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Magnetic metal–organic framework–titanium dioxide nanocomposite as adsorbent in the magnetic solid-phase extraction of fungicides from environmental water samples

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ABSTRACT

In this work, a core-shell Fe_3O_4@SiO_2@MOF/TiO_2 nanocomposite was synthesized and used to as adsorbent for magnetic solid-phase extraction (MSPE) of triazole fungicides from environmental water samples. Five triazole fungicides, namely, triadimenol, hexaconazole, diniconazole, myclobutanil, and tebuconazole, were selected as target analytes for MSPE. These analytes were quantitatively adsorbed on microspheres, and the sorbents were separated from the solution by using a magnet. The analytes were desorbed by methanol and determined through liquid-chromatography coupled with tandem mass spectrometry. The extraction parameters affecting the extraction efficiency were optimized through response surface methodology. The limits of detection and limits of quantification for the selected fungicides were 0.19–1.20 ng L^{-1} and 0.61–3.62 ng L^{-1}, respectively. The proposed method was applied to determine the concentration of fungicides in actual environmental water samples. The accuracy of the proposed method was evaluated by measuring the recovery of the spiked samples. The satisfying recoveries of the four water samples ranged from 90.2% to 104.2%. Therefore, the magnetic metal–organic framework/TiO_2 nanocomposite based MSPE is a potential approach to analyze fungicides in actual water samples.

1. Introduction

In modern agricultural systems, fungal growth can seriously damage crops or endanger the health of domestic animals or humans [1]. Fungal growth is usually killed or inhibited by fungicides, which are a class of pesticides [2,3]. When applied to crops, these pesticides remain in the environment, such as soil and water, and may contaminate food through the food chain [4,5]. Therefore, analytical methods for monitoring the level of residual fungicides should be developed to control fungicide overuse and to protect the ecological environment.

Sample pretreatment is of importance in chemical trace analysis [6]. The high extraction efficiency of target analytes from a sample matrix ensures the accuracy of analytical results. Sample pretreatments involve solid-phase sorption-based extraction methods, such as solid-phase extraction (SPE) [7], solid-phase microextraction (SPME) [8,9], micro-solid-phase extraction (μ-SPE) [10–12], and stir-bar sorptive extraction [13]. Magnetic solid-phase extraction (MSPE) is a type of dispersive SPE (*d*-SPE) [14]. In MSPE, a sorbent dispersed into a sample can be retrieved via a magnetic force. Filtration and centrifugation steps in typical *d*-SPE procedures are avoided. MSPE is also characterized by high rates of mass diffusion and transfer between a sample phase and a solid phase. It has been widely used to analyze environmental, biological, and food samples [15].

Sorbent materials have been extensively investigated in solid-phase sorption-based extraction techniques [16–18]. The sorbents can determine the selectivity of analytical methods, the extraction efficiency, the required sample volume, and organic solvent consumption. Novel sorbents have been fabricated to enhance the performance of solid-phase sorption-based extraction techniques and satisfy the requirements of highly sensitive and highly selective green analytical chemistry. Many novel nanomaterials, such as carbon nanotubes [19], graphene [20,21], metal–organic frameworks (MOFs) [22,23], molecular imprinting polymers [24], and metal oxide nanoparticles [25], have been used as sorbents in extraction. MOFs and TiO_2 have also been widely explored because of their unique chemical properties. Many MOFs have been used as

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an adsorbent in μ-SPE [26,27], SPE, SPME, and MSPE [28–32]. For example, Zhou et al. [33] used highly ordered TiO_2 nanotubes as a sorbent for u-SPE of fungicides from environmental water samples. Ouyang and coworkers [34] utilized mesoporous TiO_2 as SPME coating to determine organochlorine pesticides.

The combination of core-shell magnetic MOFs with TiO_2 has not been employed in extraction techniques. TiO_2 immobilized on MOF could potentially enhance the relatively weak physisorption forces between fungicides and MOF. On the other hand, the porous structure and open network of the MOF should enable fast molecular diffusion and thus increase the mass transfer rate of the target analytes to the TiO_2 surface. In this work, a magnetic core-shell MOF/TiO_2 nanocomposite was synthesized and then used as a sorbent in MSPE. TiO_2 was uniformly doped on the surface of core-shell Fe_3O_4@MOF microspheres to combine the intrinsic properties of MOF and TiO_2. Five fungicides, namely, triadimenol, hexaconazole, diniconazole, myclobutanil, and tebuconazole, were selected as target analytes for MSPE. These fungicides are widely used in the agricultural system and their structures were shown in Table S1. The target analytes in the samples were quantified through liquid-chromatography coupled with tandem mass spectrometry (LC–MS/MS). The extraction parameters affecting the extraction efficiency were optimized through response surface methodology (RSM). The developed method was utilized for the MSPE of fungicides from environmental water samples.

2. Experimental

2.1. Reagents and materials

Ferric chloride hexahydrate, ammonia aqueous solution, *N,N*-dimethyl formamide, andethyl alcohol were obtained from Sinopharm Chemical Reagent Co., Ltd. Tetraethyl orthosilicate (TEOS), glutaric anhydride, (3-aminopropyl) triethoxysilane, 2-methylimidazole, and tetrabutyl titanate were purchased from Shanghai SiYu Chemical Technology Co., Ltd. (Shanghai, China). Sodium acetate and ethylene glycol were obtained from Tianjin Kermel Chemical Reagent Company (China). Deionized water (18.2 MΩ cm^{-1}) obtained from a Millipore Milli-Q system (Millipore, Bedford, MA, USA) was used to prepare aqueous solutions that were utilized in subsequent experiments. Triadimenol, hexaconazole, diniconazole, myclobutanil, and tebuconazole, were purchased from the Institute of Environmental Protection and Monitoring, Department of Agriculture (Beijing, China). The standard mixtures of fungicides at 1 μg mL^{-1} concentration were prepared in HPLC-grade methanol. These standards were stored in the dark at 4 °C and were used to prepare working standard solutions. HPLC-grade methanol, acetonitrile, formic acid, and acetone were purchased from Tedia Company Inc. (Fairfield, OH, USA). All other reagents were of analytical grade.

2.2. Instrumentation

The morphology of the nanocomposite was observed through scanning electron microscopy (SEM) (SWPRA^{TM}55, Carl Zeiss MicroImaging Co., Ltd., Germany). Transmission electron microscopy (TEM) images were obtained on a JEOL Ltd. JEM-2010 spectrometer. Powder X-ray diffraction (PXRD) patterns were recorded at room temperature (298 K) on a Bruker SMART APEX CCD-based diffractometer. The specific Brunauer–Emmett–Teller (BET) surface areas of the materials was measured using an ASAP 2020 porosimeter (Micromeritics, USA). The magnetization curves of microspheres were obtained at room temperature on an MPMS-SQUID-VSM (Quantum Design, USA). Ultrasonication was conducted using a KQ2200 DB ultrasonic machine (Zhengzhou, China). The solvent was evaporated in aSY-2000 rotary evaporator (Yarong, Shanghai, China). AThermo U-3000 (Dionex, CA, USA) liquid chromatography coupled with AB Sciex Qtrap 5500 (AB SCIEX, USA) mass spectrometer was used to analyze the fungicides.

2.3. Synthesis procedure

Fig. 1 shows the synthesis procedure for the magnetic core-shell Fe_3O_4@SiO_2@MOF/TiO_2 nanocomposite. Fe_3O_4 microspheres were prepared via the solvothermal method and subsequently coated with silica shell via hydrolysis of TEOS. The detailed synthesis procedures for Fe_3O_4 and Fe_3O_4@SiO_2 were described in the Supplementary information.

2.3.1. Synthesis of Fe_3O_4@SiO_2@ZIF-8 microspheres

$Zn(NO_3)_2{\cdot}6H_2O$ (0.03 g) was typically dissolved in MeOH (10 mL) and then carboxylate-terminated Fe_3O_4@SiO_2 microspheres (0.01 mg) were added into the solution. The mixed solvents were subsequently ultrasonicated for 15 min, and a solution containing 2-methylimidazole (0.024 g) and MeOH (10 mL) was added. After 30 min of ultrasonication, the products were collected using a magnet and washed several times with ethanol and deionized water. The final products were obtained after repeating the previous step for five cycles and then dried at 60 °C for 12 h.

2.3.2. Synthesis of Fe_3O_4@SiO_2@ZIF-8/TiO_2 microspheres

Tetrabutyl titanate (50 μL) and ethyl alcohol (1 mL) were mixed and sonicated for 5 min and then Fe_3O_4@SiO_2@ZIF-8 microspheres (20 mg) dispersed in ethanol (15 mL) was added into the mixture. Deionized water (1 mL) was subsequently placed in a 20 mL Teflon-lined stainless steel autoclave and added the previous suspension. The autoclave was maintained at 160 °C for 15 h and allowed to cool down to room temperature. The final products were separated by using a magnet, washed with ethanol and deionized water, and dried at 60 °C for 12 h.

2.4. MSPE procedure

Extraction experiments were conducted in a 20 mL glass bottle. First, 10 mL of sample solutions were transferred into the bottle, and 0.5 mg of Fe_3O_4@SiO_2@ZIF-8/TiO_2 was added to the aqueous solution and mixed through ultrasonication for 30 min. An external magnet was placed inside the glass bottle to collect the sorbents and separate them from the solution. After the aqueous solution was removed, 1 mL of methanol was added to the glass to desorb the analytes through ultrasonication for a 5 min. The magnetic microspheres were collected through magnetic separation. The collected eluent was concentrated using a gentle stream of nitrogen at 30 °C. The obtained extract was diluted with methanol to obtain the final volume of 100 μL. Afterward,10 μL of the extract was subjected to LC–MS/MS analysis.

2.5. LC–MS analysis

The five selected fungicides were separated through HPLC by using an Acclaim^{TM} C_{18} column (150 mm × 2.1 mm i.d. 3 μm, 120 Å, Thermo Scientific, USA). The mobile phase was acetonitrile/deionized water acidified with 0.1% formic acid. The flow rate was 0.5 mL min^{-1}. The column temperature was kept at 30 °C. The injection volume is 10 μL. The mass spectrometer was operated in positive electrospray ionization (ESI) and MRM mode. The source temperature was 500 °C, and N_2 was used as collision gas. The capillary voltage was −4500 V. The curtain gas was set to 25 psi, and the ion source gases 1 and 2 were set to 40 psi. The HPLC gradient elution and mass spectrometer parameters, including MRM tran-