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Adsorption of pharmaceuticals on chitosan-based magnetic composite particles with core-brush topology

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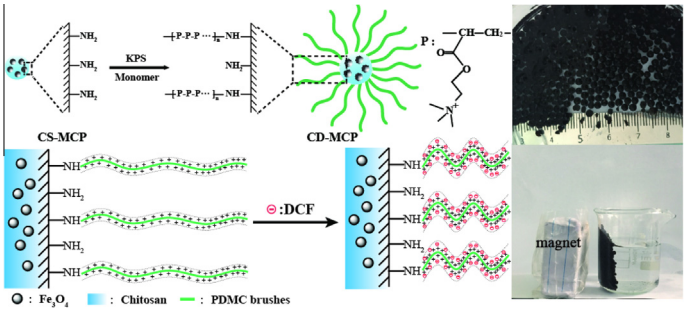
HIGHLIGHTS

- Chitosan-based magnetic composite particles with core-brush topology are synthesized.
- These particles have improved surface areas resulting from core-brush topology.
- These particles have high adsorption efficiency in the removal of diclofenac sodium.
- CD-MCP with polycationic brushes displays the highest adsorption capacities.
- Charge attraction was the intrinsic driving force promoting adsorption.

GRAPHICAL ABSTRACT



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ABSTRACT

A series of magnetic composite adsorbents with core-brush topology were prepared through grafting co-polymerization on the surface of chitosan/Fe_3O_4 composite particles (CS-MCP), and then applied for the removal of two pharmaceuticals (diclofenac sodium (DCF) and tetracycline hydrochloride) from water. Adsorption performance evaluation, including adsorption capacities from single- and binary-solute solutions at different pHs, influences of coexisting salts, desorption and reusability, demonstrated CD-MCP with polycationic brushes was a cost-effective adsorbent for DCF removal: Compared to CS-MCP, all the modified MCPs exhibited higher removal efficiencies, due to the enhanced surface areas resulting from core-brush topology; Among the modified MCPs with different surface charges, CD-MCP displayed the highest adsorption capacities, attributed to the electrostatic attraction between the positively charged brushes and the anionic contaminant's species. Adsorption mechanism was investigated from both the macroscopic (thermodynamics and kinetics) and microscopic (changes of solution pH and spectral analyses of the adsorbent after adsorption) viewpoints: Charge attraction was the intrinsic driving force; A monolayer coverage of pharmaceuticals were adsorbed onto the brushes of CD-MCP; OH^- exerted competitive adsorption effect; After adsorption, the originally extended polycationic brushes turned collapsed. The current study provided a strategy for the design of adsorbents from both topological and chemical structures.

1. Introduction

In recent years, the research focus on water contaminants has gradually shifted from conventional priority pollutants to the emerging contaminants (ECs), among which pharmaceuticals are one of the major classes [1]. According to different functions,

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pharmaceuticals can be divided into various groups, in which anti-inflammatory drugs are one kind of the most-frequently detected ones in real aquatic environment [2]. Although generally present with relatively low concentrations in water, pharmaceuticals still attracted extensive concern from both researchers and the general public, due to their properties of low biodegradability, high persistence and facile bio-accumulation [3]. Therefore, it is of significance to eliminate them from water.

To achieve such a goal, various techniques have been adopted, including adsorption, advanced oxidation, biological treatment and so on [4,5]. Among these methods, adsorption is widely applied in not only lab-scale fundamental studies but also large-scale industrial applications, because of its advantages of low cost, easy operation and no sludge formation [6]. Commonly used adsorbents are activated carbon and synthetic polymer resins, which have done many successes in the removal of organic pollutants in reported literatures [7,8]. Despite this, alternative biopolymer-based magnetic adsorbents have been gaining increasing popularity recently [9,10]: For one thing, biopolymers (such as chitosan, cellulose, starch, etc.) are renewable and environmental-friendly [11], which meet the requirements of the concept of green chemistry; For another, the magnetic carrier technology (MCT) (the most available one is to introduce Fe_3O_4 into biopolymer gel particles) can remarkably enhance water treatment efficiency [12,13]. However, when raw biopolymer-Fe_3O_4 magnetic composite particles (MCP) without appropriate modification are employed, the adsorption performance is usually unsatisfactory, because functional groups with strong adsorption capacity for targeted organic contaminants are insufficient in raw biopolymer molecules [14]. Fortunately, chemical modification on raw biopolymer-Fe_3O_4 MCP provides an approach to overcome such a drawback [15].

Etherification and esterification on hydroxyl groups, and amidation on amino groups using small-molecular reagents are intensively employed means to increase the number of functional groups on biopolymers [16,17]. Nevertheless, only one layer of desired groups at most are fixed onto the surface of MCP during each of the above processes. In order to introduce more functional groups in one modification step, grafting co-polymerization is a better choice [18]. Moreover, the modified MCP with grafted polymeric branches will have a specific "core-brush" topology where the raw MCP can be treated as the core and the post-modified polymeric branches form a brush-like outer layer. In comparison with functional groups on fully fixed biopolymer frameworks of MCP which may be affected by steric hindrance [19], the probability of functional groups on one-end-fixed brushes to contact with contaminants in water will be further heightened, as the grafted brushes are more flexible when moving in aqueous phase [20]. However, few work is now available on the elimination of pharmaceuticals using MCP with core-brush structure, to the best of authors' knowledge.

On the basis of the above ideas, the objective of this work is to synthesize several sorts of chitosan-based MCP with core-brush structure by grafting different polymeric branches onto chitosan-Fe_3O_4 MCP (CS-MCP), and to investigate their adsorption behaviors for the removal of pharmaceuticals from water. Diclofenac sodium (DCF), a typical anti-inflammatory drug [21], is selected as the targeted contaminant. Meanwhile, tetracycline (TC), a typical antibiotic which is another type of commonly available pharmaceuticals, is selected for comparison [22]. As the pharmaceuticals can exist in water in the form of anions, cations or neutral molecules at different pHs [23], three sorts of grafting branches, including polycations (poly(2-methyl acryloyloxyethyl trimethyl ammonium chloride), PDMC), polyanions (polyacrylic acid, PAA), and neutral polymer (polymethylmethacrylate, PMMA), are introduced from the viewpoint of possibly existed charge attraction between the adsorbents and the contaminants. Their application performance is systematically studied, including effects of pH and the type of functional groups on adsorption capacities, adsorption from DCF-TC mixed solution, effects of coexisting salt ions, and reusability. Finally, taking adsorption isothermal equilibrium and thermodynamics, adsorption kinetics, changes of solution pH and spectral analyses of adsorbents after adsorption into consideration, adsorption mechanism is discussed in detail.

2. Materials and methods

2.1. Materials

DCF and TC (pure drugs (Active Pharmaceutical Ingredient, API)), used as the targeted pollutants, were purchased from Aladdin Industrial Co. Their chemical structures and basic physicochemical parameters are provided in Supporting Information Fig. S1 and Table S1, respectively. Chitosan, with a deacetylation degree of 95% and a viscosity-average molecular weight of 2.0×10^5 g/mol, was purchased from Shanghai Yuanye Biological Technol. Co. Ltd. All other chemicals were purchased from Sinopharm Chemical Reagent Co. Ltd. Ultrapure water (18.2 MΩ·cm^{-1}) was used in all the experiments.

2.2. Preparation of the MCP adsorbents with core-brush structure

CS-MCP was prepared according to authors' previous work [24] as described in Supporting Information Text S1. The MCPs with core-brush topology were prepared according to the synthesis route in Fig. 1a. Detailed steps are as follows.

40 g of wet CS-MCP after filtration was dispersed in 200 mL of water under vigorous stirring and N_2 atmosphere. Then, 10 mL of 0.05 g/mL potassium persulfate (KPS) aqueous solution was added as the initiator. After the suspension was kept for 5 min for initiation, a certain amount of a monomer aqueous solution was added dropwise with a dropping speed of 2.0 mL/min. The reaction was carried out for 3 h under N_2 at 45 °C. The solid product was filtered, washed, extracted using ethanol in a Soxhlet apparatus for 72 h to removal all the impurities, and finally kept in water for further use. The modified MCP products were marked as CD-MCP, CA-MCP and CM-MCP, respectively, according to the monomer of 2-methyl acryloyloxyethyl trimethyl ammonium chloride (DMC), acrylic acid (AA), and methylmethacrylate (MMA). All MCPs have diameters of approximate 2 mm with obvious magnetic separation property, as shown in Fig. 1(b–i). To make it possible to compare the effect of the type of functional groups on adsorption, the contents of three functional groups (quaternary ammonium groups, carboxyl groups and ester groups) are controlled similar by adjusting feed ratios in the preparation processes.

2.3. Characterization

The characterization methods of the adsorbents included Fourier transform infrared (FTIR) spectra on a Bruker Tensor-27 FTIR spectrometer within a wave number range of 650–4000 cm^{-1}, UV–vis spectra on a Hitachi UH-5300 UV–vis spectrophotometer, X-ray diffraction (XRD) on a Rigaku D/max 2500VL/PC X-ray diffractometer at a voltage of 40 kV and a current of 30 mA using Cu Kα radiation, vibrating-sample magnetometer (VSM) on a Lakeshore Cryotronic LS 7307-9303 VSM at room temperature, scanning electron microscope (SEM) a JEOL JSM-5610LV SEM with an acceleration voltage of 25 kV, transmission electron microscope (TEM) on a JOEL JEM-2100F TEM at an acceleration voltage of 200 kV, static water contact angle using the sessile drop method on a Rame-Hart-100 telescopic goniometer, elemental analysis on a vario EL III elemental analyzer, zeta potential (ZP) on a Malvern