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Methyl parathion imprinted polymer nanoshell coated on the magnetic nanocore for selective recognition and fast adsorption and separation in soils

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HIGHLIGHTS

- A uniform MIPs nanoshell was introduced to the surface of a magnetic supporter.
- The Fe_3O_4@MPIPs performed high adsorption capacity and specific recognition.
- The Fe_3O_4@MPIPs had excellent removal and detection effects for MP in soils.

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ABSTRACT

Core–shell magnetic methyl parathion (MP) imprinted polymers (Fe_3O_4@MPIPs) were fabricated by a layer-by-layer self-assembly process. In order to take full advantage of the synergistic effect of hydrogen-binding interactions and π–π accumulation between host and guest for molecular recognition, methacrylic acid and 4-vinyl pyridine were chosen as co-functional monomers and their optimal proportion were investigated. The core–shell and crystalline structure, morphology and magnetic properties of Fe_3O_4@MPIPs were characterized. The MP-imprinted nanoshell was almost uniform and about 100 nm thick. Binding experiments demonstrated that Fe_3O_4@MPIPs possessed excellent binding properties, including high adsorption capacity and specific recognition, as well as fast adsorption kinetics and a fast phase separation rate. The equilibration adsorption capacity reached up to 9.1 mg/g, which was 12 times higher than that of magnetic non-imprinted polymers, while adsorption reached equilibrium within 5 min at a concentration of 0.2 mmol/L. Furthermore, Fe_3O_4@MPIPs successfully provided selective separation and removal of MP in soils with a recovery and detection limit of 81.1–87.0% and 5.2 ng/g, respectively.

1. Introduction

The last five decades have seen extensive use of organophosphorus pesticides (OPPs) for plant protection, resulting in OPPs becoming one of the most widespread soil contaminants [1,2]. Although these compounds have relatively short lifetimes and fast degradation procedures under normal environmental conditions, their acute toxic effects, especially on non-target recipients, amplify their contribution to soil pollution [3]. Methyl parathion (MP) is one of the most hazardous insecticides used for the control of sucking and chewing insects in a very wide range of crops including cereals, fruits, vegetables, cotton, and ornamentals [4]. However, this wide use of MP creates a negative impact on the environment. During its continually release into the environment through evaporation, adsorption and souring, MP results in hazardous concentrations of pesticide and its metabolites in surface water and soils due to the low solubility and bioaccumulation properties [5,6]. Therefore, timely determination and removal of MP has become an extremely important issue.

Gas chromatography (GC) and high performance liquid chromatography (HPLC) are the primary methods for detecting MP [7,8]. However, when only trace amounts of MP are present in complex samples such as soils, fruits, humor and so on [9–13], the determination of MP become difficult because the selectivity and sensitivity of these detection methods is poor. Therefore, preconcentration and separation of samples are indispensable techniques. Methods

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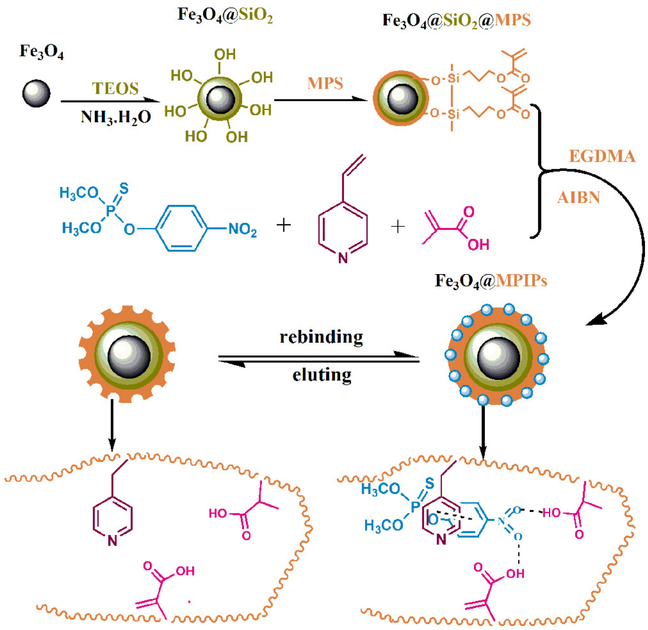

Fig. 1. Synthesis scheme for Fe$_3$O$_4$@MPIPs.

commonly used for pretreatment such as liquid–liquid extraction and solid-phase extraction, etc. [3,14], are less selective because their extractants have no specific recognition ability. It is significant to develop an artificial receptor, which can selectively recognize and adsorb methyl parathion in complex samples.

Thanks to the obvious advantages of predictable specific recognition, chemical stability, and comparatively cheap and easy preparation [15], molecular imprinting has been known as a versatile technique tailor-made toward a given target or group of target molecules. Hence, molecularly imprinted polymers (MIPs) have become a powerful tool for highly selective adsorption and detection field, where the MIPs act as molecular recognition elements [16–18]. Nevertheless, some drawbacks to traditional MIPs including incomplete template removal, low binding capacity, slow mass transfer and slow solid–liquid phase separation rate of the extractant with the solution have restricted their widespread application.

Adopting a surface imprinting approach that produces a MIPs nanoshell on a solid support provides a solution to the above disadvantages. Over the past decade, magnetic iron oxide nanomaterials have attracted significant interest because of their unique physical and chemical properties that enable them to be easily isolated from a matrix by using an external magnetic field instead of centrifuging and filtrating. The strong potential for biological and environmental applications makes these nanomaterials ideal candidates for use as the solid support for MIPs [19]. By encapsulating magnetic components into MIPs, specific molecular recognition can be combined with magnetic properties to obtain a novel solid phase extraction material with highly selective recognition, fast adsorption, and fast kinetic separation.

Based on this approach, this paper developed a new method to synthesize a magnetic molecularly imprinted solid phase extractant, then applied this MIPs to preconcentrate MP from soil samples. Methacrylic acid and 4-vinyl pyridine were chose as the functional monomers, owing to their ability to form hydrogen-binding interactions and π–π accumulation effect with MP within the imprinting polymer. Magnetic Fe$_3$O$_4$ nanoparticles (MNPs) were adopted as the substrate material, and the core–shell magnetic MP imprinted polymers (Fe$_3$O$_4$@MPIPs) were fabricated using a layer-by-layer self-assembly process (Fig. 1). The prepared Fe$_3$O$_4$@MPIPs were then characterized, and their adsorption behaviors were investigated and compared to non-imprinted polymers (NIPs).

2. Materials and methods

2.1. Materials

MP (98%), methamidophos (98%), malathion (98%), and simetryn (98%) were purchased from Sima-lab company (Tianjin, China). Nano-iron oxide (Fe$_3$O$_4$, 99%, 20 nm) was purchased from DK-lab company (Beijing, China). Methacrylic acid (MAA, 98%), 4-vinyl pyridine (4-VP, 98%), Tetraethoxysilane (TEOS, 99%), 3-methacryloyloxypropyltrimethoxysilane (MPS, 99%), ethylene glycol dimethacrylate (EGDMA, 98%), and 2, 2-azo-bisisobutyronitrile (AIBN, 98%) were obtained from Alfa Aesar (Tianjin, China). The HPLC grade organic solvents including chloroform, 2-propanol, acetic acid, and methanol were purchased from Kermel (Tianjin, China). AR grade chloroform, acetone, and concentrated ammonia aqueous solution (25 wt%) were acquired from Tianjin Chemicals Ltd.

2.2. Apparatus

HPLC analyses were performed on a Shimadzu LC-10AD pump (Kyoto, Japan) incorporating a Shimadzu SPD-10A UV–vis detector. And the determinations were performed on an analytical, reverse-phased Symmetry C18 (4.6 mm I.D. × 15 cm long, 5 mm) column (Dikema). The target compounds were characterized by transmission electron microscope (TEM) (Hitachi HT7700, Japan), Fourier transform infrared (FT-IR) (Bruker QUINOX-55, Germany), X-ray diffractometer (XRD) (Bruker D8 ADVANCE, Germany) and vibrating sample magnetometer (VSM) (Quantum MPMS XL-7, United States).

2.3. Preparation of Fe$_3$O$_4$@MPIPs

2.3.1. Synthesis of Fe$_3$O$_4$@SiO$_2$

Fe$_3$O$_4$@SiO$_2$ was synthesized according to Wang's method [20]. 300 mg of Fe$_3$O$_4$ nanoparticles were dissolved in 50 mL of 2-propanol and 4 mL of highly purified water by sonication for 15 min. Next, 5 mL of ammonium hydroxide and 2 mL of TEOS were added sequentially. The mixture was reacted for 12 h at room temperature under continuous stirring. The resultant product was separated by magnetic field, thoroughly rinsed six times with deionized water, then dried to powder in vacuum.

2.3.2. Synthesis of vinyl-modified Fe$_3$O$_4$@SiO$_2$

200 mg Fe$_3$O$_4$@SiO$_2$ was dissolved in 10 mL of deionized water by sonication for 10 min, followed by adding 1 mL of hydrochloric acid solution (0.012 mol/L). The mixture was homogenized by vigorous stirring, then 0.1 mL of MPS added. The solution was reacted for 24 h at room temperature under continuous stirring. The resultant product was collected by an external magnetic field, washed 3 times with both ethanol and deionized water, and finally dried in vacuum.

2.4. Preparation of Fe$_3$O$_4$@MPIPs and Fe$_3$O$_4$@NIPs

MP (78.9 mg), MAA (68.2 µL) and 4-VP (172 µL) were mixed in 10 mL of chloroform solvent, then refrigerated for 12 h to form a pre-assembly solution. Vinyl-modified Fe$_3$O$_4$@SiO$_2$ (100 mg), EGDMA (1.1 mL), and AIBN (25 mg) were dissolved in 30 mL of chloroform by ultrasonic vibration for 15 min, then stirred under nitrogen. The pre-assembly solution was then added to this mixture. After purging for 30 min with N$_2$, the combined mixture was sealed and vibrated on a shaking table at 300 rpm for 24 h at 60 °C.