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Bioinspired synthesis of multi-walled carbon nanotubes based enoxacin-imprinted nanocomposite membranes with excellent antifouling and selective separation properties

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ABSTRACT

Inspired from the bioadhesive surface modified technology of polydopamine (pDA) and the radical polymerization method of amphiphilic grafted copolymer (ACMO@PVDF), the bioinspired porous enoxacin-imprinted nanocomposite membranes (EINCMs) were synthesized by developing the multi-walled carbon nanotubes (MCNTs)-based nanocomposite structure. The EINCMs were prepared through immersion phase inversion method and sol–gel blot imprinted method for selective purification and separation of enoxacin. Testing results indicated that the surface physicochemical properties such as higher micropores, significantly improved hydrophilicity and enhanced antifouling ability, could be successfully obtained. Results showed that the specific adsorption capacity was markedly enhanced from 3.72 mg g^{-1}, which was for the non-imprinted nanocomposite membrane (NINCMs), to 31.56 mg g^{-1} for the imprinted one. In addition, the imprinting factor β was proved as high as 4.44 and the perm-selectivity of membrane was also measured in the form of separation factor γ, which was calculated as 6.03. Furthermore, the rebinding capacities reached about over 90. 36% of the initial adsorption capacity after 5 cycles of adsorption/desorption. The rebinding capacity just only declined to 82.89% after another 5 cycles rebinding circulations. The highly stable stability and homogeneous growth of enoxacin-imprinted layers on pDA@MCNTs surfaces might probably be the reason for desirable performance and stability. The as-obtained results could be concluded that this synthesis method would provide wastewater treatments containing enoxacin with a highly stable and selective separation performance.

1. Introduction

Indiscrimination abuse of antibiotics, such as enoxacin, has become a global problem because of the unpredictable threaten to public health and natural environment through human food chain. Enoxacin residues had already been found in natural waters [1,2]. Membrane based technology for wastewater treatment is one of the effective approaches, which has drawn wide attentions to develop more efficient and sustainable antibiotics-contaminated waste water treatment. As membrane based technology has been applied widely in this field, hindrances have been revealed gradually. Enoxacin or other organic–inorganic foulants will generate severely surface fouling, which will limit the long term performance such as permeability, selectivity and stability of membranes. Therefore, it is necessary to develop an effective fouling mitigation strategy with wide spread applications, low operation cost, and high selectivity for the separation of enoxacin remains from waste water [3,4].

Molecularly imprinted polymers (MIPs) with high selectivity had been synthesized on membranes to prepare molecular imprinted membranes, with specific recognition sites [5,6]. Mixed matrix membranes (MMMs) have attracted a great deal of attentions owing to the incorporation of nanomaterials into membranes. Because of the strong hydrophilicity, abundant pore channels, large surface area, and effective anti-fouling property of nanomaterials, MMMs have increasingly incorporated in several waste water treatment processes [7,8]. However, implementation of these technologies still face some limitations, some membranes are hydrophobic, low mechanical or poor anti-fouling [9–11], which will be not conducive to the separation of template molecules and membrane reusability. Therefore, this may still be a challenge to improve the above properties [12,13].

Multi-walled carbon nanotubes (MCNTs) are allotropes of carbon with cylindrical nanostructure, which are famous for unique

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large surface area, chemical inertness, a large amount of oxygen-containing functional groups and excellent mechanical and thermal properties [14–16]. With these numerous outstanding properties, MCNTs have received extensive applications in various fields. Therefore, MCNTs-based membranes could combine with the advantages both of membranes and MCNTs, which exploit features such as well-ordered porous structures, fast water transport, durability, anti-fouling performance, self-cleaning functionality, easy functionalization, and low energy consumption [17–20]. However, the MCNTs presented hydrophobic property and their stability were rarely studied in references, so the hydrophilicity, stability and reusability of MCNTs-based membranes still need to be studied.

Inspired by the bioadhesive surface modified technology, the combination of MCNTs and membrane imprinting technology would show significant potentials on improvement of selective separation performance. Messersmith and his co-workers found that the dopamine (DPA) presented a great surface adherent material for hydrophilic coatings of membrane surfaces, which improved the hydrophilic and stability of membranes. In addition, the polydopamine (pDA) could be regarded as both functional monomer and cross linker, which would create well distribution and stable imprinted cavities during the imprinting process [21–25]. Through the inspiration of bioadhesive property of mussel protein, pDA layer could be coated on the surface of materials, which would be regarded as interfacial adhesives [26]. The homogeneously dispersed pDA layers synthesized by self-polymerization would wrap on the surface of the membranes, which formed a secondary reaction platform for the further modification [27]. This bioadhesive methodology not only largely improved the anti-fouling performance and hydrophilic property, but also uniformly formed the composite nano-layers to improve chemical stability.

In the previous work, the anti-fouling behaviors have been enhanced with increased hydrophilicity, porosity, enhanced permeability, and changed pore structure [28,29]. Acryloylmorpholine (ACMO) is similar to a biocompatible poly (ethylene glycol), which has advanced hydrophilic properties, low toxicity, and biocompatible [30]. ACMO also showed resistance of protein adsorption, good anti-fouling performance [31]. The ACMO monomers have identified unique features such as hydrophilic nature, electrical neutrality, hydrogen-bond acceptors, and donors [32,33]. With these outstanding properties of ACMO, the preparation of porous membranes could be an effective strategy to improve the hydrophilicity. The hydrophilic chain of the copolymer also could facilitate the formation of large membrane pores during the membrane preparation process [6].

Herein, a facile bioinspired method was proposed to prepare porous enoxacin-imprinted nanocomposite membranes (EINCMs) for the selective separation enoxacin from waste water. Enoxacin was used as the template molecules, and a sol–gel blot imprinted method was proposed to obtain the dopamine-modified carbon nanotubes (pDA@MCNTs). After polyvinylidene fluoride (PVDF) powders being treated by the potassium hydroxide (KOH), the PVDF main chains were then grafted with ACMO monomers to form the graft copolymer (ACMO@PVDF). Whereafter, enoxacin-imprinted pDA@MCNTs reacted with different dosages of ACMO@PVDF copolymers to form the final MMMs. The schematic illustration for the formation process was shown in Scheme 1. In addition, the morphologies of ENICMs presented well-ordered porous structures, rough surface structures, which generated excellent hydrophilic and antifouling properties. And the as-prepared EINCMs also possessed great rebinding abilities and perm-selectivity for enoxacin. As been proved by experimental results, this novel composite membrane effectively enhanced the performance of hydrophilicity, anti-fouling performance, binding capacity, and permselectivity.

2. Experimental section

2.1. Materials

Poly (vinylidene fluoride) (PVDF, molecular weight of 110,000) powder and polyvinylpyrrolidone (PVP, molecular weight of 58,000, K29-32) were obtained from Sinopharm Chemical Reagent (Shanghai, China). Multi-walled carbon nanotube (MCNTs, 95%, Aladdin), Tris (hydroxymethyl) aminomethane (Tris–HCl, 99%, Aladdin), tetraethyl orthosilicate (TEOS, 98%, Aladdin), dopamine (98%, Aladdin), 1-Methyl-2-pyrrolidinone (NMP, 99%, Aladdin), Acryloylmorpholine (ACMO, 98%, Aladdin), azo-bis-isobutryronitrile (AIBN, 99%, Aladdin), N, N-Dimethylfomamide (DMF, Aladdin), Enoxacin (98%, MACKLIN), (3-Aminopropyl) triethoxysilane (APTES, 99%, Aladdin), Bovine serum albumin (BSA, 96%, Aladdin) were used as received. All chemicals used in the synthetic process were at least analytical grade.

2.2. Characterization

The micromorphology of different membranes was observed by field emission scanning electron microscopy (SEM, S-4800, Japan). Transmission electron microscopy (TEM) was performed on an F20 S-TWIN electron microscope (Tecnai G2, FEI Co.) with a 200 kV accelerating voltage. The membrane surface roughness was investigated by AFM (Solver P47 Atomic Force Microscopy, Russia) using tapping mode in the range of scanning area of 10 μm × 10 μm at room temperature in air. Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra for functional groups were collected on an FT-IR Nicolet560 (Nicol, U.S.). To test the surface chemical composition of membranes, X-ray photoelectron spectroscopy (XPS) was recorded using a monochromatized Al Kα-X-ray source with an ESCALAB 250 spectrometer. Sonication was performed using a Branson digital 450 W sonifier. In order to measurement the hydrophilic of membranes were obtained by contact angle measurement (CA, KSV CM200, Finland). The UV–visible (UV-3600, Japan) spectrophotometer was used for the determination the amount of template molecules and structural analogue and BSA adsorption amount.

2.3. Preparation of pDA@MCNTs

A hydrophilic pDA coating was synthesized by self-polymerization of dopamine at room temperature. The dopamine solution (2.0 mg mL^{-1}) was prepared by dissolving dopamine into Tris–HCl aqueous solution (pH = 8.5). After that, the MCNTs were dispersed uniformly into the above prepared dopamine solution, and the mixture was stirred at room temperature for 6 h. After reaction process, the pDA modified MCNTs (pDA@MCNTs) were rinsed into DI water to remove any unreacted residues before dried under the vacuum at 40 °C.

2.4. Synthesis of enoxacin-imprinted pDA@MCNTs through sol–gel blot modification method

According to the sol–gel blot modification method, we used enoxacin as the template compound to synthesize enoxacin-imprinted pDA@MCNTs. Briefly, 0.3 mmol of enoxacin, 0.2 mL of APTES and ethanol mixed solution was stirred at room temperature for 30 min, the 0.8 mL of TEOS, 0.5 mL of ammonia spirit and 0.5 g of pDA@MCNTs were put into the mixed solution stirred for 12 h. Finally, the enoxacin-imprinted pDA@MCNTs was removed from the reaction system and washed away the unreacted and redundant molecules with ethanol before dried to constant weight.