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Adsorption and degradation of norfloxacin by a novel molecular imprinting magnetic Fenton-like catalyst☆



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ABSTRACT

In this study, a novel magnetically separable adsorbent, molecular imprinting magnetic γ -Fe₂O₃/crosslinked chitosan composites (MIPs), were prepared by a microemulsion process. Adsorption and Fenton-like oxidative degradation of a model pharmaceutical pollutant norfloxacin (NOR) by using MIPs were investigated. Various characterization methods were used to study the properties of MIPs, and it is suggested that the hydroxyl groups are the main adsorption sites for NOR. MIPs present better selective adsorption for NOR than its reference antibiotic sulfadiazine. The NOR adsorption data can be well fitted by Langmuir isotherm model and pseudo-second-order kinetic model. The optimum pH range for NOR adsorption is 7–10. In addition, the MIP-catalyzed Fenton-like system (MIPs/H₂O₂) exhibits remarkably faster removal rate for NOR than the case of γ -Fe₂O₃/H₂O₂. The result indicates that MIPs will be a good functional material in decontamination of pharmaceutical wastewaters since MIPs can be magnetically recycled after the treatment.

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1. Introduction

Fluoroquinolones can inhibit the proliferation of many Gram-negative and Gram-positive bacteria [1], so they have been widely used in human medicine. However, as a result of antibiotic overuse, public concern about fluoroquinolones has been greatly increasing in the past decades. The environmental concern of fluoroquinolone residuals in the aquatic environments is not only on their potential to increase antibiotic resistance, but also on their unfavorable ecotoxicity profile [2]. It has been reported that conventional biological processes (wastewater treatment plants) are incapable to remove antibiotic pollutants [3–5].

Advanced oxidation processes (AOPs), commonly with the highly reactive hydroxyl radical ([•]OH) as the main oxidative species, are efficient alternatives for degrading bio-refractory antibiotics [6]. As the second strongest oxidant after F₂ ($E = 2.8$ V), [•]OH can oxidize target compounds non-specifically at high reaction rate [7,8]. Fenton reaction is one of the popular AOPs and has attracted much attention because of its distinct advantages, such as high efficiency and stability to treat a wide range of substances and free of secondary pollution [9].

Molecular imprinting technology allows synthesis of polymers with specific recognition ability towards target pollutants, selectively

removing low-concentration contaminants in the presence of other substances that are thousands of times more abundant than the targets [10]. Previous studies have showed that many contaminants can be gathered and removed by using molecular imprinting adsorbents, which are prepared by using contaminants themselves as templates, e.g. pharmaceuticals [11,12], synthetic dyes [13] and PAHs [14].

Chitosan is a deacetylated product of chitin, which is one of the most abundant polysaccharide in the world. Raw [15], grafted [16] and cross-linked [17] chitosan used as economical adsorbents are drawing great attention and showing significant adsorption potential for removal of various contaminants. Amino (–NH₂) and hydroxyl (–OH) functional groups on chitosan chains serve as electrostatic interaction and coordination bonds in the process [18,19]. However, the difficulty in separating those powdery adsorbents from the system limits their applications. To solve this problem, chitosan powder is combined with magnetic materials. With the assistance of magnetic field, the material can be easily separated from the effluent [20]. γ -Fe₂O₃ is widely used as magnetic material due to their excellent magnetic properties, chemical stability and biocompatibility [21].

Compared to common adsorption materials, molecularly imprinted polymers (MIPs) exhibit high selectivity and affinity for low concentration template molecules [19]. To our best knowledge, combining Fenton reaction with magnetic MIP materials in pharmaceutical decontamination has been scarcely studied. Therefore, in this study, magnetic iron oxide nanoparticles coated with molecular imprinting chitosan are prepared. A typical antibiotic fluoroquinolone, norfloxacin (NOR), is chosen as the target pollutant to evaluate the characteristics of MIPs for their selective adsorption and catalyzing Fenton-like oxidation of antibiotic pollutant. The objectives are to: (a) synthesize a novel magnetic γ -Fe₂O₃/

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crosslinked chitosan composite (MIPs) through a microemulsion process, (b) investigate the adsorption capacity for NOR of MIPs, and (c) explore the oxidation of NOR in the MIP-catalyzed Fenton-like system.

2. Materials and Methods

2.1. Materials

Chitosan (Molecular mass $2.1 \times 10^5 \text{ g} \cdot \text{mol}^{-1}$, degree of deacetylation 80.0%–95.0%) was purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Norfloxacin ($\text{C}_{16}\text{H}_{18}\text{FN}_3\text{O}_3$, molecular mass $319.34 \text{ g} \cdot \text{mol}^{-1}$, purity $\geq 98.0\%$) and sulfadiazine were purchased from Tokyo Chemical Industry Co., LTD (Japan). Their chemical structures are displayed in Fig. 1. Other chemicals were of analytical grade and used without further purification. All solutions were prepared by deionized water.

2.2. Preparation of MIPs

Magnetic $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles were prepared by hydrothermal coprecipitation of Fe^{2+} and Fe^{3+} ions in the presence of ammonia solution (NH_4OH), according to literature [22]. $2.68 \text{ g FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $3.11 \text{ g FeCl}_3 \cdot 6\text{H}_2\text{O}$ were dissolved in 250 ml deionized water. The solution was thoroughly mixed at room temperature for 30 min , followed by increasing pH rapidly to $11 (\pm 0.1)$ with the addition of ammonia solution (25%). The obtained $\gamma\text{-Fe}_2\text{O}_3$ precipitates were multiplied, washed with deionized water and then collected and dried in an oven.

The preparation procedure of MIPs is described as follows. 4 g chitosan and 1.5 g $\gamma\text{-Fe}_2\text{O}_3$ are dispersed into 300 ml $100 \text{ mg} \cdot \text{L}^{-1}$ NOR solution with continuous stirring for 12 h . The mixture is washed and dissolved in 80 ml 2% (volume percentage) of acetic acid solution. The solution is dispersed slowly into a medium composed of 200 ml paraffin and 4 ml emulsifier (Span 80), with mechanical agitation for 30 min . 2 ml methanol (37.0%–40.0%, volume percentage) is dropped slowly into the above reaction system. After 1 h , 2 ml glutaraldehyde (25%, volume percentage) is added and the solution is stirred for 2 h . Then the solution pH is adjusted to $10\text{--}11$ by using $0.5 \text{ mol} \cdot \text{L}^{-1}$ NaOH and kept for 2 h . The obtained particles are collected by a magnet and then washed with petroleum ether, ethanol and distilled water three times separately. Template molecule NOR is removed by washing with $0.5 \text{ mol} \cdot \text{L}^{-1}$ NaOH. The resultant MIPs are finally dried in an oven prior to the adsorption and degradation experiments. Corresponding non-imprinted polymers (NIPs) were prepared similarly but without the addition of template.

2.3. Characterization of MIPs

X-ray diffraction (XRD) patterns of samples were obtained in ambient air at room temperature using a Bruker advanced D8 diffractometer. X-ray photoelectron spectrometry (XPS) analysis was carried out by using an Axis-Ultra DLD-600W electron spectrometer. Scanning electron microscopy (SEM) analysis was conducted by a Nova NanoSEM 450 instrument. Magnetic hysteresis loops were obtained at room temperature using a Lackshore EM4-HVA vibrating sample magnetometer.

TG–DTG (Q600 SDT) analysis was performed under a nitrogen atmosphere from $25 \text{ }^\circ\text{C}$ to $800 \text{ }^\circ\text{C}$ with a heating rate of $10 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$. Fourier transform infrared (FT-IR) spectra were measured at room temperature on a Bruker Vertex 70 Fourier Transform instrument.

2.4. Batch adsorption experiments

Batch NOR adsorption experiments were carried out using a HZS-H thermostated shaker (Harbin Donglian Electronic Technology Development Co., LTD) at $110 \text{ r} \cdot \text{min}^{-1}$. Adsorption volume of solution was 20 ml and 30 mg MIPs were used in each adsorption. The initial solution pH was about 5 and specific temperature was kept in the reaction for 24 h . Then the suspension was filtered through $0.45 \text{ }\mu\text{m}$ membranes before the analysis. NOR concentration was determined by using a high performance liquid chromatography (LC-15C, Shimadzu), equipped with a C18 column ($4.6 \text{ nm} \times 250 \text{ nm}$) and a UV detector. The mobile phase was a mixture of phosphoric acid (87% , $0.03 \text{ mol} \cdot \text{L}^{-1}$, pH 3 ± 0.1 , adjusted by triethylamine) and acetonitrile (13%), with a flow rate of $0.8 \text{ ml} \cdot \text{min}^{-1}$. The detector temperature was set at $35 \text{ }^\circ\text{C}$ and the wavelength was set at 278 nm .

The amount of adsorption q_t ($\text{mg} \cdot \text{g}^{-1}$) is calculated by

$$q_t = \frac{(c_0 - c)V}{W} \quad (1)$$

where c_0 and c are the initial and instantaneous NOR concentrations ($\text{mg} \cdot \text{L}^{-1}$), respectively, W is the mass of adsorbent (g), and V is the volume of solution (L).

2.5. NOR degradation experiments

In a typical experiment for MIP-catalyzed NOR degradation, the initial concentrations of NOR, MIPs and H_2O_2 were $5 \text{ mg} \cdot \text{L}^{-1}$, $0.6 \text{ g} \cdot \text{L}^{-1}$ and $0.03 \text{ mmol} \cdot \text{L}^{-1}$, respectively. Initial pH was adjusted to 3 by using $0.25 \text{ mol} \cdot \text{L}^{-1}$ HCl or NaOH. After mixing at least for 30 min to achieve adsorption equilibrium, the reaction commenced with the addition of H_2O_2 . Samples were taken out at specific time intervals and $50 \text{ }\mu\text{l}$ methanol was used to quench the reaction. All samples were filtered through $0.45 \text{ }\mu\text{m}$ membranes before the analysis.

3. Results and Discussion

3.1. Characterizations of MIPs

Fig. 2 shows six XRD diffraction peaks of $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles at 2θ of 30.26° , 35.64° , 43.34° , 53.84° , 57.36° and 62.96° , corresponding to (220), (311), (400), (422), (511) and (440) lattice planes of $\gamma\text{-Fe}_2\text{O}_3$ [23]. Typical diffraction peaks of $\gamma\text{-Fe}_2\text{O}_3$ remain after embedding into MIPs. It indicates that $\gamma\text{-Fe}_2\text{O}_3$ in the MIPs keeps its intrinsic phase of maghemite.

It should be noted that the XRD patterns of Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ are analogous [24]. High resolution XPS spectrum of Fe 2p from MIPs is presented in Fig. 3. A difference in the binding energy (BE) of 3.5 eV is clearly observed when comparing the satellite of FeO (BE = 715.5 eV , purely

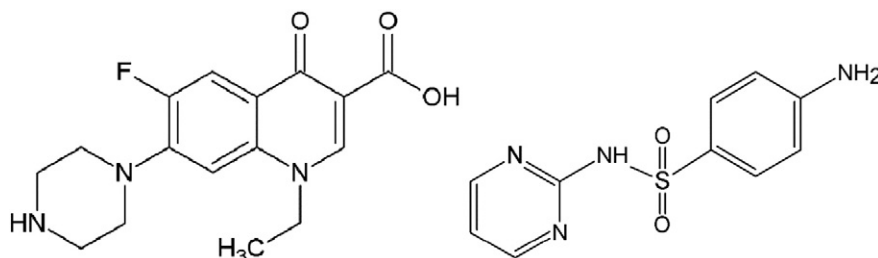


Fig. 1. Chemical structures of norfloxacin (left) and sulfadiazine (right).

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