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Insights into high-efficiency molecularly imprinted nanocomposite membranes by channel modification for selective enrichment and separation of norfloxacin

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ABSTRACT

A facile, yet efficient method was proposed here to prepare the novel molecularly imprinted nanocomposite membranes (MICMs) with high adsorption capacity and rapid selective separation aiming at targeting norfloxacin. The MICMs were prepared by vacuum filtering directly pre-synthesized norfloxacin-imprinted nanocomposites to the regenerated cellulose membranes, which utilized adequately the dual-function effect of dopamine as crosslinking agent and functional monomer. Moreover, the best adsorption capacity and separation factor of MICMs toward target can reach up to 25.35 mg/g and 4.43, respectively, which were far superior to that of non-imprinted nanocomposite membranes (NICMs) (6.38 mg/g and 1.0, respectively). Meanwhile, the perm-selectivity (the permeability factor β values were also more than 15.2). And this work provided an exemplary guidance for the treatment of fluoroquinolones antibiotics pollutants in water environment.

1. Introduction

Over the past decades, antibiotic pollutants in water have drawn considerable attention owing to the untold damage to human health and environment. Norfloxacin, as an outstanding representative of the third generation of synthetic fluoroquinolones antibiotics, has been applied diffusely in clinical medicine due to its broad spectrum antimicrobial, lower toxicities and less allergic reaction. As a result, the extensive use of norfloxacin brought about residues in livestock products and subsequently posed adverse health risks to humans. In order to resolve environmental pollution problems, it is urgent to adopt a rapid, specific and sensitive method for detecting and separating norfloxacin in water environment [1–2].

The treatment technologies of antibiotics pollutants in water environment were mainly photocatalysis [3], electrolysis [4], oxidation [5], bio-degradation [6] and other methods [7]. However, many of them usually displayed some disadvantages, such as high cost, tedious procedures, weaker sensitivity and so on. It is very necessary to develop the new technology with high efficiency, fast separation, and good regenerability for enriching and separating norfloxacin. Membrane separation technology (MST) has been widely used in production process due to its advantages of high efficiency, energy conservation, and fast operation, but the traditional membrane separation materials are still incapable of realizing the high-efficient selective separation and lacking of specific recognition ability [8–11].

As we have already known, molecularly imprinted materials can effectively selectively recognize the targeting molecules [12–14]. For instance, the molecularly imprinted polymers (MIPs) exhibited short time preparation, high selectivity, and the chemical and mechanical stability, which were regard as the tempting alternative for the selective separation of target molecules [15–18]. However, the single MIPs have a few deficiencies including reclamation difficulty in water and slow leaching of the template from the polymer matrix. Therefore, if MIPs are introduced into inorganic–organic hybrid membranes to construct the novel molecularly imprinted nanocomposite membranes (MICMs), it will overcome the shortcomings of single MIPs, and maintain the double superiorities of the continuously separating ability of inorganic–organic hybrid membranes and the specific recognition ability of MIPs [11,19–21].

Recently, it was reported that the organic materials were used as a matrix with adding inorganic materials such as iron

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oxide, TiO_2 nanospheres, and graphene to improve the magnetic conductivity, the hydrophilic, specific surface area of the functional organic membranes, which greatly broaden the application fields of organic membranes [22–25]. Therefore, TiO_2 nanospheres and porous regenerated cellulose membranes (RCMs) were considered to design and fabricate inorganic–organic hybrid membranes, which were expected to obviously enhance adsorption ability of MICMs toward target molecules [26–30]. Meanwhile, the polydopamine-based imprinted by norfloxacin serving as MIPs was decorated on the surface of TiO_2 nanospheres so as to improve the selectivity and recognition ability of MICMs for norfloxacin molecules. Polydopamine can also be used as a functional monomer and cross-linker, which might create well-distributed and stable molecularly imprinted cavities during the imprinting process [31–35].

To this end, TiO_2 nanospheres coated with polydopamine imprinted by norfloxacin were first prepared by making the best of dual-function effect of dopamine as both cross-linker and functional monomer. The MICMs were then synthesized by modification of the norfloxacin-imprinted nanocomposites in the channel of the porous RCMs via vacuum filtration. Meanwhile, the adsorption and separation mechanism were discussed in detail. Consequently, these obtained MICMs exhibited the superior adsorption capacity, separation efficiency and selective recognition ability for norfloxacin molecules, which were undoubtedly beneficial to efficient and long-term water treatment.

2. Materials and methods

2.1. Materials

Commercial regenerated cellulose membranes (RCMs) (0.45 μm average pore size, a diameter of 25 mm) were purchased from Sartorius. Tris(hydroxymethyl) aminomethane (Tris–HCl, 99%,), norfloxacin (99%), dopamine (98%), ammonia solution (28%–30%), titanium nitride (TiN, 99.9%), hydrogen peroxide (H_2O_2, 30%), were purchased from Aladdin Reagent (Shanghai, China) and used as received. All chemicals used in the synthetic process were at least analytical grade. Deionized water was used for the whole experimentation processes.

2.2. Preparation of TiO_2 nanospheres

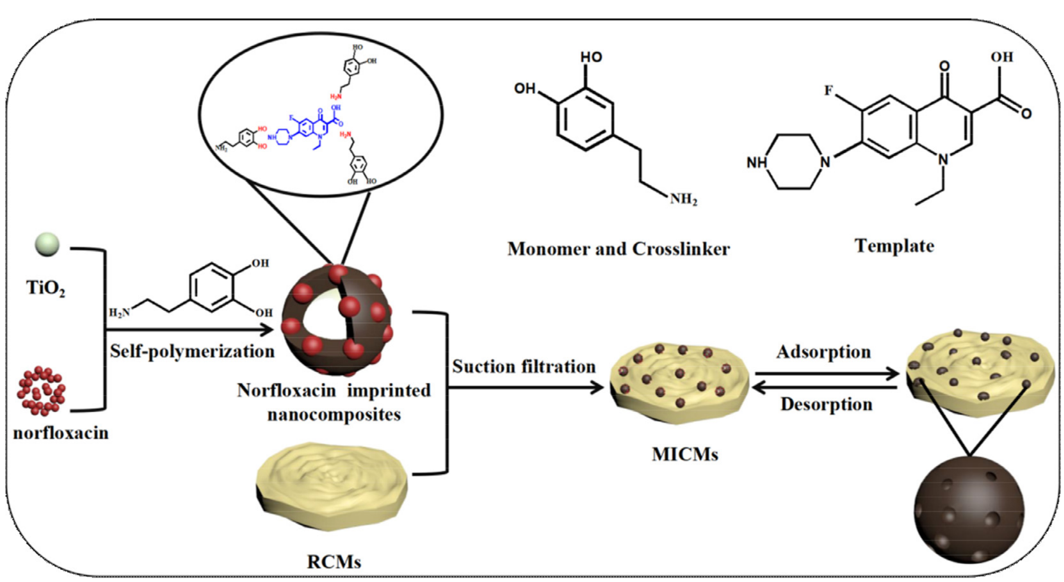
The preparation of TiO_2 nanospheres was produced by the hydrolysis method [36]. In a typically synthesis, commercial TiN powders (0.25 g) were dispersed in distilled water (60 mL). Then $NH_3 \cdot H_2O$ (8 mL) and hydrogen peroxide solution (8 mL) were poured into the above mixture with magnetic stirring for 1 h. When the TiN nanopowders were fully dissolved, transparent yellow solution was obtained. Afterward, the above obtained transparent yellow solution (40 mL) and ethanol (100 mL) were mixed and reacted in a round-bottomed flask for 12 h under reflux condition at 80 °C. At last, the achieved white precipitates were collected by centrifugation at 3552 g and washed with deionized water and anhydrous ethanol at least 3 times. Then the samples were dried under vacuum at 40 °C to obtain amorphous TiO_2 nanospheres.

2.3. Fabrication of norfloxacin-imprinted nanocomposites

Typically, in a norfloxacin-imprinted nanocomposites synthesis, the obtained TiO_2 nanospheres (0.2 g) were dispersed in 50 mL Tris–HCl (pH = 8.5) aqueous solution, and followed by ultrasonic for 5 min, then norfloxacin (20 mg) was added. The achieved mixture was stirred constantly for 1 h. Afterward, dopamine (100) mg was added to the above obtained solution to undertake the self-assembling process. The reaction system continued to be vigorously stirred at room temperature for 3 h, which resulted in the construction of norfloxacin imprinted polydopamine layer on the surface of TiO_2. The suspension was collected by centrifugation at 3552 g, washed with deionized water three times to ensure that surplus polydopamine particles and all unreacted dopamine were discarded. At last, the norfloxacin-imprinted nanocomposites were dried at 35 °C in a vacuum oven for further use. The schematic diagram of the experiment was given in Scheme 1. Non-imprinted nanocomposites were prepared in parallel, following the same experimental procedure as for imprinted particles, getting rid of the presence of the template molecule.

2.4. Fabrication of norfloxacin molecularly imprinted nanocomposite membranes

The norfloxacin molecularly imprinted nanocomposite membranes were fabricated by vacuum-assisted filtration process and



Scheme 1. Schematic illustration of constructing MICMs for selective recognition and separation of norfloxacin.