



Enhanced adsorption of pharmaceuticals onto core-brush shaped aromatic rings-functionalized chitosan magnetic composite particles: Effects of structural characteristics of both pharmaceuticals and brushes

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ARTICLE INFO

Article history:

Received 5 July 2017

Received in revised form

22 September 2017

Accepted 18 October 2017

Available online 23 October 2017

Keywords:

Core-brush shaped adsorbents

Pharmaceuticals

pH resistance

Enhanced adsorption

π -Electron-containing interaction

Electrostatic attraction

ABSTRACT

Core-brushes shaped chitosan/Fe₃O₄ composite particles (CS-MCPs) have been demonstrated applicable in the removal of pharmaceuticals due to the large amounts of functional groups on branches and heightened approachability of flexible branches to contaminants. To further enhance adsorption capacity (Q_e) and pH-resistance, novel representative core-brushes shaped aromatic rings-functionalized CS-MCPs were used for adsorption of typical pharmaceuticals (norfloxacin, tylosin and diclofenac sodium (DCF)). For norfloxacin and tylosin, modified CS-MCP with polyanions (poly(sodium p-styrenesulfonate)) branches exhibited high Q_e (165 mg/g and 134 mg/g, respectively); whereas for DCF, modified CS-MCP with polycations (poly(p-vinylbenzyl trimethylammonium chloride)) branches is favored (151 mg/g). Due to existence of phenyl groups on branches, Q_e remained high levels in a wide pH range, proving improved pH-resistance. Considerable resistance against coexisting pharmaceuticals and inorganic ions, as well as reusability, of the adsorbents, were found. Physico-chemical analyses, instrumental characterizations and theoretical calculations demonstrated that electrostatic attraction and π -electron-containing interactions contributed to adsorption: charged ends of contaminants were fixed to oppositely charged part of branches; whereas other fragments of pharmaceutical molecules bound with π -electrons of phenyls on branches. The novel core-brush shaped biopolymer-based MCPs showed potential in water treatment and guidance for designing the brush characteristics was provided according to pharmaceutical characteristics.

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1. Introduction

Large-scale use of pharmaceuticals has given rise to serious biological accumulation and frequent detection of these materials in natural aquatic system (Liu et al., 2016; Wang et al., 2016). Due to

the negative impacts of pharmaceuticals on both human health and ecosystem even at very low concentrations, effective technologies to remove such contaminants are urgently needed, among which adsorption is believed to be one of the most cost-effective methods (Alqadami et al., 2017; Dhoble et al., 2011; Shen et al., 2011).

Many sorts of adsorbents (such as activated carbon (Jawad et al., 2017b, 2017c; Pan et al., 2017), synthetic polymeric resins (Li et al., 2017a; Zhang et al., 2017), biopolymer-based materials (Donia et al., 2008; Galhoum et al., 2017; Song et al., 2016a) and so on) have been reported in the removal of organic contaminants. Among them, biopolymer-based adsorbents gain intensive attention in recent years due to their unique molecular characteristics, abundant raw

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materials, relatively low cost, and low secondary-pollution risk. Chitosan (Jawad et al., 2017a; Mubarak et al., 2017), one of the important biopolymer and an organic waste product of the shellfish industry, is widely used in engineered adsorbents due its abundant amino and hydroxyl groups. Moreover, magnetic particles (Li et al., 2017b; Song et al., 2016b) (for example, the most commonly used Fe_3O_4) can be facilely carried in biopolymer matrix, endowing fast magnetic solid-liquid separability of the obtained magnetic composite particle (MCP) adsorbents. Although biopolymer-based MCPs have achieved much success (Lu et al., 2017), further improving adsorption capacities is always a development trend of new adsorbents. To achieve these goals, one commonly applied strategy is chemical modification of biopolymers.

Since large amounts of hydroxyl and/or amino groups are often available in biopolymer molecules, etherification, esterification and amination (Zhang et al., 2016c) are traditionally used methods for introducing functional groups onto biopolymers. However, the above methods can only introduce a limited number of expected functional groups onto the surface of on biopolymer-based MCPs. By contrast, grafting copolymerization (Liu et al., 2015; Thakur and Thakur, 2014) provides a better means: On the one hand, more functional groups can be introduced by grafting copolymerization in one step; On the other hand, the obtained modified MCPs, with specific core-brush structure (Zhang et al., 2016a) where the raw MCP is the core and the post-modified polymer branches are treated as brushes, have heightened approachability of branches to contaminant molecules in water, which is believed to be favored for enhanced adsorption.

On the basis of the above idea, in authors' previous work (Zhang et al., 2016a), a series of core-brush shaped chitosan-based MCPs (CS-MCPs) with polyacrylic acid derivatives as brushes were synthesized. The obtained MCPs exhibited higher adsorption capacities toward diclofenac sodium (DCF, a typical anti-inflammatory drug) than the raw MCPs and most of reported adsorbents, due to strong electrostatic attraction and enhanced approachability between the brushes and contaminants. Despite this, two points worthy of further improvement cannot be neglected: (i) The adsorption capacity of the obtained MCPs demonstrated notable pH sensitivity, i.e. the adsorbents could only be used in a very narrow pH range, as coexisting H^+ or OH^- ions also exerted electrostatic attraction to adsorbents, generating competitive adsorption; (ii) more kinds of pharmaceuticals, besides DCF, with various structural characteristics should be considered to extend the application field of adsorbents. To overcome the first weak point, introducing aromatic-ring groups onto adsorbents for enhancing π - π interactions (Abdul et al., 2017; Zhu et al., 2016) to contaminants is expected to be useful, since most pharmaceutical molecules consist conjugated π -electron structures and π - π interaction is more difficult to be affected by coexisting inorganic ions than electrostatic attraction. As for the second point, the brush characteristics of the core-brush shaped MCPs should be adjusted according to the pharmaceutical molecules.

Consequently, the objective of the current research was to comparatively study the effect of brush characteristics on adsorption behaviors and mechanism of three typical pharmaceuticals onto a series of novel representative core-brushes shaped aromatic rings-functionalized CS-MCPs, with polystyrene derivatives as brushes. Norfloxacin (NOR, a typical quinolone), tylosin (TYL, a typical macrolide) and DCF were selected as targeted pharmaceuticals. The core-brushes shaped adsorbents had brushes of polycations (poly(*p*-vinylbenzyl trimethylammonium chloride)), neutral polymer (polystyrene), and polyanions (poly(sodium *p*-styrenesulfonate)), and thus were marked as PSC-MCP, PSN-MCP, and PSA-MCP, respectively. The adsorption behaviors of different adsorbents for both single- and binary-solute solutions at various

pHs, effect of coexisting inorganic ions, and reusability of the adsorbents were systematically investigated. Adsorption mechanism was explored *via* macroscopic physico-chemical analyses, microscopic instrumental characterizations and theoretical calculations.

2. Materials and methods

2.1. Materials

NOR, TYL and DCF (pure drugs (Active Pharmaceutical Ingredient, API); chemical structures and basic physicochemical parameters provided in Supporting Information Fig. S1 and Table S1) were purchased from Aladdin Industrial Co. Chitosan power (deacetylation degree: 95%; viscosity average molecular weight: 2.0×10^5 g/mol) was purchased from Shanghai Yuanye Biological Technol. Co. Ltd. All other reagents were purchased from Sino-pharm Chemical Reagent Co., Ltd. Ultrapure water ($18.2 \text{ M}\Omega \text{ cm}^{-1}$) was used in all the experiments.

2.2. Preparation of MCPs

The synthetic route is shown in Fig. 1 (a). 2.43 g of chitosan power, 5.64 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 2.07 g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ were fully dissolved in 150 mL of water. Then, the mixture was added dropwise into 500 mL of 3 mol/L NaOH ethanol-water (volume ratio between ethanol and water was 1:2) solution under mechanical stirring and N_2 atmosphere. The obtained precipitate was filtered and washed by water for three times. After that, the precipitate was placed into 750 mL of 0.5 g/L glutaraldehyde solution under mechanical stirring for crosslinking at 25 °C for 24 h. The solid after filtered and washed with ethanol and distilled water was CS-MCP.

10 g of the filtered wet CS-MCP was dispersed in 50 mL of water under N_2 atmosphere and mechanical stirring. Then, 2.5 mL of 0.05 g/mL potassium persulfate solution was added. 5 min later, a certain amount of a monomer solution was added dropwise. The mixture was mechanical stirred under N_2 at 45 °C for 3 h. After filtered, washed, extracted using ethanol in a Soxhlet apparatus for 72 h, the solid product with diameters of approximate 2 mm and notable magnetic separation properties was finally placed in water for further use. Basic physicochemical parameters of these adsorbents were listed in Table 1.

Detailed characterization methods of these MCPs were provided in Supporting Information Text S1.

2.3. Adsorption assay

Adsorption experiments were conducted in conical flasks in an air-bath incubator with a shaking speed of 140 rpm. Kinetics experiments showed that 12 h was long enough for reaching adsorption equilibrium, and therefore, 12 h of shaking was selected. Experimental temperature was 298 K unless specified. The relative humidity of laboratory is 50%–65%. Initial pharmaceutical concentration was 100 mg/L unless specified. Initial solution pHs were adjusted using 0.1 M HCl or NaOH solution. Since DCF is insoluble at $\text{pH} < 4$, the lowest pH value in the adsorption tests of DCF is 4. Otherwise, this value is set to be 2, as all MCPs in this study were stable (without Fe ions loss) at $\text{pH} > 2$.

The concentrations before and after adsorption were analyzed by UV-vis spectrophotometer. The determination wavelengths were 270, 276 and 290 nm for NOR, TYL and DCF, respectively. The adsorption capacity, Q_e (mg/g), was calculated as follows:

$$Q_e = (C_0 - C_e)V/m \quad (1)$$

where C_0 and C_e (mg/L) are the initial and final pharmaceutical

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