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A novel molecularly imprinted material based on magnetic halloysite nanotubes for rapid enrichment of 2,4-dichlorophenoxyacetic acid in water

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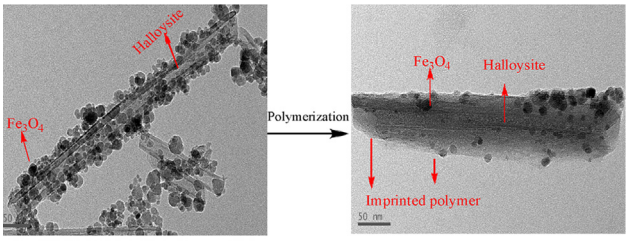
HIGHLIGHTS

- Successful preparation of a novel type of magnetic halloysite molecularly imprinted material.
- Rapid enrichment for 2,4-dichlorophenoxyacetic acid in water.
- This material possesses high adsorption capacity and specific recognition to 2,4-dichlorophenoxyacetic acid.
- Magnetic halloysite were synthesized by co-precipitation method.

GRAPHICAL ABSTRACT



MHNTs MHNTs@MIP

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ABSTRACT

A new type of magnetic halloysite nanotubes molecularly imprinted polymer (MHNTs@MIP) based on halloysite nanotubes (HNTs) with embedded magnetic nanoparticles was introduced in this study. MHNTs@MIP was prepared through surface imprinting technology, using 2,4-dichlorophenoxyacetic acid (2,4-D) as a template, 4-vinylpyridine as the monomer, divinylbenzene as cross-linking agents, and 2,2-azodiisobutyronitrile as initiator. MHNTs@MIP was characterized by Fourier Transform Infrared Spectrometer, transmission electron microscopy, X-ray diffraction, and vibrating sample magnetometer. MHNTs@MIP exhibited rapid and reliable analysis with supermagnetic properties, as well as repeated use and template-specific recognition. The adsorption capacity of magnetic halloysite nanotubes non-imprinted polymer (MHNTs@NIP) and MHNTs@MIP was 10.3 mg/g and 35.2 mg/g, respectively. In the detailed discussion on specific selectivity, MHNTs@MIP can be applied as an adsorbent for sample pre-treatment extraction and obtain high recoveries of about 85–94%. After extraction, high-performance liquid chromatography was used to detect 2,4-D residue in water.

1. Introduction

2,4-Dichlorophenoxyacetic acid (2,4-D) is a widely-used herbicide or plant growth regulator in agriculture. Despite its toxicity to many organisms, 2,4-D has been used and monitored for several decades. Presently, an increasing number of countries are concerned about its continued use, and the residues of 2,4-D in grain, fruit, and vegetables are strictly limited. Thus, establishing an efficient method for separation and extraction of 2,4-D is important. Several methods have been described for the determination of 2,4-D in different samples, including surface-enhanced Raman scattering, chemiluminescent ELISA [1], and high-performance

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liquid chromatography (HPLC) [2]. The HPLC-based method is the universal procedure for the quantitative determination of 2,4-D [3]. However, an enrichment step is necessary prior to detection using HPLC [4]. Various traditional sample pretreatment methods, such as liquid-liquid extraction waste a considerable amount of organic solvents. Molecularly-imprinted polymers (MIPs) can be used as a good material for sample pretreatment, has attracted significant attention because of their excellent selectivity and high affinity, in the same manner as antibodies.

The synthesis of MIPs is a process wherein a functional monomer and crosslinker are co-polymerized with the template. Removing the template exposes the binding sites that satisfy the shapes and sizes of the template molecule and can rebind the analyte from multi-component systems with very high specificity [5]. MIPs have many potential applications and advantages in fields, such as biomimetic sensors [6], catalysis [7], and separation [8].

Considering the mass transfer limitations on conventional bulk polymerization technology and the elution difficulty because of the embedding depth of template molecule, surface imprinting has been introduced. Inorganic nanoparticles, such as SiO_2 [9–11], Al_2O_3, carbon nanotubes (CNTs) [12], and Fe_3O_4 [13,14], are new functional supports that possess small size and large specific surface area, and are used as effective absorbents for surface imprinting. For imprinted polymers, the participation of Fe_3O_4 microspheres may offer a more facile method than the conventional centrifugation or filtration to achieve a rapid separation. However, Fe_3O_4 microspheres have several disadvantages, such as an easy tendency to aggregate and the leakage of magnetism. A new support material called halloysite nanotubes (HNTs) has recently been introduced. HNTs have the chemical formula of $Al_2Si_2O_5(OH)_4{\cdot}nH_2O$ [15,16], similar to kaolinite, except for the presence of an additional water monolayer between the adjacent clay layers [17,18]. HNTs are composed of gibbsite (Al–OH) octahedral sheet groups on the internal surface and siloxane (Si–O–Si) groups on the external surface. HNTs are highly useful because they are obtained from natural, biocompatible sources with eco-friendly properties [19], which has been proven when the toxicity of halloysite was tested after 48 h of incubation with fibroblast and human breast cells [20]. At the same time, HNTs also exhibit excellent characteristics, such as large volume, large surface, and adequate hydroxyl groups [21]. In recent years, the function of HNTs modified by acid activation [22], embedding, and chemical modification [23] have gained the interest of many researchers because of their inherent hollow nanotube structure and differing outside and inside chemistry. Therefore, the combination of Fe_3O_4 and HNTs can yield a promising support material that possesses the excellent magnetic properties of Fe_3O_4 and the surface of the HNTs. However, the size of the Fe_3O_4 particles produced by hydrothermal method is about 200–300 nm [24], which may block the Si–O–Si group or cannot adhere on the HNT surface [25]. This phenomenon may affect the grafting rate of the silane coupling agent and the molecular imprinting polymer coated in magnetic halloysite nanotubes (MHNTs) [26–28]. To protect the efficient Si–O–Si group and obtain magnetic properties, a one-step co-preciptation method has been introduced for preparing MHNTs [29,30].

In this work, MHNTs@MIP has been successfully developed. First, a one-step co-precipitation method was used to prepare MHNTs composites with iron (III) and iron (II) salts. Second, MHNTs were surface-modified by MPTES, which introduced double bonds onto the surface of MHNTs to form sites for polymerization. Third, MHNTs@MIP was synthesized by precipitation-polymerization method, using vinyl-modified MHNTs as support material, 2,4-D as template, 4-Vinylpyridine as the functional monomer, divinylbenzene as the crosslinker, and 2,2-azobisisobutyronitrile as the initiator. This work has been proposed to develop a new facile, environment-friendly, and sensitive method based on MHNTs@MIP as selective extraction sorbents for the detection of 2,4-D in water.

Table 1
Binding energies (ΔE) of the optimized complex of 2,4-D with 4-VP and MMA at the ratio of 1:4.

Complex	ΔE calculated by DFT method (10^5 kJ mol^{-1})
2,4-D-4-VP	−38.2
2,4-D-MMA	−36.4

2. Experimental

2.1. Reagents and apparatus

Halloysite nanotubes (HNTs) were supplied by Zhengzhou Jinyangguang Co., Ltd. (Henan, China). Iron (III) chloride hexahydrate ($FeCl_3{\cdot}6H_2O$), iron (II) chloride tetrahydrate ($FeCl_2{\cdot}4H_2O$), polyvinylpyrrolidone (PVP) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China); 2,4-dichlorophenoxyacetic acid (2,4-D), (4-chloro-2-methylphenoxy) acetic acid (MCPAc), phenoxyactic acid (POAc) were obtained from J & K Chemical Limited (Beijing, China) 3-methacryloxypropyltrimethoxysilane (MPTES) and divinylbenzene (DVB) were purchased from Aladdin Company (Shanghai, China). 4-Vinylpyridine (4-VP) was purchased from Aladdin Company (Shanghai, China) and distilled under vacuum before use and kept at −20 °C in the dark. 2,2-Azobisisobutyronitrile (AIBN) was purchased from Sigma-Aldrich and purified by recrystalization from ethanol. All chemicals were of analytical reagent grade, except for methanol and acetonitrile which was of high-performance liquid chromatography (HPLC) grade. All water was doubly distilled before use.

2.2. Instruments and HPLC method

The instruments used in this study were as follows: UV-2450 Spectrophotometer (Shimadzu, Japan). FT-IR spectra were employed to determine infrared spectra (Nicolet, America). Morphology and size distribution of the MHNTs and MHNTs@MIP were obtained at 20.0 kV using JEM-2100F TEM (JEOL, Japan). Particle phases were characterized using a Rigaku D/max22500 XRD with Cu Ka radiation (Rigaku Ltd., Japan). Magnetic properties were recorded using a VSM (Lake Shore Ltd.) at room temperature. Chromatographic measurements were performed using an EasySepTM-1010 HPLC (Unimicro Technologies Co., Ltd., Shanghai, China) with a 2010A LC liquid delivery pump and a 2010A UV detector. The Column was C-18 column (4.6 mm × 250 mm) at the temperature of 30 °C. The mobile phase was acetonitrile–water–acetic acid (50:50:1, v/v/v) at the flow rate of 1.0 mL/min. We selected 230 nm as the detection wavelengths. The sample volumes for injection were all 20 μL.

2.3. Computational selection of functional monomers for molecular imprinting

The geometries of 2,4-D, MAA, 4-VP, and two possible configurations of 1:1 and 1:4 template–monomer molecular systems were optimized by applying relatively accurate DFT method at the B3LYP/6-31G(d) level by the Gaussian05 program package using a Chem3D workstation with a Windows operating system [31]. The minimum binding energies between the optimized conformations of 1:*n* template–monomer complexes are listed in Table 1. The most stable template–monomer complexes were searched through