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Metal organic frameworks (MOFs) for magnetic solid-phase extraction of pyrazole/pyrrole pesticides in environmental water samples followed by HPLC-DAD determination

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Abstract

Magnetic metal-organic frameworks (MOFs, [MIL-101]) were prepared and used as magnetic solid-phase extraction (MSPE) adsorbents for preconcentration of four kinds of pyrazole/pyrrole pesticides (flusilazole, fipronil, chlorfenapyr, and fenpyroximate) in environmental water samples, followed by high-performance liquid chromatography-diode-array detector (HPLC-DAD) determination. Several variables affecting MSPE efficiency were systematically investigated, including amount of MIL-101, extraction time, sample pH, salt concentration, type of desorption solvent and desorption number of times. Under optimized conditions, excellent linearity was achieved in the range of 5.0–200.0 $\mu\text{g/L}$ for flusilazole and fipronil, and 2.0–200.0 $\mu\text{g/L}$ for chlorfenapyr and fenpyroximate, with correlation coefficients $r > 0.9911$. Limits of detection and quantification were 0.3–1.5 $\mu\text{g/L}$ and 1.0–5.0 $\mu\text{g/L}$, respectively. The intra-day and inter-day precision (relative standard deviation, $n=6$, %) at three spiked levels were 1.1–5.4% and 3.9–7.8% in terms of peak area, respectively. The method recoveries at three fortified concentration levels ranged from 81.8–107.5% for reservoir water samples, 81.0–99.5% for river water samples, and 80.2–106.5% for seawater samples. The developed MOFs based MSPE coupled with HPLC method proved to be a convenient, rapid and eco-friendly alternative to the sensitive determination of pyrazole/pyrrole pesticides with high repeatability and excellent practical applicability.

Keywords: Metal-organic frameworks (MOFs), Magnetic solid-phase extraction, Pyrazole, Pyrrole, Water samples

1. Introduction

Flusilazole, fipronil, chlorfenapyr, and fenpyroximate as pyrazole/pyrrole derivatives, are mainly used as weeding herbicides and pesticides with high efficiency, good sterilization ability and low toxicity. They have been recommended to replace highly toxic organophosphorus pesticides as the first choice by a large number of chemical experts. This kind of pesticides have been widely used in rice, vegetable, fruit trees and ornamental plants for comprehensive prevention and control of pests. However, they still exhibit toxic or other undesirable side effect on non-target organisms [1]. Extensive or inappropriate use can cause soil and water pollution, and thus harm human health. Therefore, increased monitoring efforts are required. Due to their trace level presence and wide distribution in complex water environment, it is necessary and important to develop simple, sensitive, and rapid methods for the determination of pyrazole/pyrrole pesticides.

The most common analytical methods for pyrazole/pyrrole pesticides are gas chromatography-mass spectrometry (GC-MS) [2], gas chromatography-electron capture detector (GC-ECD) [3] and high-performance liquid chromatography-ultraviolet or diode-array detector (HPLC-UV/DAD) [4,5] because of the compounds' high boiling point and intense UV absorption. However, for low concentration of pyrazole/pyrrole pesticides in water, UV detector cannot provide high sensitivity without enrichment prior to analysis. Therefore, pretreatment techniques are imperative for the enrichment and cleanup of pyrazole/pyrrole pesticides in environmental samples in order to achieve the ideal determination sensitivity and effectively eliminate matrix interferences from complex samples. Currently reported pretreatment techniques for pyrazole/pyrrole pesticides from environmental water samples mainly include solid-phase extraction (SPE) [3,6–8], solid phase microextraction (SPME) [2], and dispersive liquid–liquid microextraction (DLLME) [3]. SPE, due to its high recovery, short extraction time, high enrichment factor, low consumption of

organic solvents, and ease of automation and operation, has been widely used to concentrate organic compounds in water samples. In SPE, the choice of adsorbents is very important for obtaining high-enrichment efficiency [9]. For example, using multi-walled carbon nanotubes (MWCNTs) as adsorbent of SPE, our group has developed an efficient method for the determination of four pyrazole/pyrrole pesticides in environmental water samples by HPLC-DAD [10].

Magnetic SPE (MSPE), as a relatively new mode of SPE based on the adsorption and release of target analytes by a small amount of magnetic nanoparticles dispersed in solution, has attracted much interest and attained wide applications [11–14]. The magnetic nanoparticle-adsorbed target compounds can be easily collected by an external magnetic field without additional centrifugation or filtration of samples [15]. Also, metal-organic frameworks (MOFs), crystalline solids consisting of metal ions coordinated by organic ligands to form rigid three dimensional frameworks, have received increasing concerns owing to their unique properties such as high surface area, high pore volume and chemical tenability [16–18], making them especially useful in gas storage, separation, chemical sensing, drug delivery, and heterogeneous catalysis applications. As SPE adsorbents, MOFs have shown very strong adsorption of various targets. Yan's group used MOFs [Cu(4-C₅H₄N-COO)₂(H₂O)₄] as on-line SPE adsorbents for the enrichment of polycyclic aromatic hydrocarbons (PAHs) in coal fly ash and water [19]. However, the fine particle of MOFs could produce high column resistance, so typical SPE mode is not suitable for most MOFs. Interestingly, the combination of MSPE and MOFs can resolve this problem. Then they reported MSPE of PAHs with the MOFs of MIL-101 as adsorbents in environmental water samples [20]. Chen et al. [21] used Fe₃O₄@MIL-100 core-shell magnetic microspheres as the sorbent for MSPE of polychlorinated biphenyls at trace levels in environmental water samples. Bagheri et al. [22] synthesize MOFs [(Fe₃O₄-Pyridine)/Cu₃(BTC)₂] as novel

sorbents for determination of palladium in environmental samples. Zhang et al. [23] used $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{UiO-66}$ microspheres for MSPE of domoic acid (DA) in shellfish samples, and established a method for the determination of DA combined with HPLC–MS/MS. Wang et al. [24] evaluated $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-MOF-177}$ as an advantageous adsorbent for MSPE of phenols in environmental water samples. Consequently, the magnetic MOFs materials as new SPE adsorbents have become popular because of the advantages such as super large surface area of MOFs and convenient operation of MSPE.

Inspired by those studies, herein, we purposed to use the magnetic MIL-101 MOFs as MSPE adsorbents and combined with HPLC for determination of the four typical pyrazole/pyrrole pesticides (flusilazole, fipronil, chlorfenapyr, and fenpyroximate) in environmental water samples. The properties of the MOFs as MSPE adsorbents were investigated and several key influence factors including amount of MIL-101, extraction time, sample pH, salt concentration, type of desorption solvent and desorption number of times were studied in detail for high MSPE efficiency. The MSPE-HPLC method was validated and applied to the simultaneous separation and determination of four pyrazole/pyrrole pesticides in reservoir water, river water and seawater samples.

2. Experimental

2.1. Reagents and materials

All chemicals were of at least analytical grade. $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Sinopharm Chemical Reagent Co. Ltd, China), terephthalic acid (Sinopharm Chemical Reagent Co. Ltd), and hydrofluoric acid (Fuyu, Tianjin, China) were used to prepare MIL-101. Ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, Sinopharm Chemical Reagent Co. Ltd.), glycol (Fuyu, Tianjin, China), polyethylene glycol (Alfa Aesar), and anhydrous sodium acetate (Aibi, Shanghai, China) were used to prepare magnetic Fe_3O_4 microparticles. Tetraethylorthosilicate (TEOS,

Alfa Aesar) was used for further modification of the magnetic Fe₃O₄ microparticles. All solvents, including methanol, ethyl acetate, acetonitrile and acetone were of HPLC grade. Methanol, acetonitrile and acetone were purchased from TEDIA (USA). Ethyl acetate was purchased from Tianjin Guangfu Fine Chemicals Institute (China). Anhydrous sodium sulfate and sodium chloride were purchased from Jiangsu Powerful Function Chemical Co., Ltd. (China). Ammonium hydroxide was supplied by Laiyang Chemical Industry (Shandong, China). Formic acid was offered by Fuyu of Tianjin (China). Dimethylformamide (DMF) was from Aladdin. Stock solutions of 1,000 mg/L of fipronil dissolved in acetone, 100 mg/L of fenpyroximate dissolved in acetone, 100 mg/L of flusilazole dissolved in acetone and 100 mg/L of chlorfenapyr dissolved in n-hexane were purchased from National Research Center for Certified Reference Materials (Beijing, China), which were all stored at -20 °C. Then, the four-mixture standard solution at 10 mg/L for individual pesticide was prepared by using methanol to dilute the stock solutions, and working solutions were prepared daily by appropriate dilution of the above-prepared standard solution with ultrapure water before use. Ultrapure water (18.2 MΩ cm) was obtained from a model Synergy 185 ultra pure water system (Millipore, USA).

Real water samples were collected from the Qingdao Jihongtan Reservoir and the Baisha River, and seawater samples were from the coastal zone area of Qingdao City (China). All the water samples were filtered through 0.45-μm membrane (Tianjin Jinteng Experiment Equipment Ltd, Co., Tianjin, China) and stored in brown glass bottles at 4 °C prior to analysis.

2.2. Apparatus

HPLC experiments were carried out on an Agilent 1100 liquid chromatographic system consisting of a quaternary delivery pump, an auto-sampler, a thermostatic column compartment and a DAD detector. A personal computer equipped with Agilent ChemStation

for HPLC was used to process the chromatographic data. An analytical ZORBAX SB-C₁₈ (100 × 4.6 mm, 5 μm) was used to analyze the pesticides at room temperature. The sample injection volume was 20 μL. Absorbance was monitored at 215 nm. The mobile phase was a gradient prepared from acetonitrile and water. Gradient elution conditions were as follows: 0–12 min, isocratic 55% acetonitrile; 12–20 min, isocratic 75% acetonitrile. The flow rate was 1 mL/min. Under these optimum conditions, all studied pesticides were well resolved from each other.

Characterization of magnetic MIL-101 was conducted on a Fourier-transform infrared spectrometry (FT-IR, Frontier, Perkin Elmer, USA), X-ray diffractometer (XRD) (Bruker D8 Advance) and a Tescan XM 5136 scanning electron microscope (SEM, Tescan, Czech Republic).

2.3. Preparation of magnetic MIL-101

2.3.1. Preparation of magnetic Fe₃O₄@SiO₂

Firstly, the magnetic Fe₃O₄ microspheres were synthesized using a reported solvothermal reduction method [25]; secondly, the Fe₃O₄ microspheres were modified with TEOS. Briefly, 1.35 g of FeCl₃·6H₂O and 3.6 g of NaAc was dissolved in 40 mL of ethylene glycol, followed by adding 1.0 g of polyethylene glycol. The mixture was stirred vigorously for 30 min and then sealed in a 50 mL teflon-lined stainless-steel autoclave. The autoclave was heated and maintained at 200 °C for 14 h, then was cooled to room temperature. The black Fe₃O₄ microspheres were washed several times with ethanol and dried at 100 °C for 6 h in oven. 120 mg of the prepared magnetite microspheres was dispersed in 240 mL of ethanol by sonication for over 30 min. 12 mL of 28% (v/v) ammonia, 15 mL of ultrapure water and 400 μL of TEOS were added into the microspheres solution. Finally, the mixture was placed into a 40 °C water bath and vigorously stirred for 2 h. Then the product was dried under vacuum at 100 °C for 4 h, which was marked as magnetic Fe₃O₄@SiO₂.

2.3.2. Synthesis of MIL-101

The MOFs of MIL-101 were synthesized according to that reported [26] with slight modification. Briefly, 3.2 g of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 1.328 g of terephthalic acid and 0.8 mL of 40% hydrofluoric acid were mixed in 38 mL of ultrapure water. The obtained mixture was sealed in a teflon-lined stainless-steel autoclave. Then, the autoclave was heated and maintained at 200 °C for 8 h. After the autoclave was cooled to room temperature, the synthesized MIL-101 was sequentially washed with DMF and hot ethanol, and collected via centrifugation at 10000 rpm for 5 min. The procedure was repeated three times to remove the unreacted terephthalic acid from MIL-101. Finally, MIL-101 was dried under vacuum at 150 °C for 12 h.

2.3.3. In situ magnetization of MIL-101 for MSPE

Initially, in situ magnetization of MIL-101 was carried out according to that reported by Yan's group [17]. That is, 1.0 mg of $\text{Fe}_3\text{O}_4@ \text{SiO}_2$ and 0.4 mg of MIL-101 were placed in a 25-mL glass vial, and sequentially washed with methanol and ultrapure water. Then 20 mL of spiked water sample (the pH of the water was adjusted to 5.0 with formic acid) was taken in and dispersed into it under ultrasonication for 20 min for the magnetization of MIL-101 to form $\text{Fe}_3\text{O}_4@ \text{SiO}_2\text{-MIL-101}$ microspheres, namely magnetic MOFs for simplicity.

Then, MSPE of pesticides was performed as follows. An external magnet was attached to the outside bottom of the vial with the above-prepared $\text{Fe}_3\text{O}_4@ \text{SiO}_2\text{-MIL-101}$ microspheres in water sample, so that the magnetic MIL-101 microspheres were forced to settle to the bottom and the supernatant water was decanted and discarded. Then the $\text{Fe}_3\text{O}_4@ \text{SiO}_2\text{-MIL-101}$ was washed with 5×0.5 mL of ethyl acetate. All the ethyl acetate extracts were combined and transferred into an auto sampler vial. The collected eluate was concentrated with a gentle stream of nitrogen at room temperature, diluted to 0.5 mL with the mobile phase, and filtered through a 0.45- μm nylon membrane for HPLC analysis. The MSPE procedure is shown schematically in Fig. 1.

3. Results and discussion

3.1. Characterization of the magnetic MIL-101 microspheres

The micro-morphologies of the prepared microspheres were observed by SEM. As shown in Fig. 2, the spherical $\text{Fe}_3\text{O}_4@\text{SiO}_2$ nanoparticles were assembled onto the external surface of amorphous MIL-101 crystals. The magnetization of MIL-101 was achieved via the formation of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ -MIL-101 hybrids due to the static electric interaction between the positively charged MIL-101 and negatively charged $\text{Fe}_3\text{O}_4@\text{SiO}_2$ [20]. Therefore, magnetic responsive $\text{Fe}_3\text{O}_4@\text{SiO}_2$ -MIL-101 microspheres namely magnetic MOFs were attained, which could be separated from the matrix solution using an external magnet. Accordingly, Fig. S1 shows observations before and after the MSPE procedure. As shown, the pesticide solution became black and turbid when $\text{Fe}_3\text{O}_4@\text{SiO}_2$ -MIL-101 microspheres were dispersed (Fig. S1a), but the $\text{Fe}_3\text{O}_4@\text{SiO}_2$ -MIL-101 microspheres with adsorbed pesticides adhered to the inner side wall of the vial when the external magnetic field was applied. As a result, the turbid solution again became clear and transparent, as shown in Fig. S1b. Hence, a fast simple magnetic separation was attained.

The chemical structures of the $\text{Fe}_3\text{O}_4@\text{SiO}_2$ -MIL-101 microspheres were examined by FT-IR spectroscopy. Fig. S2 shows the FT-IR spectra of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ (a), MIL-101 (b) and $\text{Fe}_3\text{O}_4@\text{SiO}_2$ -MIL-101 (c). In Fig. S2a, the absorption peaks at 580 cm^{-1} might well result from Fe–O–Fe vibration of magnetite, and 1080 cm^{-1} could be attributed to the Si–O–Si stretching vibration of silica layer formed on the surface of magnetite particles, suggesting the formation of $\text{Fe}_3\text{O}_4@\text{SiO}_2$. In Fig. S2b, the absorption peaks at 3300 and 1000 cm^{-1} could be ascribed to O–H and C–O stretching vibration, respectively, from the MIL-101. Three peaks at $1400\text{--}1700\text{ cm}^{-1}$ very likely belonged to C=C of benzene ring and C=O stretching vibration. All the characteristic peaks for $\text{Fe}_3\text{O}_4@\text{SiO}_2$ and MIL-101 appeared in Fig. S2c, and thereby the $\text{Fe}_3\text{O}_4@\text{SiO}_2$ -MIL-101 microspheres were attained.

The $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-MIL-101}$ microspheres were also characterized by XRD. As shown in Fig. S3, the XRD pattern of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-MIL-101}$ was in agreement with the combination pattern of MIL-101 and $\text{Fe}_3\text{O}_4@\text{SiO}_2$ consistent with previous reports [20]. Therefore, the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-MIL-101}$ microspheres were successfully prepared.

3.2. Optimization of MSPE conditions

MSPE efficiency is mainly subject to the following major factors: amount of MIL-101, extraction time, sample pH, salt concentration, type of desorption solvent, and desorption number of times. In this study, these were investigated using a spiked ultrapure water sample (50 $\mu\text{g/L}$), and all the optimization experiments were conducted three times.

3.2.1. Effect of amount of MIL-101

Effect of the amount of MIL-101 on the performance of the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-MIL-101}$ for MSPE of four pesticides was investigated. The amount of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ was kept 1.0 mg, and the amount of MIL-101 was changed from 0 to 2.0 mg. Fig. 3A shows that four pesticides were hardly extracted by $\text{Fe}_3\text{O}_4@\text{SiO}_2$ without adding MIL-101. The extraction efficiency increased rapidly when the amount of MIL-101 increased from 0 to 0.4 mg, and then decreased when the amount increased from 0.5 to 1.0 mg. It may be because that excessive MIL-101 without magnetic modification adsorbed a part of pesticides which could not be collected by magnetic separation. In the following experiment, 0.4 mg of MIL-101 was employed.

3.2.2. Effect of sample pH

The pH of the sample solution plays an important role in the adsorption of the four pyrazole/pyrrole pesticides by affecting both the form of target analytes and surface binding sites of the adsorbent. When the pH value is exceeded 9.6 the zeta potential of MIL-101 is negative so that MIL-101 and negatively charged $\text{Fe}_3\text{O}_4@\text{SiO}_2$ cannot interact each other. On the other hand, the MIL-101 is unstable when the pH value is exceeded 9.6. So the effect of

sample pH on the extraction of the four pesticides was studied ranging from 3 to 9. As can be seen in Fig. 3B, the extraction efficiencies for fenpyroximate, chlorfenapyr and flusilazole increased within pH 3–5 followed by decreasing within pH > 5. For fipronil, the extraction efficiencies increased at pH 3–6 followed by decreasing at pH > 6. So, most pyrazole/pyrrole pesticides obtained the highest signals when the samples were prepared at pH 5. Therefore, sample solutions at pH 5 were used in further experiments.

3.2.3. Effect of extraction time

The effect of extraction time on extraction efficiencies for the four pesticides was shown in Fig. 3C. The peak areas of the analytes increased as extraction time increased from 5 to 20 min, and decreased with a further increase of extraction time. Thus, 20 min was chosen as the extraction time.

3.2.4. Effect of salt concentration

Salt content in water samples can change the ionic strength of the solutions or alter the diffusion rate of analytes from aqueous to solid phases. To investigate the salt effect on the extraction of pyrazole/pyrrole pesticides, various amounts of NaCl (0–100 mmol/L) was added into solution to adjust salinity. As shown in Fig. 3D, the peak areas for the four pesticides sharply decreased when the concentration of NaCl varied from 0–20 mmol/L, then leveled off from 20–60 mmol/L NaCl and slightly increased as the concentration of NaCl increased from 60 to 80 mmol/L, finally decreased as NaCl increased from 80 to 100 mmol/L. Interestingly, the highest signals were obtained when no NaCl was added. This may be because that NaCl would weaken the static electric interaction between $\text{Fe}_3\text{O}_4@\text{SiO}_2$ and MIL-101, and reduce the stability of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ -MIL-101 for MSPE. Also, the addition of NaCl would reduce mass transfer by changing the Nernst diffusion layer, probably leading to the decreased diffusion rate of the analytes to the surface of the magnetic microspheres. Therefore, no NaCl was added in the following extractions.

3.2.5. Effect of type of desorption solvent

Desorption solvent is known to be vital for MSPE efficiency. Four solvents including methanol, acetonitrile, acetone and ethyl acetate were studied as desorption solvents to examine their effects on the extraction efficiency. Fig. 3E shows that the peak areas of the four pesticides eluted by ethyl acetate were higher than those by other solvents. Therefore, ethyl acetate was adopted for eluting the four pesticides for further work.

3.2.6. Effect of desorption number of times

To investigate the effect of desorption number of times, 0.5 mL of ethyl acetate was used for eluting the four pesticides for the number of times from 1–6. The results were shown in Fig. 3F. It can be seen that the highest peak area was obtained when the four pesticides were eluted by 0.5 mL of ethyl acetate for five times. So, the desorption number of times was set at five for the remainder of this study.

3.3. Analytical performance of the magnetic MOFs based MSPE-HPLC method

Under the above-optimized MSPE conditions, the four pyrazole/pyrrole pesticides were separated well by HPLC and the analytical performance of the magnetic MOFs ($\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-MIL-101}$) based MSPE method was assessed. Seven pyrazole/pyrrole pesticide standard solutions with different concentrations (2, 5, 10, 20, 50, 100 and 200 $\mu\text{g/L}$ for individual pesticide) were obtained by serial dilution with appropriate solvents from stock solutions. Working curves were obtained using a least-squares linear regression analysis of peak area versus pesticide concentration. The method presented good linearity in the range of 5.0–200.0 $\mu\text{g/L}$ for fipronil and flusilazole, and 2.0–200.0 $\mu\text{g/L}$ for chlorfenapyr and fenpyroximate, with correlation coefficients (r) ranging from 0.9911 to 0.9973, as listed in Table 1.

The limits of detection (LODs) for the method, calculated by analyzing the spiked water sample after MSPE using a signal-to-noise ratio of 3, varied from 0.3 to 1.5 $\mu\text{g/L}$ (Table 1).

On the basis of the peak height being ten times the background noise ($S/N=10$), the limits of quantification (LOQs) were attained from 1.0 to 5.0 $\mu\text{g/L}$ (Table 1). The intra-day and inter-day precision in terms of peak area, based on six consecutive injections, are shown in Table S1. As shown, the relative standard deviations (RSDs) of peak area, obtained from a working solution containing each of the four pesticides at 5 $\mu\text{g/L}$ based on intra-day precision, were less than 5.4%, while the RSDs based on inter-day precision remained within 7.8%. Meanwhile, at 50 $\mu\text{g/L}$, the RSDs of peak area based on intra-day precision were below 3.6%, and the inter-day precisions were less than 6.1%. At 100 $\mu\text{g/L}$, the RSDs of peak area based on intra-day precision were below 3.9%, and the inter-day precisions were less than 7.7%. Thus, the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-MIL-101}$ were ideal candidate adsorbents for MSPE, and the MSPE-HPLC method was proven robust, reliable and capable of accurately quantifying pyrazole/pyrrole pesticides at trace levels.

3.4. Application of the MSPE-HPLC to real environmental water samples

To further evaluate the practical applicability of the MSPE-HPLC method, three water samples from reservoir water, river water and seawater were analyzed. HPLC chromatograms achieved for the seawater sample with and without standards addition after MSPE were displayed in Fig. 4. As seen, no endogenous selected pesticides were detected in the real water samples (Fig. 4a and Table 2), and significant peaks appeared after spiking (Fig. 4b). The recoveries were obtained by spiked real water samples with 5.0, 50.0 and 100.0 $\mu\text{g/L}$ individual pesticides, which were averaged from three replicates. As listed in Table 2, the recoveries of four pesticides ranged from 81.8–107.5% for reservoir water samples with RSDs of 1.1–7.8%, ranged from 81.0–99.5% for river water samples with RSDs of 1.8–7.7%, and ranged from 80.2–106.5% for seawater samples with RSDs of 3.1–7.8%. The developed MSPE-HPLC method was demonstrated practically feasible for the simultaneous separation and determination of trace pyrazole/pyrrole pesticides in complicated water samples.

3.5. Method performance comparison

Analytical performance of the developed MSPE-HPLC-DAD method for the detection of pyrazole/pyrrole pesticides was compared with reported GC or HPLC methods, where SPME [2], DLLME [4] or SPE [8,10] was used for the extraction of pyrazoles/pyrroles pesticides. As shown in Table S2, compared to that reported HPLC-DAD methods [4,8,10], our method presents lower LODs. The SPE-HPLC method using MWCNTs as adsorbents showed the lowest LODs [10], however, the pretreatment time of conventional SPE is nearly 4 h while the pretreatment time of MSPE only less than 30 min. Although the SPME-GC-MS method attained low LODs (0.08 $\mu\text{g/L}$) [2], only single fipronil could be detected instead of more pyrazole/pyrrole pesticides because of their high boiling points. Therefore, our developed MOFs based MSPE-HPLC method has advantages of high sensitivity, cost-effectiveness and rapid simple magnetic separation.

4. Conclusions

In conclusion, a simple, sensitive and robust method using the magnetic MOFs of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-MIL-101}$ as MSPE sorbents was successfully developed for the simultaneous determination of four pyrazole/pyrrole pesticides in environmental water samples followed by HPLC-DAD. Good extraction efficiencies and low LODs/LOQs were obtained. The analysis requires no complicated devices, since the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-MIL-101}$ could be separated quickly from solutions by an external magnet. The processes of enrichment, separation, and release for four pyrazole/pyrrole pesticides were convenient, rapid, cost/labor-effective and eco-friendly. The developed MSPE-HPLC-DAD method provided great potential to analyze pyrazole/pyrrole pesticides in real water samples.

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Table 1. Related analytical parameters of the magnetic MOF-MSPE-HPLC method for determination of four pyrazole/pyrrole pesticides.

Pyrazole/pyrrole pesticides	Regression equation ^a	Correlation coefficient (r)	Linear range (µg/L)	LOD (µg/L)	LOQ (µg/L)
Flusilazole	$y = 0.2380x + 2.664$	0.9911	5.0–200.0	1.5	5.0
Fipronil	$y = 0.1358x + 4.090$	0.9957	5.0–200.0	1.4	4.7
Chlorfenapyr	$y = 0.5077x + 0.9727$	0.9973	2.0–200.0	0.3	1.0
Fenpyroximate	$y = 0.5194x + 7.725$	0.9967	2.0–200.0	0.3	1.0

^a x means concentration of pesticides (µg/L), y means peak area.

Table 2. Determination of four pyrazole/pyrrole pesticides and method recoveries in real water samples.

Pyrazole/pyrrole pesticides	Spiked ($\mu\text{g/L}$)	Reservoir water		River water		Seawater	
		Found ($\mu\text{g/L}$)	Recovery (%)	Found ($\mu\text{g/L}$)	Recovery (%)	Found ($\mu\text{g/L}$)	Recovery (%)
Flusilazole	0	ND ^a		ND		ND	
	5.0	4.5	90.0 ^b \pm 1.7 ^c	4.1	81.0 \pm 7.7	4.1	81.4 \pm 3.7
	50.0	44.3	88.5 \pm 2.7	43.3	86.6 \pm 3.7	45.3	90.5 \pm 4.7
	100.0	88.1	88.1 \pm 6.9	83.3	83.3 \pm 2.3	89.1	89.1 \pm 6.3
Fipronil	0	ND		ND		ND	
	5.0	4.8	96.0 \pm 4.1	4.1	82.2 \pm 4.1	4.0	80.2 \pm 4.5
	50.0	53.1	106.2 \pm 4.1	43.2	86.3 \pm 6.1	46.1	92.3 \pm 3.1
	100.0	103.2	103.2 \pm 5.9	85.4	85.4 \pm 5.7	95.1	95.1 \pm 5.7
Chlorfenapyr	0	ND		ND		ND	
	5.0	4.5	90.3 \pm 4.7	4.4	87.4 \pm 4.9	4.4	88.4 \pm 4.8
	50.0	47.6	95.7 \pm 3.0	48.9	97.7 \pm 2.3	47.8	95.7 \pm 3.7
	100.0	92.8	92.8 \pm 1.1	98.8	98.8 \pm 1.8	95.7	95.7 \pm 2.3
Fenpyroximate	0	ND		ND		ND	
	5.0	4.1	81.8 \pm 7.8	4.4	87.0 \pm 3.8	4.1	82.0 \pm 7.8
	50.0	53.8	107.5 \pm 5.0	49.8	99.5 \pm 4.8	53.8	106.5 \pm 6.0
	100.0	94.9	94.9 \pm 5.3	96.3	96.3 \pm 2.9	101.8	101.8 \pm 3.3

^a Not detected.^b Average value from triplicate individual experiments.^c Relative standard deviation, $n = 3$.

Figure captions

Fig. 1. Schematic illustration of the MSPE procedure for pyrazole/pyrrole pesticides.

Fig. 2. SEM image of the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-MIL-101}$.

Fig. 3. Effect of (A) Amount of MIL-101, (B) sample pH, (C) extraction time, (D) salt concentration, (E) type of desorption solvent and (F) desorption number of times on the extraction efficiency of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-MIL-101}$ microspheres MSPE for four pyrazole/pyrrole pesticides. Extraction conditions: sample volume, 20 mL; concentration of each pesticide, 50 $\mu\text{g/L}$. (A) Extraction time, 20 min; sample pH, 5.0; desorption solvent, 0.5 mL of ethyl acetate; desorption number of times, five. (B) Amount of MIL-101, 0.4 mg; extraction time, 20 min; desorption solvent, 0.5 mL of ethyl acetate; desorption number of times, five. (C) Mass of MIL-101, 0.4 mg; sample pH, 5.0; desorption solvent, 0.5 mL of ethyl acetate; desorption number of times, five. (D) Mass of MIL-101, 0.4 mg; extraction time, 20 min; sample pH, 5.0; desorption solvent, 0.5 mL of ethyl acetate; desorption number of times, five. (E) Amount of MIL-101, 0.4 mg; sample pH, 5.0; extraction time, 20 min; desorption volume, 0.5 mL, desorption number of times, five. (F) Mass of MIL-101, 0.4 mg; sample pH, 5.0; extraction time, 20 min; desorption solvent, ethyl acetate.

Fig. 4. HPLC chromatograms of four pyrazole/pyrrole pesticides in real seawater samples after MSPE without spiking (a) and with spiking (b). Peak identification: (1) flusilazole, (2) fipronil, (3) chlorfenapyr, and (4) fenpyroximate. Extraction conditions were the optimal condition.

Fig. 1.

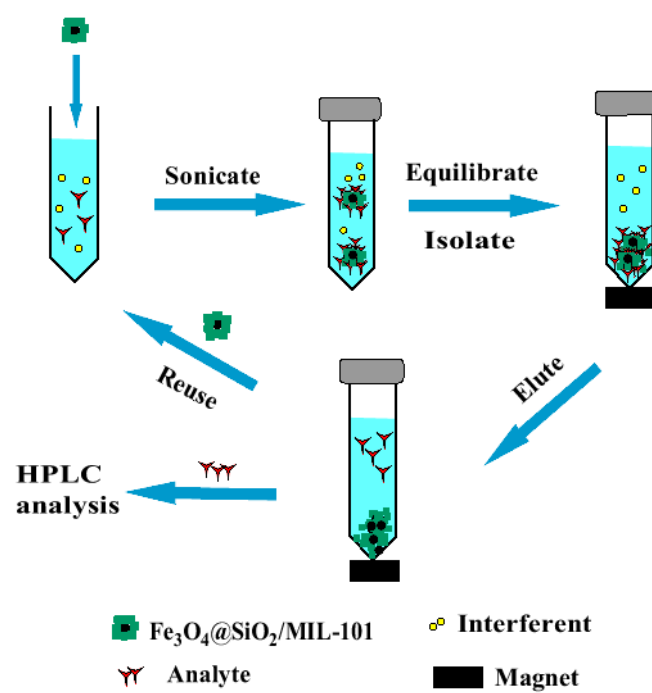
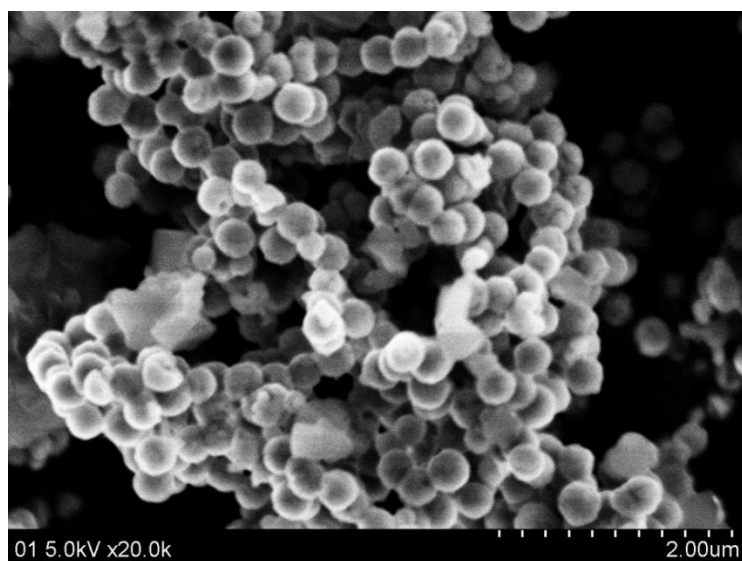


Fig. 2.

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Fig. 3.

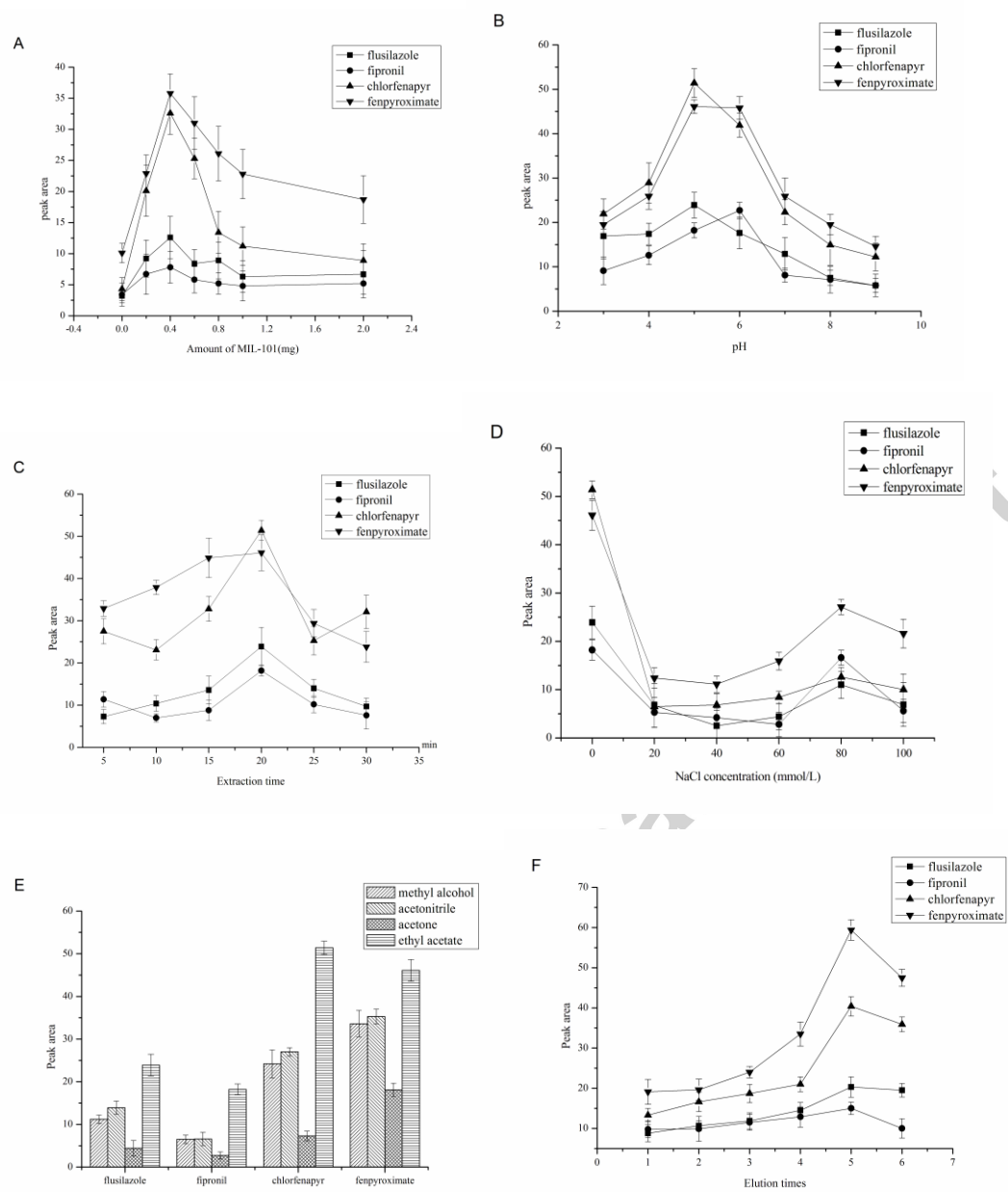
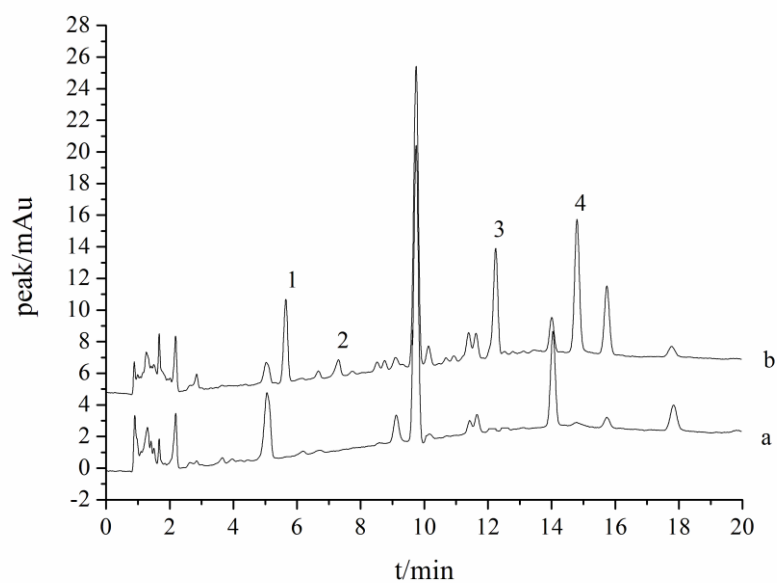
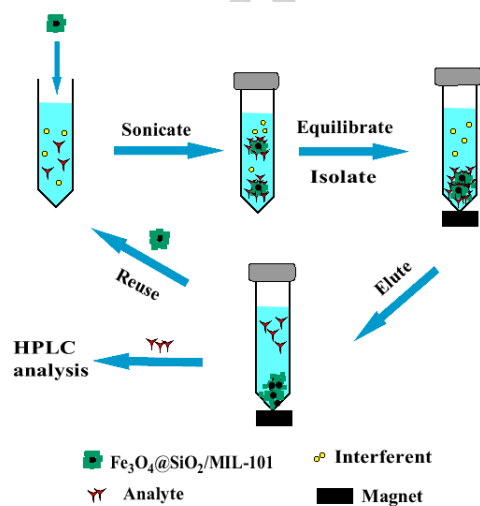


Fig. 4.



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Highlights

- Magnetic metal-organic frameworks (MOFs, [MIL-101(Cr)]) were prepared.
- The magnetic MOFs proved effective for MSPE of four pyrazole/pyrrole pesticides.
- The MSPE process was convenient, rapid and eco-friendly.
- The developed MSPE-HPLC-DAD method was suitable for complicated water samples.

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