

Biomass ferulic acid-derived hollow polymer particles as selective adsorbent for anionic dye



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ABSTRACT

In the present study, naturally occurring ferulic acid (FA) is used for the first time as raw material to copolymerize with maleic anhydride (MAH) for fabricating bio-based hollow polymer particles (BHPs). After consecutive reaction with ethylenediamine and HCl, BHPs were transformed to ammonium-functionalized BHPs (BHP-NH₃⁺) which were identified by SEM, TEM, FT-IR and XPS measurements. BHP-NH₃⁺ served as high-performance selective adsorbent for removal methyl orange (MO), a model anionic dye from water. Detailed adsorption studies reveal that the adsorption of MO onto BHP-NH₃⁺ better fits the pseudo-second-order kinetics model and the adsorption isotherm can be well-described by Langmuir isotherm model with a maximum adsorption capacity of 952 mg/g at pH 7. The removal of MO can maintain a high level in a wide pH range (from 5 to 10). Desorption tests demonstrate that the adsorbent after adsorbing MO can be facily regenerated to recover both the dye and adsorbent with high efficiency (over 95%) in basic solution (pH 11). Moreover, the biobased adsorbent shows high reusability and stability over five adsorption/desorption cycles.

1. Introduction

Water pollution and resource shortage have received increasing concerns nowadays. As common pollutants in water environment, organic dye contaminants, which are highly visible and aesthetically unpleasant, pose a significant threat to human and other organisms because of their toxicity and carcinogenicity [1–3]. Hence, eliminating these organic dyes from effluents before their discharge is environmentally necessary and urgent. To remove dyes from wastewaters, various treatment processes have been developed, including physical separation [4,5], chemical precipitation [6], biological treatments [7] and adsorption [8]. Among the currently available techniques, adsorption technology is highly promising for dye removal because of its operation simplicity, high efficiency, flexibility, and insensitivity to toxic substances [9–12]. So far numerous kinds of adsorbents have been developed, including carbon-based materials [13,14], silica gels [15], kaolin [16], magnetic particles [17] and polymeric adsorbents [18–20]. Among the adsorbents, polymeric adsorbents have received much attention for dye removal due to their perfect mechanical property and facile regeneration for repeated uses [21,22]. However, most of these polymeric adsorbents are prepared by nonrenewable materials, which

is not desirable for sustainable development. Thus, new high-efficiency adsorbents from renewable biomass such as chitosan [23], β -cyclodextrin [24] and methyl isoeugenol [25] have been gathering rapidly increasing attention in recent years. Among the various biobased adsorbents, those derived from lignin have been regarded as one of the most ideal candidates [26]. Different from the biomass derived from crops, lignin is abundant in wood and annual plants and cannot serve as human's food [27,28], which circumvents the concern about the preparation of adsorbents from lignin competing with human feeding. Unfortunately, the complex structures of lignin limit the development of lignin-based materials. This situation stimulates emerging interest in the derivatives from lignin, exemplified by ferulic acid.

As a category of natural phenolic compound, ferulic acid (FA) exists in many plant cell walls [29,30] and especially can be derived from lignin [31]. The chemical structure of FA comprises a skeleton of cinnamic acid along with phenolic group and methoxy group. Due to the existence of hydroxyl and carboxylic acid groups in the structure, various FA-based polymers with a wide range of thermomechanical properties have been synthesized via condensation polymerizations recently [31–36]. In addition, the conjugated carbon-carbon double bond in FA structure also can be converted into polymers via addition

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polymerization. Unfortunately, because of the 1,2-substituted structures as well as the antioxidant phenolic groups, FA hardly undergoes direct radical polymerization [37,38]. Alternatively, after decarboxylation (the product called 4-vinylguaiacol, 4VG) and protection of phenol groups, the protected monomers derived from FA (named as protected 4VGs) could be radically polymerized into high molecular weight polymers [39–41]. However, the protected 4VGs have never been designed for preparing hollow polymer particles yet. Polymeric particles especially hollow particles have attracted considerable attention due to their unique properties and advantages such as surface functionality, surface permeability and encapsulation property [42–45]. In our previous studies, biomass adsorbents derived from *trans*-anethole, a typical biomass from crops, have been well designed and prepared [46,47]. To further exploit the potential uses of lignin, in the present work, a novel type of bio-based hollow particles was prepared using methacrylate-protected 4VG (4-vinylguaiacol methacrylate, 4VGMA) and maleic anhydride (MAH) and served as selective adsorbent. Herein, of special notice is that MAH can also be regarded as a renewable material because nowadays it can be prepared from biomass 5-hydroxymethyl furfural [48]. Therefore, the present study not only extends largely the potential uses of FA, but also provides a novel type of biomass based polymeric hollow particles.

In the present contribution, FA was judiciously used as raw material to prepare monomer 4VGMA (Scheme 1). 4VGMA was further used to prepare bio-based hollow particles via hard-templating method as shown in Scheme 2. Following the strategy, core/shell particles were prepared by using 4VGMA, MAH and PMV (polymer particles derived from MAH and vinyl acetate) template through precipitation polymerization. After removing the template, the as-prepared bio-based hollow particles (BHPs) were converted to ammonium functionalized BHPs (BHP-NH₃⁺) after consecutive reaction with ethylenediamine and HCl. The resulting BHP-NH₃⁺ was investigated to evaluate the adsorption property towards negatively charged dye, using methyl orange (MO) a model. The hollow and porous structure provides the obtained BHP-NH₃⁺ with high specific surface area while the mesoporous channels act as a fast diffusion path for dye adsorption and the subsequent desorption. Meanwhile, the high density of ammonium groups on the mesoporous shell can serve as effective binding sites for the selective and pH-responsive removal of anionic dye. Furthermore, with the assistance of carboxyl groups, the reported adsorbents can be rapidly and flexibly regenerated under mild conditions (in weak alkaline solution, pH 11).

2. Experimental

2.1. Materials

N,N-Dimethylformamide (DMF), anhydrous diethyl ether, anhydrous ethanol, and acetone were purchased from Beijing Chemical Reagents Company (China) and distilled by standard methods. Ethylenediamine and triethylamine (TEA) were purchased from Tianjin Fuchen Chemical Reagents Factory and used without further treatment. Methacryloyl chloride (from Alfa Aesar), ferulic acid (FA, from Adamas), maleic anhydride (MAH, from TCI), methyl orange (MO, from Alladin) and methylene blue (MB, from Ciba) were used as received. 2,2'-Azobisisobutyronitrile (AIBN, from Aldrich) was purified by

recrystallization from methanol. Water was freshly deionized before use.

2.2. Measurements

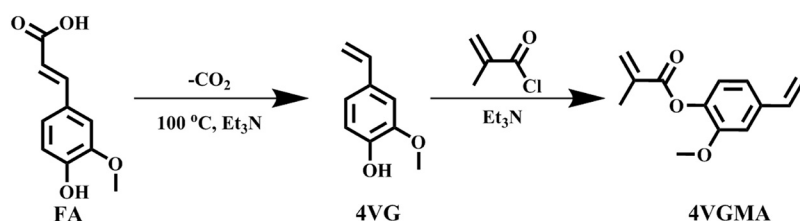
FT-IR spectra (KBr pellet) were measured using a Nicolet NEXUS 670 spectrophotometer. ¹H NMR (nuclear magnetic resonance, 400 MHz) spectra were measured in CDCl₃ by using a Bruker AV400 spectrometer at 20 °C, with tetramethylsilane (TMS) as internal standard. The surface morphology of all particles was investigated by S-4800 electron microscope (SEM, Hitachi) while the hollow structure was observed by transmission electron microscope (TEM, Hitachi H-800). For SEM measurement, the samples were fixed on conductive adhesive tape, while for TEM, the samples were fixed on copper wire mesh. Methyl orange content and methylene blue content were determined by a UV–vis spectrophotometer (Shanghai Jinghua756MC). X-ray photoelectron spectroscopy (XPS spectra) was performed in a Thermo Fisher Scientific ESCALAB 250 spectrometer with an X-ray source of monochromated Al Kα 150 W, and the pass energy is 200 eV for survey and 30 eV for high resolution scans. Elemental analysis was performed on a Vario EL cube (Elementar Analysensysteme GmbH). The specific surface area and pore diameter of BHP-NH₃⁺ were determined by using a Quadrasorb SI analyzer (Quantachrome Instruments, Boynton Beach, FL, USA).

2.3. Synthesis of 4-vinylguaiacol (4VG)

Monomer 4-vinylguaiacol (4VG) was synthesized according to the method in literature [38]. Ferulic acid (FA, 10 g, 52 mmol) was dissolved in DMF (30 mL). Into this solution, TEA (15 mL, 104 mmol) was added and then the mixture was heated to 100 °C under stirring. After 3 h, the reaction mixture was cooled to room temperature and then diluted with diethyl ether and washed with 1 M HCl aqueous solution three times. The organic layer was dried over anhydrous Na₂SO₄ and then evaporated to yield 4VG. Further purification was conducted by distillation to give 4VG as colorless liquid (yield 78%).

2.4. Synthesis of 4-vinylguaiacol methacrylate (4VGMA)

4-Vinylguaiacol methacrylate (4VGMA) was synthesized by the reaction of 4VG and methacryloyl chloride. 4VG (4.56 g, 30 mmol) and TEA (3.03 g, 30 mmol) were dissolved in diethyl ether (45 mL) and then charged into a three-necked round-bottomed flask. Methacryloyl chloride (3.6 g, 35 mmol) dissolved in diethyl ether (15 mL) was added dropwise at 0 °C under continuous stirring. Then the reaction mixture was heated to room temperature for 12 h under a nitrogen atmosphere. After reaction, the mixture was filtered to remove triethylamine hydrochloride and then washed with 5% NaOH solution and deionized water three times to remove any unreacted reagents. The organic layer was then dried over anhydrous Na₂SO₄ and distilled under reduced pressure to give the crude product. The product was purified by column chromatography on silica gel with hexane/ethyl acetate (9/1, v/v) as the eluent to give 4VGMA (yield, 75%).



Scheme 1. Synthesis of 4VGMA derived from naturally occurring ferulic acid.

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