Journal of Membrane Science 490 (2015) 120–128

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

A self-protected self-cleaning ultrafiltration membrane by using polydopamine as a free-radical scavenger

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ARTICLE INFO

Article history:
Received 5 February 2015
Received in revised form
23 April 2015
Accepted 25 April 2015
Available online 5 May 2015

Keywords:
TiO_2
Polydopamine
Self-cleaning membrane
Polysulfone
Free-radical scavenger

ABSTRACT

Herein, a free-radical scavenger platform was first utilized to prepare self-cleaning ultrafiltration membranes. First, a polydopamine (PDA) layer was attached onto the surface of a polysulfone (PSf) supporting membrane via dopamine's self-polymerization. Then, amine-functionalized TiO_2 (TiO_2-NH_2) nanoparticles were chemically bonded with the PDA layer via amine-catechol adduct formation. Consequently, a self-protected TiO_2/PDA/PSf composite ultrafiltration membrane with self-cleaning property was obtained. The photocatalytic TiO_2 was decorated on the TiO_2/PDA/PSf surface. Compared with the conventional TiO_2+PSf membrane prepared by a blending method, the TiO_2/PDA/PSf membrane enlarged the contact area between the photocatalytic nanoparticles and contaminants and hence had improved efficiency of photocatalytic degradation. In addition, the interlayer PDA, acting as a free-radical scavenger, protected the PSf supporting membrane from being attacked by free radicals during UV irradiation. Therefore, such a sandwich-like structure bestowed both good self-cleaning property and performance stability upon the TiO_2/PDA/PSf ultrafiltration membrane. We found that the TiO_2/PDA/PSf ultrafiltration membrane still possessed excellent permeability and separation ability even after a nine-day UV irradiation, while the performance of the TiO_2+PSf one began to deteriorate after only one-day UV irradiation. Therefore, we believe that the free-radical scavenger platform is a promising approach to prepare self-cleaning membranes with good performance stability.

1. Introduction

With the fast development of modern society, there is an increasing requirement for clean and abundant water resources. Consequently, the enthusiasm for research on membrane separation techniques is rapidly growing in the recent years. Compared with conventional water-purification technologies, membrane separation techniques have unique and fascinating advantages, such as energy saving, high efficiency and removal capacity, environmental and commercial benefit [1]. However, membrane fouling manifested as a flux decline and/or an increase in transmembrane pressure in the pressure-driven membrane process is still a main barrier to the greater use of membrane separation techniques [2,3]. Enormous efforts are underway on fouling mitigation and membrane cleaning involving pre-treatment of the feed solution, optimization of module arrangement and process conditions, and periodic cleaning. However, these methods increase manufacturing cost and complexity of the operation process. Surface modification of membrane is another effective way to diminish membrane fouling, especially, via increasing the hydrophilicity of membrane. Recently, considerable efforts go to the development of physical and/or chemical modifications to bestow a self-cleaning property upon the composite membranes [2–5].

One of the commonly used methods is to introduce photocatalytic nanoparticles, like TiO_2, into the membrane matrix to degrade contaminants during water treatment process [4,6–10]. By simply adding TiO_2 particles into the casting solution, You obtained a TiO_2-incorporated poly(vinylidene fluorite) (PVDF) membrane [6]. The improved membrane hydrophilicity bestowed a good antibacterial property upon the composite membrane. Later, You and his co-workers plasma-grafted poly(acrylic acid) (PAA) onto the surface of PVDF membrane to locate abundant bonding sites for TiO_2 [9]. By dipping the PAA-modified PVDF membrane into an aqueous TiO_2 dispersion, TiO_2 mainly existed on the membrane surface, tremendously enhancing the membrane hydrophilicity and the protein anti-fouling property [9]. Zhang revealed that pre-treating PVDF membrane with cetyltrimethyl ammonium bromide also benefited the loading of TiO_2 on the surface and inner pores of the membrane. The as-prepared TiO_2+PVDF composite membrane had decreased protein adsorption capacity [11]. Self-assembling TiO_2 particles onto the membrane surface merely with the aid of coordinate bonds with the OH groups on the membrane surface is another effective way to prepare

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http://dx.doi.org/10.1016/j.memsci.2015.04.056
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TiO_2-modified self-cleaning membranes [3]. Besides, thermally induced phase separation method was also employed to incorporate TiO_2 particles into PVDF matrix [12]. Other types of polymers, such as polysulfone (PSf) and chitosan, were also used as the materials of membrane matrix, and other kinds of TiO_2, like TiO_2 nanotubes, were also employed when preparing self-cleaning membranes [13].

To be specific, when incident photons are absorbed by TiO_2, excited electrons in the conduction band and holes in the valence band will first emerge, followed by the formation of hydroxyl and oxygen radicals [1]. The self-cleaning property comes from the reactions between the free radicals and contaminants [2]. However, the practicability of this kind of self-cleaning membranes greatly depends on their service life under long-term ultraviolet (UV) irradiation as well. There is an often-ignored fact in the existing literatures that the polymer chains of membrane matrix would also be broken down by free radicals during the self-cleaning process. Under this circumstance, the composite membrane would be dramatically damaged, resulting in a significant decrease in its separation capability and thermal–mechanical stability [2]. In our opinion, it is unreasonable to merely derive the self-cleaning property of a membrane at the expense of its performance stability.

Herein, a free-radical-scavenger platform was first utilized in the preparation of self-cleaning ultrafiltration membranes. Polydopamine (PDA), a bio-inspired polymer, can facilely self-polymerize to form a controlled thin and stable layer on virtually all types of materials' surface [14]. A novel TiO_2/PDA/polysulfone (TiO_2/PDA/PSf) composite ultrafiltration membrane was prepared in this study by first attaching PDA onto the surface of a PSf supporting membrane and then chemically bonding amine-functionalized TiO_2 (TiO_2-NH_2) with the PDA layer through the amine-catechol adduct formation [14–16]. Such an intermediate PDA layer with similar chemical structure as that of eumelanin [17–20], serving as a free-radical scavenger, protected the PSf supporting membrane against UV irradiation [17]. Meanwhile, under this circumstance, TiO_2 mainly existed on the membrane surface, enlarging its contact area with contaminants to optimize its efficiency of photocatalytic degradation. Thereby, an ultrafiltration membrane with both good self-cleaning property and excellent performance stability was successfully obtained here. Besides, the influences of TiO_2 and PDA contents on membrane performance were also discussed in this study.

2. Experimental

2.1. Materials

TiO_2 nanoparticle (diameter: 21 nm) was obtained from Degussa. 3-Aminopropyltriethoxysilane (APS) and dopamine were provided by Sigma Aldrich. Tris(hydroxymethyl)aminomethane (Tris), ninhydrin, KH_2PO_4 and K_2HPO_4 were purchased from Aladdin. Dimethyl sulfoxide (D-DMSO) was purchased from Cambridge Isotope Laboratories Inc. (D-99.9%). Unless otherwise stated, all the other reagents were purchased from commercial suppliers and used as received without further purification.

2.2. Preparation of TiO_2-NH_2

760 mg TiO_2 was dispersed in 150 mL absolute ethanol, followed by being ultrasonicated for 10 h to obtain a white and homogeneous mixture. After that, 1 g APS dissolved in 50 mL absolute ethanol was added into this TiO_2 dispersion drop by drop (1 drop/s), and the whole system was vigorously stirred at 80 °C for another 6 h [1]. Subsequently, the product was obtained via centrifugation and then washed with absolute ethanol for several times before being vacuum-dried.

2.3. Preparation of PDA/PSf and TiO_2/PDA/PSf composite ultrafiltration membranes

PSf supporting membranes were prepared by a phase intrusion method. First, 1 g PSf powder was mixed with 6.7 mL N-methyl pyrrolidone (NMP) and vigorously stirred under 90 °C until PSf were completely dissolved. After removing air bubbles, the PSf/NMP solution was casted onto a clean glass plate. Subsequently, the system was horizontally immersed into deionized water under 30 °C for at least 24 h to completely remove NMP and hence solidify the membrane structure. To prepare PDA/PSf and TiO_2/PDA/PSf composite membranes, PSf supporting membranes were first immersed into a 0.2 wt% dopamine buffer solution (Tris–HCl, pH=8.8) for 5 or 15 min [2,3]. After that, the membranes were carefully rinsed with water for several times and then immersed into IPA for 30 min to remove any unbound and/or loosely-bound PDA. Then, the membranes were immersed into water for at least 30 min to exchange IPA out of the membrane [2,3]. Such membranes were named as "PDA-5/PSf" or "PDA-15/PSf" composite membranes, respectively. Subsequently, the obtained PDA-5/PSf and PDA-15/PSf membranes were put into 0.05 wt% TiO_2-NH_2 dispersion (Tris–HCl buffer solution, pH=8.8) under 35 °C for 120 min [3,4]. At last, the TiO_2/PDA-5/PSf and TiO_2/PDA-15/PSf composite membranes were rinsed with water for several times and then stored in water. In the following sections, unless otherwise stated, "TiO_2/PDA-5/PSf" and "TiO_2/PDA-15/PSf" refer to the membranes with ~0.4 wt% and ~1.5 wt% TiO_2 loading, respectively (please see Section 3.2).

2.4. Preparation of TiO_2+PSf composite ultrafiltration membrane

TiO_2+PSf composite ultrafiltration membrane was prepared by a blending and solution casting approach. First, a PSf/NMP solution was obtained via the same procedure as described above. After that, 0.5 wt% TiO_2 nanoparticles were added into the PSf/NMP solution and then sonicated for 12 h to obtain a homogeneous dispersion. The TiO_2 content was determined according to the amount of PSf. The Then, the TiO_2+PSf membrane was prepared by the same phase intrusion method as that in the preparation of PSf supporting membranes [21].

2.5. Characterizations

The Fourier transform infrared spectroscopy (FT-IR) spectra were measured on a Nicolet Nexus 470 spectrometer with a resolution of 4 cm^{-1} and 64 scans. The thermogravimetric analysis (TGA) measurements were performed under air atmosphere with a Perkin Elmer Thermal Analyzer at a heating rate of 20 °C min^{-1}. The Raman spectra were collected on a Renishaw inVia Reflex micro-Raman spectrometer with 785 nm laser excitation. The transmission electron microscopy (TEM) images were recorded on a JEOL JEM2100 TEM instrument operated under an acceleration voltage of 200 keV. The surface and cross-sectional morphologies of membranes were observed with a scanning electron microscopy (SEM, XL 30 ESEM-TMP PHILIP). All the SEM samples were coated with gold before the SEM observation. The atomic force microscopy (AFM) measurements were conducted by using a Multimode Nano 4 in a tapping mode.

The flux of pure water and 0.5 g/L BSA solution (PBS buffer solution, pH=7.4) of the PSf, PDA-5/PSf, PDA-15/PSf, TiO_2/PDA-5/PSf, TiO_2/PDA-15/PSf and TiO_2+PSf membranes were measured in a cross-flow membrane module at an operation pressure of 0.2 MPa. The flux was calculated according to the equation $F = V/(At)$, where V means the total volume of the permeated solution, A is the membrane area and t represents the operation time. The rejection to BSA was calculated by the following equation: $R = 1-(C_p/C_f)$, where C_f and C_p are concentrations of the feed and permeation solutions, respectively. Both C_p and C_f were determined by a Shimadz