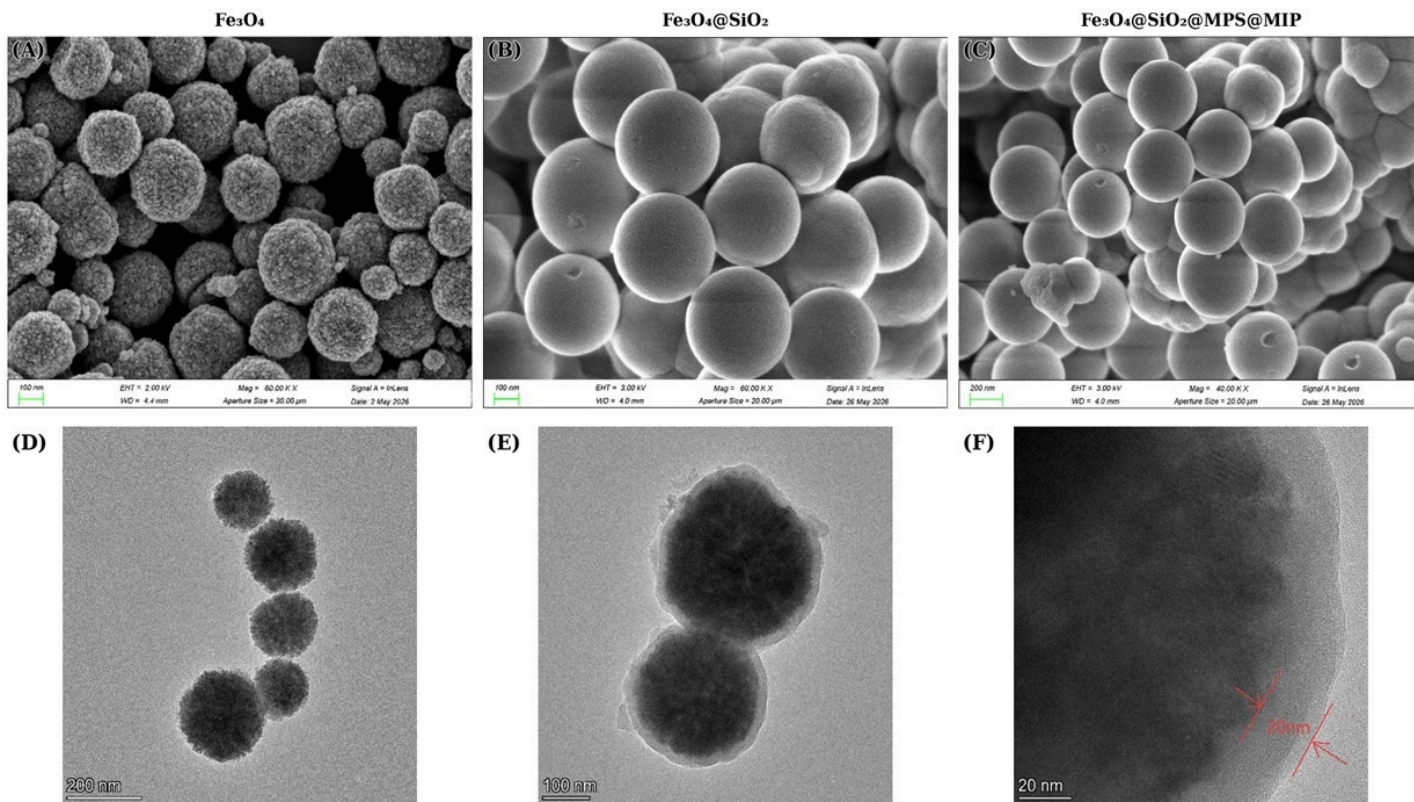


Figure 2

SEM images of (A) Fe_3O_4 , (B) $\text{Fe}_3\text{O}_4@\text{SiO}_2$, and (C) $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS@MIP}$; TEM images of (D) Fe_3O_4 , (E) $\text{Fe}_3\text{O}_4@\text{SiO}_2$, and (F) $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS@MIP}$.

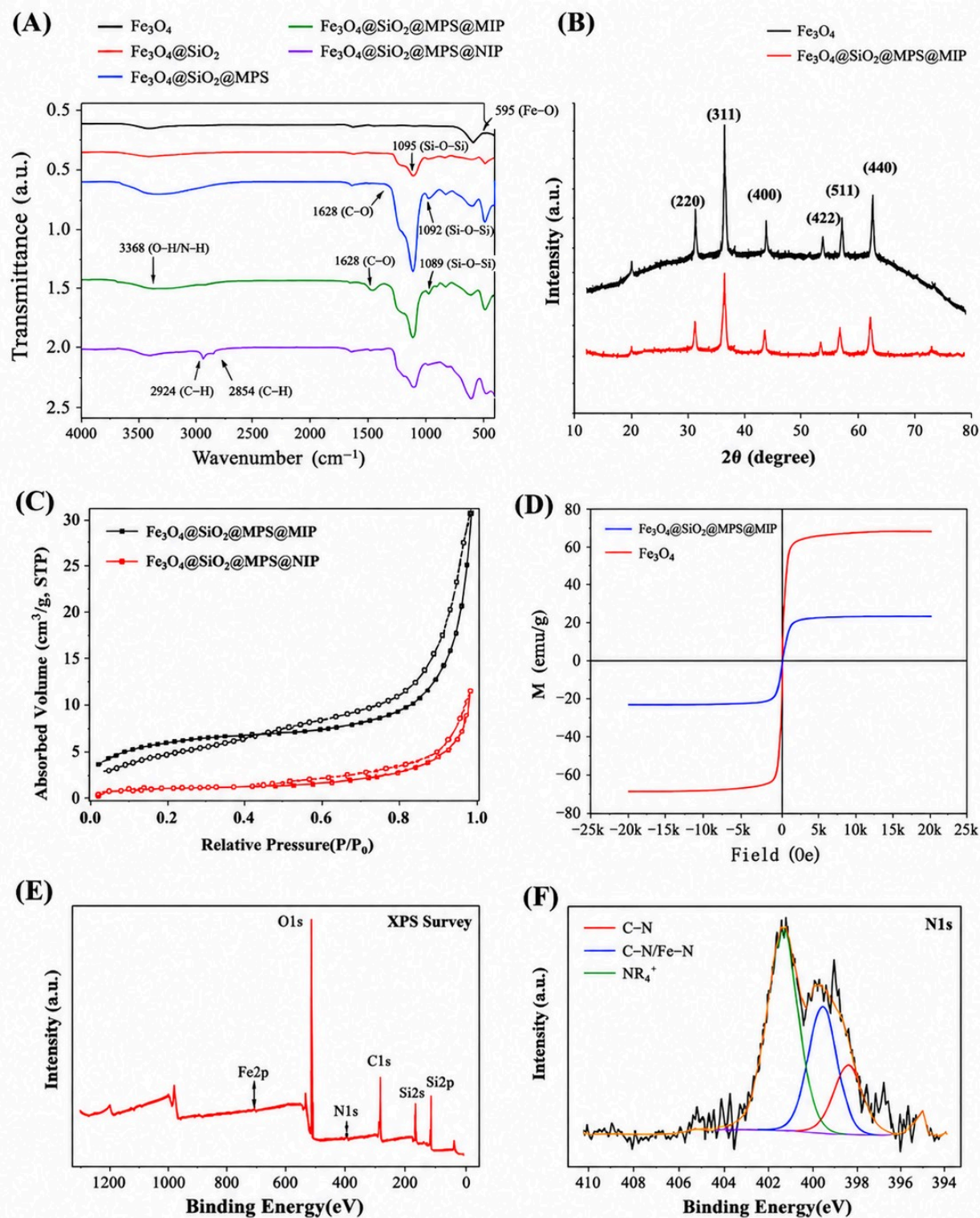


Figure 3

Characterization of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@MIP$ and the corresponding intermediate materials: (A) FTIR spectra of Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{SiO}_2$, $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}$, $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@MIP$, and $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@NIP$; (B) XRD patterns of Fe_3O_4 and $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@MIP$; (C) N_2 adsorption-desorption isotherms of Fe_3O_4 and $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@MIP$; (D) magnetic hysteresis curves of Fe_3O_4 and $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@MIP$; (E) XPS survey spectrum of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@MIP$; and (F) high-resolution N 1s XPS spectrum of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@MIP$.

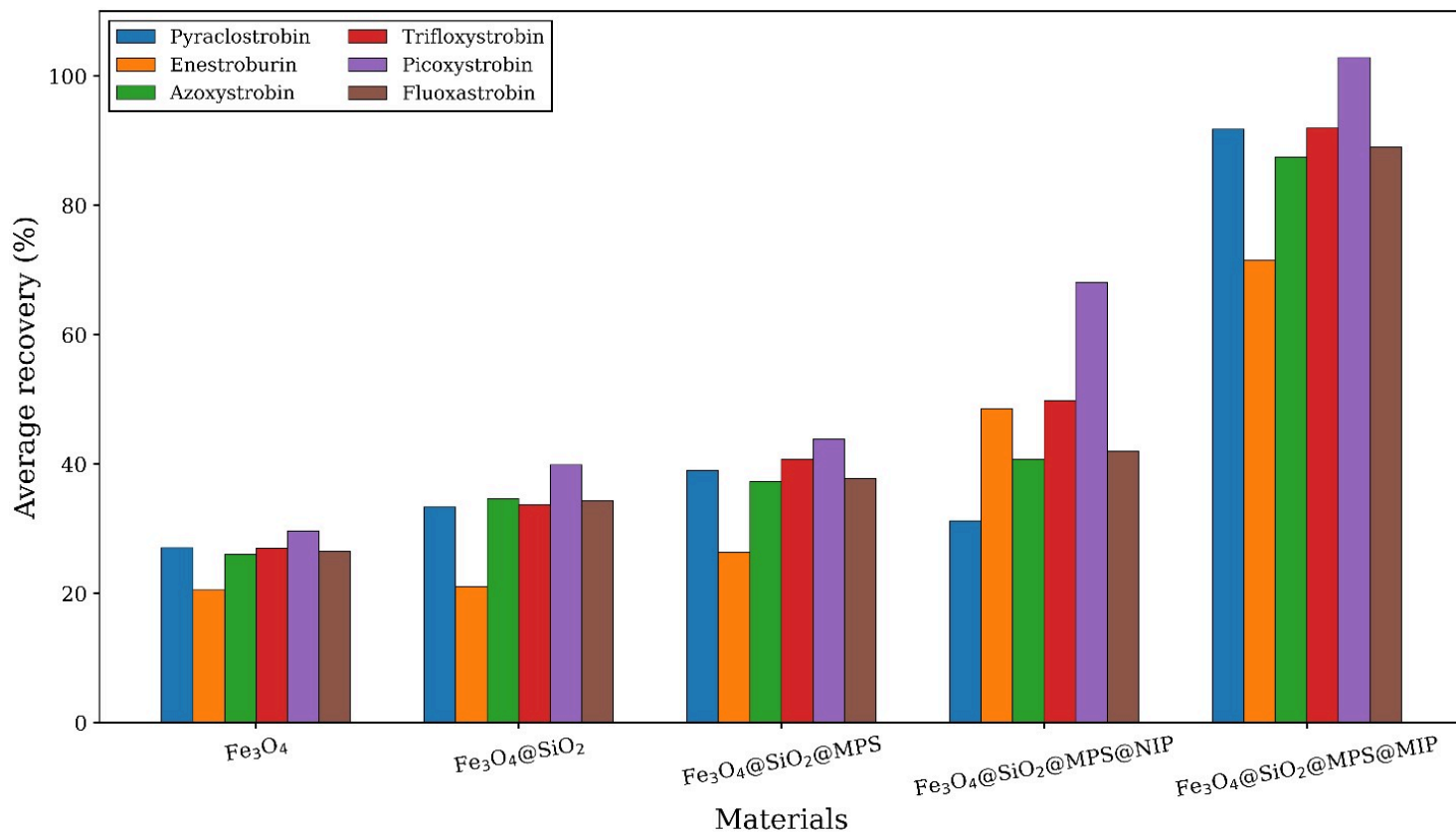


Figure 4

Selectivity and extraction performance of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@ \text{MIP}$: (A) comparison of the recoveries of the six strobilurin fungicides obtained using Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{SiO}_2$, $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}$, $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@ \text{NIP}$, and $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@ \text{MIP}$.

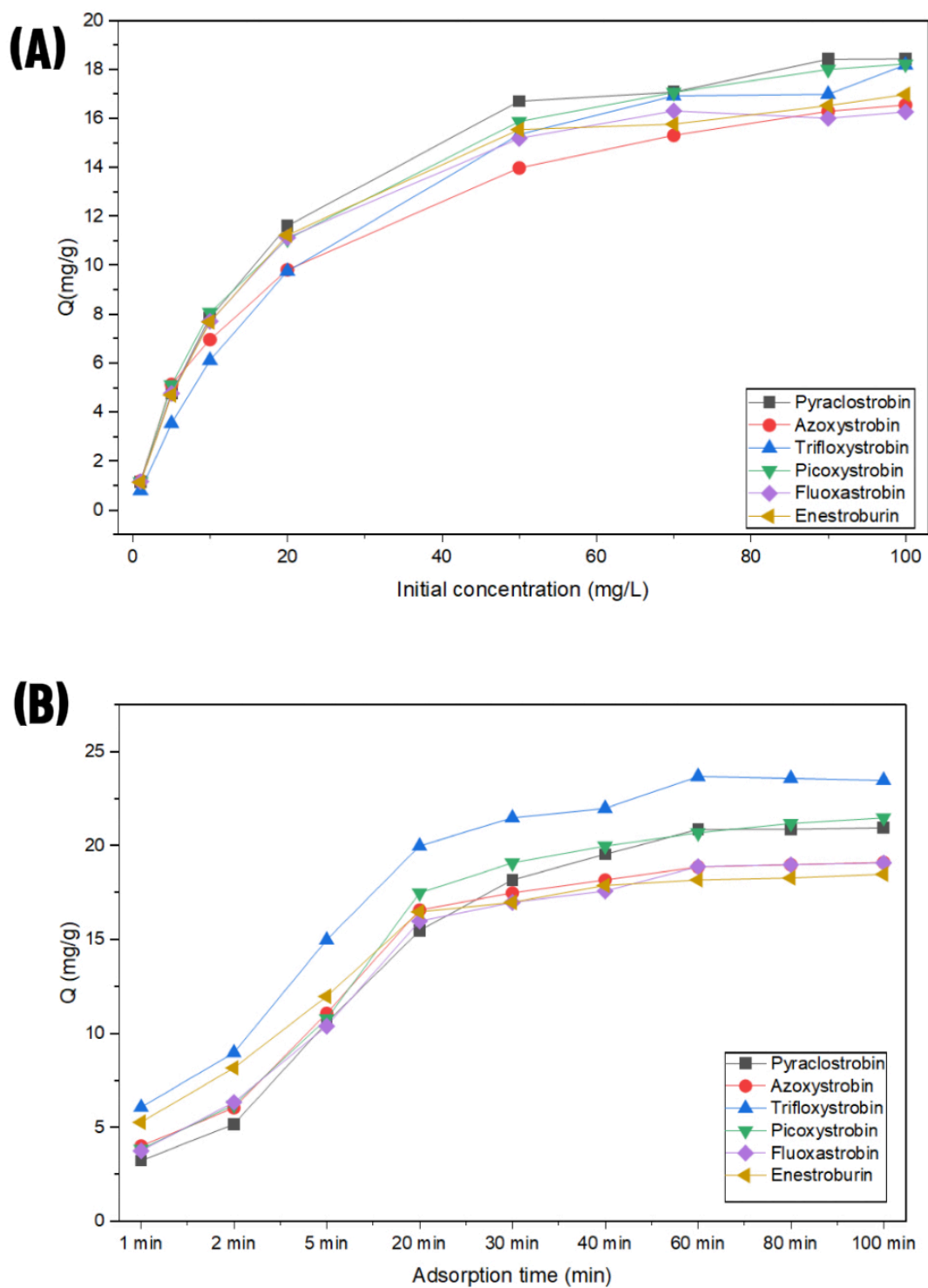


Figure 5

Adsorption performance of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MPS}@\text{MIP}$ toward the six strobilurin fungicides under adsorption conditions: (A) equilibrium adsorption capacities at different initial analyte concentrations and (B) adsorption kinetic curves at different contact times.

Supplementary Files

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