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A thin-film nanocomposite nanofiltration membrane prepared on a support with in situ embedded zeolite nanoparticles

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ABSTRACT

A novel approach to fabricating thin-film nanocomposite (TFN) nanofiltration membranes was reported in this study. It involved the preparation of a polysulfone support in situ embedded with zeolite nanoparticles followed by interfacial polymerization to form the polyamide layer. Compared with the TFN membranes prepared by the conventional method (TFN-C), the new TFN membrane (TFN-I) had higher loading and more uniform dispersion of nanoparticles in the polyamide layer. The nanoparticles incorporation resulted in an increase of surface roughness but no change of surface hydrophilicity. The TFN-I membrane doubled the water permeability compared with the control membrane (TFC). The TFN-I membrane had a similar rejection of $MgSO_4$ (>93% at 150 psi) and negatively charged pharmaceuticals (PhACs) with TFC, but a reduced rejection of NaCl and a slightly lower rejection of neutral and positively charged PhACs of small molecular weights. The TFN-I membrane performed much better than the TFN-C membrane. The demonstrated performance of TFN-I could be due to the internal pores of zeolite nanoparticles, the increased membrane surface roughness and, though undesirable, the microporous defects between the nanoparticles and the polyamide matrix. The newly developed approach is highly promising for the fabrication of TFN nanofiltration and reverse osmosis membranes of improved performance by incorporating various nanoparticles.

1. Introduction

Nanofiltration (NF) is currently gaining its popularity and acceptance worldwide in advanced treatment of impaired surface water and groundwater to produce drinking water of higher qualities [1–5]. Compared with reverse osmosis (RO) membranes, most NF membranes are designed to have a higher molecular-weight-cut-off (MWCO) (usually within 200–2000 Da) and resultantly a higher water permeability. Accordingly, NF membranes are generally used to “selectively” remove water impurities at relatively low applied pressures, which include multivalent ions (e.g. calcium, magnesium and sulfate ions) and natural organic matter which can otherwise cause a lot of aesthetic and toxicological problems [6]. In addition, NF has been increasingly reported in recent studies for its applications to remove arsenic, fluoride and trace organic compounds (TrOCs) (pharmaceuticals (PhACs), personal care products, endocrine disrupting compounds, disinfection by-products, etc.) [7–12].

Similar to RO membranes, most NF membranes are fabricated as a thin film composite (TFC), consisting of a polyamide thin layer formed via interfacial polymerization (IP) of monomer reactants on a porous polysulfone support [13]. In brief, the polysulfone support is first pre-saturated with an aqueous solution of the diamine monomers and then brought into contact with an organic solution of the acyl chloride monomers. The performance of a TFC membrane, including the water permeability and the separation ability, is primarily determined by the physicochemical properties of the polyamide layer, which in turn are controlled by the conditions adopted for the IP process. The improvement of the TFC NF membrane performance is therefore mainly through the optimization of the IP process conditions [14,15]. Some of the notable efforts are the use of alternative or combined monomers [16,17] and doping of additives to the monomer solutions [18].

The improved performance of TFC membranes can also be potentially achieved by incorporating nanoparticles into the polyamide layer to form thin film nanocomposite (TFN) membranes [19–22]. By dispersing the nanoparticles in either the organic solution or the aqueous solution, or both, they will be consequently incorporated into the polyamide layer during the IP process. A number of nanoparticles were demonstrated to endow the TFN

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membranes with an enhanced water permeability, which was attributed to the hydrophilic nature and the negative surface charges of the incorporated nanoparticles. Moreover, some nanoparticles, e.g. zeolite and mesoporous silica and carbon nanotube, are supposed to be able to provide preferential flow path for water. However, one probable drawback of many TFN membranes is the deteriorated rejection ability. It is resulted both from the lack of sufficient cross-linking between the nanoparticles and the active monomers and, more problematically, from the agglomeration of nanoparticles in the polyamide layer leading to the formation of "defects". Many types of nanoparticles have a strong tendency to agglomerate in the monomer solutions. A lot of recent studies were devoted to increasing the dispersibility of nanoparticles mainly by surface modifications, some of which were proved to be fairly successful [19,23].

Recently, we found that zeolite nanoparticles (and probably other nanoparticles) could be uniformly embedded to the polysulfone ultrafiltration (UF) membrane surface [24] by employing the in situ embedment approach [25]. The coverage ratio of zeolite nanoparticles on the UF membrane surface could be higher than 40%, but no substantial particle agglomeration was observed. In addition, the zeolite nanoparticles-embedded UF membranes demonstrated a higher water permeability than the control, indicating that the membrane pores were negligibly blocked by the particles. Moreover, the embedded nanoparticles were tightly anchored (but not totally buried) into the polysulfone matrix, settling the problem of either loss or clustering of nanoparticles when applying the rubber roller or air knife to remove the excessive amine solution. It thus appears that the zeolite nanoparticles-embedded UF membranes could serve as an ideal support for the fabrication of TFN membranes with no need of dispersing nanoparticles in either monomer solution. It was believed that, if the nanoparticles were to become an integral part of the active layer and the active layer structure were optimized, the TFN membrane would have an enhanced water permeability with little compromise of the rejection performance. We report the innovative approach to the fabrication of TFN NF membranes in this paper. Performance of the TFN membrane was evaluated in terms of the water permeability and the ability in rejecting both inorganic salts (sodium chloride and magnesium sulfate) and TrOCs in consideration of more applications of NF in this area.

2. Materials and methods

2.1. Membrane fabrication

Preparation of the zeolite nanoparticles-embedded UF membrane (denoted as the TFN-I support hereafter) and the bare UF membrane (denoted as TFC support) was described in our previous publication [24]. In brief, the cast solution contained 15% polysulfone, 8% polyvinylpyrrolidone and 77% anhydrous 1-methyl-2-pyrrolidinone all by weight. The thickness of the cast solution film was set at 200 μm. A deionized (DI) water bath was used for the formation of the TFC support, while a water bath containing the Linde type L (LTL) zeolite nanoparticles (80 nm in size, NanoScape AG, Germany) at 500 mg/L was used to form the TFN-I support [25]. The temperature of both water baths was 35 °C. Under these conditions, the pore size of the TFC support was measured to be ~30 nm (Fig. 1a) and the coverage ratio of zeolite nanoparticles on the TFN-I support was determined to be ~49% (Fig. 1b) by analyzing the scanning electron microscope (SEM) images using the ImageJ software [24].

The polyamide layers of the TFN-I and TFC membranes were prepared via the IP process (Fig. 2). The diamine monomer was piperazine (PIP, Sigma-Aldrich, USA), which was dissolved in deionized water at a weight concentration of 1.0%, while the acyl chloride monomer was trimesoyl chloride (TMC, Sigma-Aldrich, USA) dissolved in hexane (Sigma-Aldrich, USA) at a weight concentration of 0.2%. Each of the TFN-I and TFC supports with an area about $10 \times 8\ \text{cm}^2$ was first soaked in the PIP solution for 4 min, ensuring the penetration of PIP monomers into the pores of the support. An air knife (UEB 0150 V7SG, PNR, China) with compressed nitrogen (at 1 bar) was used to remove the excessive PIP solution from the surface of the support by slowly moving from one end to the other in 30 s. Afterwards, a volume of 15 mL of the TMC solution was poured onto the top surface of the support to allow the polymerization between PIP and TMC for 1 min. A dry curing process was proceeded in an oven at 80 °C for 5 min immediately after the polymerization reaction. The synthesized TFN NF membrane was denoted as TFN-I500 (which means that the membrane support was fabricated by using the in situ embedment approach with 500 mg/L nanoparticles in the water bath).

TFN NF membranes were also fabricated following the conventional method [26]. The same procedure was adopted except that the bare UF membrane was used as the support (denoted as the TFN-C support, same with the TFC support) and the aqueous PIP solution also contained LTL zeolite nanoparticles. (It was observed that the zeolite nanoparticles had a better dispersibility in water than in hexane.) The zeolite concentrations were 500 mg/L and 1000 mg/L, and the obtained TFN NF membranes were denoted as TFN-C500 and TFN-C1000, respectively. All NF membranes were stored in DI water at 4 °C prior to characterization of the properties and test of the performance.

2.2. Membrane characterization

The membrane surface morphologies were imaged under an SEM (Quanta 200F, FEI, USA) at 15 kV in high vacuum mode. The air-dried membrane specimens each with an area of $5 \times 5\ \text{mm}^2$ were sputter-coated with ~15 nm of Au/Pd (Precision etching and coating system 682, Gatan, USA) before SEM observation.

The membrane cross sections were characterized with a transmission electron microscope (TEM) (H-7650, Hitachi, Japan) at an acceleration voltage of 80 kV. The membrane samples were first embedded in Type 812 epoxy resin, and sliced into TEM sections (70 nm thick) by using a Leica EM UC6 Ultramicrotome (Leica, Wetzlar, Germany).

Atomic force microscope (AFM, Veeco Nanoscope 5, USA) was applied to determine the surface roughness of the membranes with a scanning area of $5 \times 5\ \mu\text{m}^2$ for each image. The membrane roughness values reported in this paper were averaged from at least three different spots and expressed as root-mean-square roughness (RMS or R_q), average roughness (R_a) and surface area difference (SAD). SAD is the difference between the three-dimensional surface area and two-dimensional projected surface area of the image. All three parameters were obtained using the AFM analysis software (NanoScope Software 7.20, USA).

X-ray photoelectron spectroscopy (XPS) scan was performed on each NF membrane using an XPS spectrometer (ESCALAB 250Xi, Thermo Fisher) with Al Kα radiation as the X-ray source. The pass energy was 100.0 eV. For each survey measurement, five survey scans sweeping over 0–1000 eV electron binding energy with a resolution of 1 eV were averaged. The spot size was $500 \times 500\ \mu\text{m}^2$.

The membrane surface hydrophilicity was indicated by water droplet contact angle, which was measured using a video-supported measuring instrument (OCA20, Dataphysics, Germany) according to the sessile-drop method [27]. A minimum of 10 measurements were carried out at different spots of each membrane to obtain the averaged contact angle value. In consideration of the influence of surface roughness on contact angle measurement,