



Well-defined magnetic surface imprinted nanoparticles for selective enrichment of 2,4-dichlorophenoxyacetic acid in real samples

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ABSTRACT

Superparamagnetic core-shell molecularly imprinted polymer nanoparticles (MIPs) were prepared via surface initiated reversible-addition fragmentation chain transfer (si-RAFT) polymerization for the selective recognition of 2,4-dichlorophenoxyacetic acid (2,4-D) in real samples. The construction of uniform core-shell structure with a 50 nm MIP layer was successfully accomplished, which favored mass transfer and resulted in fast recognition kinetics. The static equilibrium experiments revealed the satisfied adsorption capacity and imprinting efficiency of Fe₃O₄@MIP. Moreover, the Fe₃O₄@MIP exhibited high selectivity and affinity towards 2,4-D over structural analogues. The prepared Fe₃O₄@MIP nanoparticles were used for the selective enrichment of 2,4-D in tap water and Chinese cabbage samples. Combined with RP-HPLC, the recoveries of 2,4-D were calculated from 93.1% to 103.3% with RSD of 1.7–5.4% (n = 3) in Chinese cabbage samples. This work provides a versatile approach for fabricating well-constructed core-shell MIP nanoparticles for rapid enrichment and highly selective separation of target molecules in real samples.

1. Introduction

2,4-dichlorophenoxyacetic acid (2,4-D) is one of the first commercial artificial auxin herbicides and still widely used nowadays [1]. 2,4-D is acting as a kind of stimulated auxin to promote cell division and elongation at low concentrations. At high concentrations, it is a kind of herbicide to control broad-leaf growth [2]. However, 2,4-D can lead to serious contamination and damage to humans and animals relevant to cancer risks, neurologic disease, reproductive risks, and immunotoxicity [1]. The maximum contaminant levels (MCL) of 2,4-D in drinking water are set as 30 µg/L by WHO [3] and 70 µg/L by US EPA [4]. The maximum residue limits (MRL) of 2,4-D in Chinese cabbage are set as 0.05 mg/kg by EU [5]. Owing to the complexity of matrix and the low concentration of 2,4-D existed, it is necessary to find an effective way for rapid and selective enrichment and separation of 2,4-D in real samples.

Molecularly imprinted polymers (MIPs) have been widely recognized as promising materials with selective binding cavities that are complementary in shape, size and alignment of functional groups for the rebinding of target molecules [6]. Their tailor-made nature allows MIPs for the recognition of a wide range of targets, including small

molecules and biomacromolecules. With the advantages of chemical and physical stability, long usage and low cost, MIPs have been successfully applied in many fields, such as separation [7–10], biosensors [11–13], catalysts [14,15], and biomedical materials [16–20]. However, MIPs are still suffering from several problems, such as incomplete template removal, slow mass transfer, poor site accessibility, or heterogeneous distribution of binding sites, which limit the wide application of MIPs [21,22].

Surface imprinted strategy [23] provides an effective way to deal with the limitations mentioned above. Compared to traditional bulk imprinted strategy, surface imprinted strategy has significant advantages, such as high template removal efficiency, fast mass transfer, controllable and regular shape, and good accessibility to the target species [24]. Moreover, MIP materials with magnetic property are superior for easy handling and fast separation since they can be easily collected and isolated by an external magnetic field. Fabrication of MIPs on superparamagnetic nanoparticles gives access to smart materials with dual functions of target recognition and magnetic separation [25–27].

Surface imprinted strategy has been applied for the construction of several MIPs for the selective enrichment and separation of 2,4-D.

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Zhang et al. prepared hydrophilic hollow MIP microparticles to adsorb 2,4-D in aqueous media with photo- and thermo-responsive template binding and release behaviors [28]. Chen et al. prepared a molecular imprinting-based turn-on ratiometric fluorescence sensor for detection of 2,4-D based on photo induced electron transfer [29]. Zhao et al. prepared monodispersed macroporous core-shell molecularly imprinted particles for the selective separation of 2,4-D in environmental water [30]. However, surface imprinted polymers were rarely applied in the enrichment of 2,4-D in complex samples. Most of them were only applied in water samples which are cleaner and have less interference.

Surface initiated reversible-addition fragmentation chain transfer (si-RAFT) polymerization, a kind of controlled/living radical polymerization method, is emerging as an appealing approach for grafting well-defined surface imprinted polymers on nanoparticles [31]. In this study, the novel superparamagnetic core-shell MIP nanoparticles for 2,4-D were prepared via si-RAFT polymerization for the detection of 2,4-D in tap water and Chinese cabbage samples. The Fe_3O_4 nanoparticles were compactly encapsulated with a SiO_2 layer via sol-gel reaction. The well-defined MIP for 2,4-D was further fabricated on the surface of $\text{Fe}_3\text{O}_4@SiO_2$. The $\text{Fe}_3\text{O}_4@MIP$ nanoparticles were characterized by transmission electron microscopy (TEM), Fourier-transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD). The magnetic property of $\text{Fe}_3\text{O}_4@MIP$ was investigated using vibrating sample magnetometer (VSM). The adsorption and separation properties were further characterized by adsorption kinetics experiments, static equilibrium experiments and selectivity experiments. Additionally, the practical application of $\text{Fe}_3\text{O}_4@MIP$ nanoparticles was used to selectively enrich 2,4-D from tap water and Chinese cabbage samples.

2. Experimental

2.1. Reagents and materials

Trisodium citrate, sodium acetate, anhydrous ferric chloride, ethylene glycol, ethyl alcohol, aqueous ammonia, tetraethyl orthosilicate (TEOS), toluene, acetone, sodium hydroxide, trichloromethane, hydrochloric acid, 2-propanol, hexane, N,N-dimethylformamide (DMF) and acetic acid were obtained from Beijing Chemical Works (Beijing, China). 3-aminopropyltrimethoxysilane (APTMS), 1-dodecanethiol, methyltriethylammonium chloride, 4-vinyl pyridine (4-VP), ethylene glycol dimethacrylate (EGDMA), 2,2'-azoisobutyronitrile (AIBN), trifluoroacetic acid (TFA) with HPLC grade, 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) and butyl 2,4-dichlorophenoxy acetate (2,4-D-OBu) were purchased from J&K Scientific Ltd. (Beijing, China). 2,4-dichlorophenoxyacetic acid (2,4-D) was obtained from Aladdin Industrial Corporation (Shanghai, China). Carbon disulfide was obtained from Sinopharm Chemical Reagent Beijing Co., Ltd. (Beijing, China). Methanol and acetonitrile with HPLC grade were purchased from Thermo Fisher Scientific Inc. (Massachusetts, USA). Benzoic acid (BA) was obtained from Wuhan Chemical Organic Synthesis Factory (Wuhan, China). O-(6-Chloro-1-hydrocibenzotriazol-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphat (HCTU), 1-Hydroxybenzotriazole (HOBt), N,N-Diisopropylethylamine (DIPEA), 1,3-Dicyclohexyl-carbodiimide (DCC) and phosphoric acid with HPLC grade were purchased from Sigma-Aldrich Co. LLC. (St. Louis, MO, USA). Ultrapure water was obtained from Milli-Q water purification system (Millipore, Massachusetts, USA). 4-VP and EGDMA were distilled under reduced pressure to remove stabilizer. All other reagents were analytical grade and used without further disposal.

2.2. Synthesis of Fe_3O_4 nanoparticles and surface modification

A complete description of the synthesis procedures for Fe_3O_4 nanoparticles and RAFT agent S-1-dodecyl-S'-(α,α' -dimethyl- α'' -acetic

acid) trithiocarbonate (TTCA), the coating of SiO_2 layer on the Fe_3O_4 nanoparticles and the amine functionalization of $\text{Fe}_3\text{O}_4@SiO_2$ nanoparticles is available in [Supplementary materials](#).

TTCA was modified on the surface of $\text{Fe}_3\text{O}_4@SiO_2@NH_2$ nanoparticles via amide bond formation. The coupling procedures were as follows: $\text{Fe}_3\text{O}_4@SiO_2@NH_2$ nanoparticles (0.3 g), HCTU (0.066 g), HOBt (0.022 g), TTCA (0.06 g) and DIPEA (0.0565 mL) were added in anhydrous DMF (5 mL). The mixture was sonicated for 15 min and stirred at room temperature for 24 h. The produced $\text{Fe}_3\text{O}_4@TTCA$ nanoparticles were separated by magnetic collection and washed with DMF and methanol for three times, respectively, followed by dried under vacuum.

2.3. Preparation of $\text{Fe}_3\text{O}_4@MIP$ and $\text{Fe}_3\text{O}_4@NIP$ nanoparticles

4-VP and EGDMA were used as the functional monomer and cross-linker, respectively. Before the polymerization, 2,4-D (0.0442 g) and 4-VP (86 μL) were dissolved in acetonitrile (20 mL) and stirred at room temperature for 12 h. Then $\text{Fe}_3\text{O}_4@TTCA$ nanoparticles (100 mg) was dispersed into the solution under ultrasonication, followed by adding EGDMA (451 μL) and AIBN (10 mg). After frozen by cold trap, the mixture was vacuumized for 15 min and purged with N_2 gas to remove oxygen. Then a two-step polymerization was carried out. The pre-polymerization was kept at 50 $^\circ\text{C}$ for 6 h, followed by normal polymerization at 65 $^\circ\text{C}$ for 12 h. The resultant $\text{Fe}_3\text{O}_4@MIP$ nanoparticles were magnetically separated and sequentially washed with acetonitrile and methanol for three times, respectively. The template molecules existing in $\text{Fe}_3\text{O}_4@MIP$ nanoparticles were removed by acetic acid-methanol (4:6, v/v) until no templates were detected by HPLC. Then $\text{Fe}_3\text{O}_4@MIP$ nanoparticles were washed with methanol until neutral, followed by dried under vacuum.

The $\text{Fe}_3\text{O}_4@NIP$ nanoparticles were prepared under the same condition only without the addition of the template 2,4-D.

2.4. Characterization

Morphological characteristic of the nanoparticles was determined with JEM-2100(UHR) lanthanum hexaboride transmission electron microscope (JEOL, Tokyo, Japan). Magnetic properties were carried out by a 7410 vibrating sample magnetometer (VSM, Lake Shore, Cryotronics Inc., Ohio, USA). Fourier transform infrared (FT-IR) spectroscopy data were obtained with a Tensor-27 FT-IR spectrometer (Bruker, Germany) with the spectra scanned from 4000 to 400 cm^{-1} in the transmission mode, accumulating 32 scans at a resolution of 4 cm^{-1} . X-ray photoelectron spectroscopy (XPS) characterization was performed with an ESCALab220i-XL electron spectrometer from VG Scientific (London, UK) using 300 W AlK α radiation. Thermogravimetric analysis (TGA) was performed using Perkin-Elmer Pyris 1TG analyzer (PE, USA) to determine the weight loss. X-ray diffraction (XRD) patterns were measured in the range of $2\theta = 20\text{--}80^\circ$ by step scanning on the Rigaku D/MAX-2500 diffractometer (Rigaku Co., Japan) with Cu K α radiation.

2.5. HPLC analysis

Chromatographic analysis was performed on a Shimadzu Prominence UFLC system (Shimadzu, Kyoto, Japan) consisting of two LC-20AD pumps, a SPD-M20A diode-array detector, a CTO-20A oven, and a SIL-20A auto sampler. The detection wavelengths were 282 nm for 2,4-D, 228 nm for BA and 2,4-D-OBu, and 223 nm for 2,4,5-T. A Dikma Diamonsil C₁₈ HPLC column (250 mm \times 4.6 mm, 5 μm , Dikma Technologies Inc. Beijing, China) was employed. The mobile phase used for the analysis of 2,4-D and its three analogues BA, 2,4,5-T and 2,4-D-OBu was methanol-water (90:10, v/v, pH 3.0, adjusted with phosphoric acid). The flow rate was 1.0 mL/min.

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