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Ultrafiltration membranes with ultrafast water transport tuned via different substrates

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HIGHLIGHTS

- PSf membranes with high performance were obtained via adjusting the substrate property.
- Ultrahigh water permeability (>13,000 L/m^2 h per MPa) was achieved via loose NWFs (36.2 g/cm^2) as substrate.
- No sacrifice of rejection.
- Excellent anti-fouling property was achieved via loose NWFs (36.2 g/cm^2).
- More porous membranes with larger pore size were obtained by relatively hydrophobic substrate.

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ABSTRACT

A series of self-supporting and substrate-supporting polysulfone (PSf) ultrafiltration (UF) membranes was fabricated using various substrates including glass plates, polypropylene random plates (PPR) and three kinds of non-woven fabrics (NWFs) via a typical phase inversion technique. Effects of the substrate hydrophilicity and structure on the membrane characteristics, morphology, separation and anti-fouling performance were systematically investigated. For self-supporting membranes, compared to glass plates, PPR facilitated more porous membranes and higher pure water permeability (L_p), permeation flux as well as anti-fouling property. NWFs density played an important role in the separation performance of the NWFs-supporting membranes. The resulting membrane with loosest NWFs exhibited an ultrahigh L_p of approximate 13,572 L/m^2 h per MPa without any sacrifice of rejection, which significantly outperformed almost all the PSf membranes with L_p of 1000–7000 L/m^2 h per MPa in literature. In addition, fouling filtration tests were performed in dead-end mode using humic acids solution followed by physical washing. More reversible rather than irreversible fouling was found in the NWFs-supporting membranes, especially for the membrane with loosest NWFs, indicating an improved anti-fouling property. This work endows the conventional PSf membranes with the outstanding properties such as ultrafast water transport and high flux recovery in an efficient and facile way.

1. Introduction

To date, membrane technology has become more and more important and covered all engineering approaches for the transport of substances between two fractions with the help of permeable membranes [1–3]. Particularly with growing concern for the scarcity of freshwater, membrane technology for water separation and purification has been consistently developed to increase the water supply in recent ten years [4]. Ultrafiltration (UF) process is considered to be an excellent replacement to the conventional water treatment technology in the most fields such as food, pharmaceutical, biotechnological, wastewater treatment [5–7] and the pretreatment prior to seawater desalination [8,9] due to its highly energy-efficient and environment-friendly UF membranes. The UF membranes with the pore size distributing in the range of 1–10 nm are able to selectively separate the macromolecules such as colloids and protein from water [10] and the separate efficiency depends on the pore structure and surface property of the UF membranes.

Blending-phase inversion is a typical and extensively-used method to fabricate a UF membrane, where a homogenous casting solution consisting of polymer and additives is casted on a suitable substrate followed by the immersion in a coagulation bath [11].

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Generally, most UF membranes available through the blending-phase inversion are limited in their relatively low separation performance due to a huge distribution in the pore size leading to a poor selectivity [12–14] or a low membrane porosity leading to a poor permeability [15,16]. Therefore, there have been extensive studies on improving the separation performance of membranes by developing advanced membrane materials and fabricating methods to control the pore size and structure of membranes [17]. Rangou et al. [15] combined the self-assembly method using PS-*b*-P4VP diblock copolymers with the non-solvent induced phase separation (SNIPS) to develop the isoporous ultrafiltration membranes with the tailored pore sizes of 20–70 nm. Then, they [18] expanded the membrane pore size (17–86 nm) via increasing the molecular weight of the PS-b-P4VP to improve the water flux from 100 to 800 L/m^2 h per bar. Choi et al. [19] employed an organic phase change material (PCM) isopentane as novel porogen to fabricate the macroporous polymeric membranes and effectively controlled the surface pore size from 350 to 550 nm by varying the PCM content. Bui et al. [20] successfully fabricated highly ordered honeycomb films with tunable pore sizes (1.45–2.89 μm) by the different volume ratios of chloroform (ChL) and MeOH as the binary mixtures of the solvent/non-solvent via spin coating. However, to the best of our knowledge, few studies were focused on the membrane pore size control via changing the substrates to improve the separation performance and anti-fouling properties of the membranes.

In this study, various substrates including glass plates, polypropylene-random (PPR) plates and three non-woven fabrics (NWFs) were employed to fabricate the polysulfone (PSf) UF membranes with tunable pore sizes, and the correlations between the substrates and the resulting membranes were investigated systematically. Glass plates with a contact angle of 15.32° and PPR plates (composed of 1–7 wt% ethylene and 99–93 wt% propylene) with a contact angle of 60.27° were employed to fabricated the self-supporting PSf membranes and to evaluate the effect of the substrate hydrophilicity on the pore structure and separation performance of the resulting membranes. NWFs with a large surface area, high thermal and chemical stabilities are extensively used as the substrates in almost all the commercial pressure-driven membranes to withstand high pressures during a practical membrane separation operation [17,21]. In our study, three types of NWFs substrates with different densities were used to fabricate the substrate-supporting PSf membranes and to investigate the effect of the substrate structure on the pore structure and separation performance of the resulting membranes. Anti-fouling behaviors of the resulting membranes were also evaluated by the fouling experiments. In addition, the membrane structure and separation performance of the self-supporting and substrate-supporting PSf UF membranes were compared. This work endows the conventional PSf membranes with the outstanding properties such as ultrafast water transport and high flux recovery, which is considered to be the most promising due to its efficiency, facility and low cost.

2. Experimental

2.1. Materials

PSf (MW ~ 50 kDa) purchased from Amoco was used as the main membrane material. N,N-dimethyl acetamide (DMAc) and polyethylene glycol 400 (PEG-400) purchased from Fuyu Fine Chemical Co. Ltd (Tianjin) were used as the solvent and pore-forming agent in the casting solution, respectively. NWFs with various densities were provided from Jiaxin Co. Ltd (Shanghai). Humic acids (HA) purchased from Sigma–Aldrich was dissolved in dilute NaOH solution (pH = 12) with stirring followed by pH adjustment to 7 with HCl to form a 5 mg/L organic foulant solution. Size distribution of HA solution was measured using Zetasizer Nano S90 (Malvern, England) by uniform dispersion in Deionized (DI) water and was presented in SI (Supporting information). DI water with a resistivity of 18.0 MΩcm was obtained using a Millipore water purification system, which was used to form a coagulation bath and rinse the membranes to remove any excess amount of chemicals on the membrane surface. Solvents and chemicals were used without further purification.

2.2. Membrane preparation

UF membranes were prepared via phase inversion method and all the casting solutions were composed of 18 wt% PSf, 8 wt% PEG-400, 0.4 wt% DI water and 73.6 wt% DMAc. The casting film was casted uniformly on various substrates separately with a home-made knife blade at a height of 150 μm and then was gently immersed into the coagulating bath for 20 min to complete the phase inversion. For the glass and PPR plates as substrate, the self-supporting membrane peeled off the substrate after phase inversion and denoted as the M-G and the M-PPR, while the substrate-supporting membranes with NWFs substrates were obtained as a whole, denoted as the M-1, the M-2 and the M-3 according to the NWFs density. The resulting membranes were kept in DI water for more than 12 h to remove residual solvent before use.

2.3. Membrane characterization

Morphologies of the substrates and the membranes were observed by scanning electron microscopy (SEM, HITACHI, S-4800). Samples were dried overnight and sputter-coated with gold nanoparticles. For examining the cross-sectional morphology of the membranes, samples were pretreated in liquid nitrogen and fractured before test.

Contact angle analysis upon the dried membrane and the NWFs surfaces was conducted by a contact angle goniometer (DSA 100, KRUSS, Germany). The sample was fixed flat on a glass slide using a double-sided tape after drying in a vacuum oven prior to the measurements. A water drop with a volume of 2 μL was dropped onto the membrane surface with a microsyringe in air and the digital image of the droplet was immediately recorded. At least five values were measured for each sample and then the average value was calculated.

Mechanical property of membranes was measured by the tensile testing equipment (SHIMAZDU, AGS-J) at room temperature. Specimens with 1 cm × 3 cm strips were stretched up to a specific elongation or fractured at a constant strain rate of 1 mm/min. Five samples at least were tested for each membrane or substrate to obtain the average value of tensile stress and elongation at break.

Average porosity (ε) of the NWFs and PSf layers was determined using gravimetric method by measuring the weight of water contained in the membrane pore, as shown in Eq. (1). First, the membrane sample was soaked in water for 24 h and weighed after mopping with blotting paper. Then the wet sample was dried in a vacuum oven at 40 °C for 24 h and weighed again. Tortuosity (τ) was determined using Archie's law (a popular empirical model) which satisfied all these conditions [22], as shown in Eq. (2) based on the ε measurements [23–25]. Five samples at least were tested for each membrane or substrate and the average value was presented in this study.

$$\varepsilon = \frac{Ww - Wd}{dA\delta} \times 100 \quad (1)$$