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Synthesis of biomass *trans*-anethole based magnetic hollow polymer particles and their applications as renewable adsorbent

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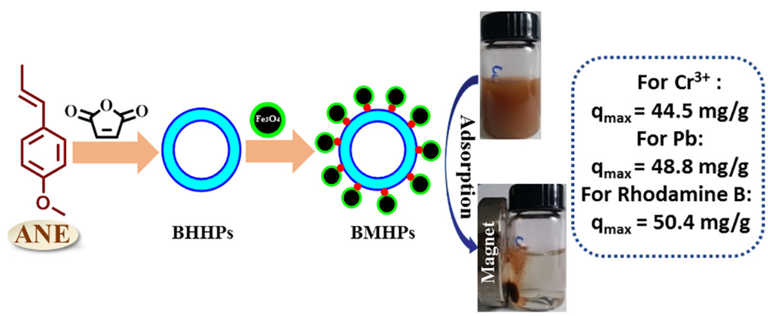
HIGHLIGHTS

- Biomass, *trans*-anethole-based magnetic hollow particles were prepared.
- The particles serve as adsorbent for removing pollutants from wastewater.
- The particles show high adsorbing capacity towards Cr^{3+}, Pb^{2+} and Rhodamine B.
- The particles demonstrate the desirable recycling ability.

GRAPHICAL ABSTRACT



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ABSTRACT

This article reports a novel type of biobased magnetic hollow particles (BMHPs) derived from a widely available biophenylpropene *trans*-anethole (ANE). To prepare BMHPs, ANE and maleic anhydride (MAH) underwent copolymerization in the presence of particulate templates to form core/shell particles. Sequential removing the cores and hydrolyzing processes provide biobased hydrolyzed hollow particles (BHHPs), which were then grafted with amino-modified Fe_3O_4 NPs. The prepared BMHPs were characterized by SEM, TEM, XRD, VSM, EDS and FT-IR techniques and further used as bioadsorbent to remove pollutants from wastewater. The maximum adsorption capacity towards Cr^{3+}, Pb^{2+} and Rhodamine B is up to 44.5, 48.8 and 50.4 mg/g, respectively. Kinetic and isothermal studies show that the adsorption is best fitted with pseudo-second order model and Langmuir isothermal adsorption. BMHPs demonstrated remarkable magneticity and can be easily separated by external magnet. Recycling use study showed that the dye-adsorbed BMHPs can be easily restored in HCl/THF mixed solution. The advantages of the new adsorbents, namely, derivative from bio-resource, high adsorption capacity, much ease in separation and regeneration recyclability, render them with promising potentials in wastewater treatment.

1. Introduction

Water contaminants with metal ions and soluble dyes, which significantly come from industrial processes, have received extensive concerns [1]. When waste water containing the pollutants is discharged directly into environment, they can cause severe health and ecological problems to aquatic life as well as human beings [2–5]. Therefore, removal of metal ions and soluble dyes prior to their discharge into environment should be mandatory. To date, many technologies such as chemical precipitation [6], membrane-based filtrations [7], biological

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treatments [8], and adsorption [9] have been explored for removing the pollutants. Among these methods, adsorption is considered as one of the most attractive methods due to the effectiveness and the ease in operation and regeneration [10–15]. Thus, a large variety of materials, e.g. clay [16], carbon-based materials [17,18], zeolite [19], and polymers [20] have been developed into adsorbents for removing water contaminants.

Among the currently available adsorbents, green bioadsorbents derived from natural biomass attract more and more attention in recent years due to their sustainability, biodegradability, and low toxicity [21]. Many bioadsorbents derived from natural polymers like chitosan [22], starch [23], and cellulose [24] and small molecular biomasses like plant oils [25], vanillin [26], β-cyclodextrin [27] have been well explored and show remarkable adsorption capacity. However, besides the adsorption capacity, ready separation of the adsorbents from treated solutions also should be highlighted, to avoid secondary pollution in practical applications [28,29]. In this regard, a judicious combination of bioadsorbent and magnetic components is expected to provide more promising adsorbents which exhibit both high adsorption capacity and recyclability [30–38].

In the aforementioned context, it is hypothesized that hollow particles combined with magnetic nanoparticles can be employed as high-performance adsorbents because they are easy to be applied and separated, together with other advantages including rapid adsorption performance and high adsorption capacity. In the previous work, interesting biobased hollow particles originated in biomass *trans*-anethole (ANE) have been prepared and used as high-performance green adsorbents [39,40]. To integrate the two concepts of "green adsorbents" and "magnetic particles", in this study a new type of hybrid biobased hollow particles (named as BMHPs below) were prepared by combining ANE-based hollow particles and Fe_3O_4 NPs. The BMHPs were used as efficient bioadsorbents for removing metal ions and soluble dyes from wastewater, irrespectively taking Cr(III), Pb(II) and Rhodamine B as examples. The adsorption kinetics and isotherm model were investigated in detail. The results show that BMHPs have high adsorption capacity for Cr(III), Pb(II) and Rhodamine B with good recyclability, so they demonstrate promising potential applications for efficient wastewater treatment. The methodology established in this work is also anticipated to provide various magnetic bioadsorbents with diverse potential applications.

2. Experimental section

2.1. Materials

$FeCl_3{\cdot}6H_2O$, $FeSO_4{\cdot}7H_2O$, and $NH_3{\cdot}H_2O$ (28%) were purchased from Beijing Chemical Reagents Company and used as received. 3-Aminopropyltriethoxysilane (APTES) and N-hydroxysuccinimide (NHS) were purchased from Alfa Aesar and used directly. 1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC·HCl) was purchased from Aladdin Reagent Co. (Shanghai, China). Biobased, hydrolyzed hollow particles (BHHPs) were prepared according to the previous work [40]. All solvents were purchased from Beijing Chemical Reagents Company and distilled by standard methods before use.

2.2. Measurements

The surface morphology of the Fe_3O_4 NPs, amino-modified Fe_3O_4 NPs, BHHPs, and biobased magnetic hollow particles (BMHPs) were observed by transmission electron microscope (TEM, Hitachi H-800) and scanning electron microscopy (SEM, Hitachi S-4800). Fourier transform infrared spectra (FT-IR) were recorded on a Nicolet NEXUS 670 spectrophotometer (KBr tablet). Magnetic characterization was measured by vibrating sample magnetometer (VSM, Lake Shore 7410). XRD patterns were carried out by using a D/max2500 VB2+/PC X-ray diffractometer. EDS and Elemental mapping before and after adsorption were performed on a JEOL JEM-200CX. Atomic absorption spectrophotometer (AAS) (Varian Spectra AA55B) and UV–vis spectrophotometer (Shanghai Jinghua756MC) were used for determining the concentrations of Cr(III), Pb(II) and Rhodamine B dye.

2.3. Synthesis of Fe_3O_4 NPs

Fe_3O_4 NPs were prepared by co-precipitation method reported in literature earlier [41]. Briefly, $FeCl_3{\cdot}6H_2O$ (2.9 g, 0.0107 mol) was dissolved in 50 ml deoxygenated water through ultrasonic process under N_2 protection. After stirring for 20 min, $FeSO_4{\cdot}7H_2O$ (1.5 g, 0.0053 mol) was added in the system and the temperature was increased to 80 °C. Then 3.75 ml of ammonium hydroxide (25%, w/w) was quickly added into the reaction mixture. A black precipitate of Fe_3O_4 NPs immediately formed. After completing the reaction, the product was collected and washed by ethanol three times. After drying in a vacuum overnight, Fe_3O_4 NPs were obtained.

2.4. Preparation of amino-modified Fe_3O_4 NPs

Amino-modified Fe_3O_4 NPs were prepared according to the previous work [42]. The whole procedure was conducted under N_2 atmosphere. Typically, Fe_3O_4 NPs (1 g) were added in a three-neck flask containing 50 ml of anhydrous isopropanol. When the temperature of reaction system was increased to 70 °C, APTES (2 ml) was injected to the reaction solution under vigorous stirring. Six hours later, the product was collected and washed by ethanol three times. After drying in an oven at 60 °C for 24 h, amino-modified Fe_3O_4 NPs were obtained.

2.5. Preparation of biobased magnetic hollow particles (BMHPs)

Briefly, 20 mg of the BHHPs was dispersed in 20 ml of deionized water with stirring. Then, 20 mg of amino-modified Fe_3O_4 NPs was added to the reaction flask. 30 min later, 4 ml of EDC·HCl solution (5 mg/ml, deionized water as solvent) and 4 ml of NHS solution (6 mg/ml, deionized water as solvent) were simultaneously added into the reaction flask at 60 °C. 10 h later, the product was isolated with assistance of a magnet and washed with ethanol three times to remove the unreacted BHHPs. After drying under vacuum at 60 °C overnight, biobased magnetic hollow particles (BMHP) were obtained.

2.6. Adsorption performance

Cr(III) and Pb(II) were taken as representatives of toxic metal ions while Rhodamine B was taken as a model for soluble dyes to explore the adsorption capacity of BMHPs, because the three adsorbates are typical pollutants causing serious environmental problems. Adsorption experiment was performed as follows. An aqueous solution of each pollutant was prepared first (100 mg/L), from which 10 ml of the solution was taken and charged in a glass bottle. Then 10 mg of BMHPs was added in the bottle. Adsorption proceeded for a determined time at room temperature. After the adsorption was complete, the supernatant was separated with the assistance of a magnet and the residual pollutant concentration was investigated by AAS and UV–vis spectrophotometer. The removal percentage of adsorbate (R) was calculated by the following equation:

$$R\% = \frac{(C_0 - C_e)}{C_0} \times 100\% \tag{1}$$

In the above equation, C_e is the equilibrium concentration (mg/L) of pollutant while C_0 is the initial concentration. The two parameters, C_e and C_0 keep unchanged in meaning below.

2.7. Equilibrium isotherm

For isothermal study, Langmuir isotherm model was investigated in