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Recognizing removal of norfloxacin by novel magnetic molecular imprinted chitosan/γ-Fe_2O_3 composites: Selective adsorption mechanisms, practical application and regeneration

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ABSTRACT

A novel magnetic molecular imprinting composites (MICs) were successfully synthesized through cross-linked chitosan and γ-Fe_2O_3 particles, and the selective removal of aqueous NOR was demonstrated. The γ-Fe_2O_3 particles embedded in MICs were still of intrinsic crystal and complexed with both amino and hydroxyl groups of chitosan. Adsorption behavior of NOR onto MICs could be described by the pseudo-second-order kinetic and the Langmuir isotherm model. Excellent selective NOR adsorption was identified with competition of sulfadiazine (SD), ofloxacin (OFL) and phenol, respectively. It could be ascribed to the memory cavities for NOR molecules, as well as the formation of triple intermolecular hydrogen bonds with suitable angle and length. Furthermore, application feasibility of MICs in NOR-spiked municipal wastewater treatment plant (WWTP) effluent was investigated. Competing with the effluent organic matters (EfOM), effective adsorption performance of NOR could be still obtained. Effect of humic and fulvic acid-like organics could be effectively reduced, while adsorption of tryptophan-like substances was slightly enhanced. In addition, it was found that Fenton-like oxidation instead of NaOH washing would be more appropriate for the multiple regenerations of MICs. The former would reserve more memory cavities and lead to oxidative decomposition of the desorbed NOR into micromolecular organics of low environmental impacts.

1. Introduction

In the past decades, the abuse of fluoroquinolone antibiotics (FQs) in human and veterinary medicine has obtaining broad attentions. Majority of consumed antibiotics were excreted into the surface water, groundwater or soils in unchanged and active forms [1]. Although the concentrations of residual antibiotics in the environment are very low, usually ppb to ppt level, it can lead to human organismslesion and increased bacterial resistance [1,2]. Therefore, removal of FQs in the aquatic environment is of significant importance. Since pharmaceutical pollutants are general biorecalcitrant, available physiochemical technologies such as adsorption [3], photodegradation [4], ozone [5] could be effective alternatives for removing FQs. Among them, adsorption technology is proved to be a harmless, simple and economical method in treating FQs wastewaters [3,6,7]. Chitin is the second most abundant natural biopolymer in the world [8]. As the most important chitin derivative, chitosan shows great potential application in aquatic environment due to its biocompatibility, non-toxicity, and adsorption properties. It has been proved to be a promising environmental friendly adsorbent material [8–11].

However, the difficulty in separating chitosan-based adsorbents from treated effluents has become great challenges to limit their practical applications. Magnetically separation technologies have been developed recently to separate powdery adsorbents from aqueous solutions. Numerous studies have been put on the combination of magnetic particles and non-magnetic matrix materials e.g. organic polymers and SiO_2 [12]. Due to the quick response to an external magnetic field and a superior sensitivity for magnetic detection, the magnetic composite materials can offer innovative prospects in various applications, including magneto filtration of catalysts, purification of proteins, and adsorption of harmful environmental pollutants [13,14].

Specific and efficient adsorptive removal of trace pollutants should be also a great challenge to many common adsorbents such

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as activated carbons and hydrotalcites [15]. It was reported that the adsorption amount of 17β-estradiol on activated carbon in river water and in secondary effluent was about one-thousandth of that in pure water [16]. Apparently, the adsorption sites of the absorbents would be mostly occupied by environmental interfering substances (e.g. natural organic matters), leading to poor removal efficiencies of target trace recalcitrant pharmaceuticals. Molecular imprinting (MI) is a novel and powerful technology for preparing advanced materials that have the ability to recognize a particular compound [15,17–20]. It has been widely used for selective separation purposes in solid-phase extraction [19], biomimetic sensors [20] and adsorption removal of pollutants [15,17]. Yu et al. [10] has also successfully synthesized a chitosan-based molecularly imprinted polymer using template perfluorooctane sulfonate (PFOS) and confirmed its high selectivity and molecular recognition for adsorption of PFOS in the presence of its analogues. But the possible selective binding mechanisms have not been clearly revealed. In the 1990's, a "gate effect" model was first proposed to illustrate the possible selective mechanism and further confirmed in recent years [21,22]. Therein, the template is analogized to the "key", corresponding with the binding site of molecular imprinted polymer which is analogized to the "lock". However, the selective recognition mechanisms for chitosan-based MI materials are still needed to be clarified.

In this study, a novel magnetic MICs was developed by cross-linked chitosan and γ-Fe_2O_3 particles. Norfloxacin (NOR), a typical FQ pollutant was chosen as the template and target pollutant to be investigated for its selective adsorption onto the MICs. The objectives were to: (a) synthesize MICs of selective ability for NOR adsorption and characterize its properties, (b) investigate the adsorption behaviors of NOR onto MICs and NICs (counterpart without molecular imprinting), (c) verify the selectivity performance of MICs in three binary solutions i.e. NOR/SD, NOR/OFL and NOR/phenol, (d) clarify the selective adsorption mechanisms of NOR onto MICs, (e) investigate the application feasibility of MICs in a NOR-spiked municipal WWTP effluent (EfOM solution), (f) compare the efficiencies of two regeneration methods, i.e. Fenton-like oxidation (H_2O_2) and chemical (NaOH) washing.

2. Materials and methods

2.1. Chemicals

Purified norfloxacin ($C_{16}H_{18}FN_3O_3$, ⩾98.0%) was purchased from Tokyo Chemical Industry Co., Ltd (Tokyo, Japan). Ofloxacin ($C_{18}H_{20}FN_3O_4$, ⩾98.0%) and sulfadiazine ($C_{10}H_{10}N_4O_2S$, ⩾98.0%) were obtained from Aladdin Industrial Corporation (Shanghai, China). Chitosan (deacetylation: 80.0–95.0%), $Fe(NO_3)_3 \cdot 9H_2O$ (⩾98.0%), glutaraldehyde (25.0%), tartaric acid (⩾99.5%), liquid paraffin and span 80 were acquired from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Other used chemicals were analytical grade. All solutions in this study were prepared in deionized water.

2.2. Synthesis procedures of MICs

γ-Fe_2O_3 particles was synthesized by a method reported by Hsiang et al. [23]. MICs based on the γ-Fe_2O_3 particles could be prepared as follows. First, 4 g chitosan and 1.5 g γ-Fe_2O_3were added into a vessel containing 300 mL of 100 mg/L template NOR solution. During the imprinting process, the solution was well-mixed overnight and its pH was kept at about7. Then the mixture were filtered and thoroughly washed with deionized water. The obtained matters were completely dissolved in 80 mL acetic acid solution (2%, v/v) with continuous sonication of 30 min. The solution was then slowly dispersed into a mixed medium of 200 mL paraffin and 4 mL Span 80, with simultaneous mechanical agitation for 60 min, followed by the addition of 2 mL glutaraldehyde (25%, v/v) for cross-link with 3 h. Afterwards, the solution pH was adjusted to 11 by 0.5 M NaOH and kept for 2 h. Prior to the magnetically collection, the obtained MICs were washed repeatedly in a sequence of petroleum ether, ethanol and deionized water. The NOR templates were thoroughly removed by using 0.5 M NaOH. Then MICs were freeze dried overnight for further use. The corresponding non-imprinted composites (NICs) were also prepared similarly but without the addition of NOR template.

2.3. Experimental procedures

2.3.1. Batch adsorption experiments

All adsorption experiments were conducted in a series of 20 mL serum bottles put in a temperature controlled shaker (HZS-H, Shanghai) at 25 °C. For kinetic experiments, suspensions with 40 mg composites (MICs or NICs) and 20 mL NOR solution (35 mg/L) were continuously shaken at 25 °C. At predetermined interval, water samples were taken out and sent for the NOR analysis after filtered by 0.45 μm membranes. For isotherm experiments, 40 mg composites (MICs or NICs) were added into a series of 20 mL solutions prepared with different initial NOR concentrations from 5 to 35 mg/L. The suspensions were shaken for 24 h at 15, 25, and 35 °C. Afterwards, NOR concentrations in the supernatant were examined. For the experiments of pH effect, specific initial pH values (3, 5, 7, 9 and 11) were adopted and the adsorption experiments were conducted similarly.

2.3.2. Selective adsorption experiments

The selective adsorption experiments for MICs and NICs were carried out in three types of solutions with binary pollutants, i.e. NOR and one of SD, OFL and phenol. Concentrations of the substances were kept at 0.11 mM. Prior to the adsorption, 40 mg composites were added into 20 mL solution with predetermined binary pollutants. The suspension were then shaken at 25 °C for 24 h. Afterwards, the supernatants were withdrawn and filtered for analysis of the specific pollutants.

To test the application feasibility of the prepared MICs, selective NOR removal was investigated in NOR-spiked EfOM solutions. According to a previous literature [24], EfOM powders were obtained by isolating the secondary effluent of a local municipal wastewater treatment plant (WWTP) using reverse osmosis. Details of the procedures can be found in the supplementary materials. During the preparation of a typical NOR-spiked EfOM solution, the maximum fluorescence emission intensities of the two components (NOR and EfOM) were maintained in the same order of magnitude. The selective removal experiments were conducted in the presence of 40 mg of MICs or NICs within 20 mL solutions. After shaking 24 h at 25 °C, the supernatants were withdrawn and filtered, followed by the EEMs and UV–Vis examinations. In addition, it is recognized that concentrations of NOR in municipal wastewater or urban storm water are commonly in the range of high ng/L to 1 mg/L. But for the purpose of demonstrating material performance efficacy and ultimate equilibrium capacity, higher concentrations (4–20 mg/L) were utilized in this study. It is recognized that the equilibrium adsorption capacity will be higher than that reported at concentrations of real environmental interest. Likewise, capacity differences between imprinted and non-imprinted material may less than that reported when considering concentrations of environmental interest.

2.3.3. Regeneration experiments

Two regeneration methods were adopted in this study, i.e. NaOH (0.5 M) washing and Fenton-like oxidation ($pH = 3$, $C_{H2O2} = 1$ mM). In either method, 40 mg composites (MICs or NICs)