



High flux nanofiltration membranes based on interfacially polymerized polyamide barrier layer on polyacrylonitrile nanofibrous scaffolds

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ARTICLE INFO

Article history:

Received 29 April 2008

Received in revised form

28 September 2008

Accepted 18 October 2008

Available online 25 October 2008

Keywords:

Nanofiber

Interfacial polymerization

High flux

Nanofiltration

ABSTRACT

Electrospun polyacrylonitrile (PAN) nanofibrous scaffold was used as a mid-layer support in a new kind of high flux thin film nanofibrous composite (TFNC) membranes for nanofiltration (NF) applications. The top barrier layer was produced by interfacial polymerization of polyamides containing different ratios of piperazine and bipiperidine. The filtration performance (i.e., permeate flux and rejection) of TFNC membranes based on electrospun PAN nanofibrous scaffold was compared with those of conventional thin film composite (TFC) membranes consisting of (1) a commercial PAN ultrafiltration (UF) support with the same barrier layer coating and (2) two kinds of commercial NF membranes (i.e., NF90 and NF270 from Dow Filmtec). The nanofiltration test was carried out by using a divalent salt solution (MgSO_4 , 2000 ppm) and a cross-flow filtration cell. The results indicated that TFNC membranes exhibited over 2.4 times more permeate flux than TFC membranes with the same chemical compositions, while maintaining the same rejection rate (ca. 98%). In addition, the permeate flux of hand-cast TFNC membranes was about 38% higher than commercial NF270 membrane with the similar rejection rate.

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1. Introduction

Polymeric membranes have been widely used at different levels of water purification [1,2]. Perhaps, the most challenging utilization of polymeric membranes in water purification is desalination, where the chemical functionality and physical structures of the membranes (e.g. reverse osmosis (RO) membranes to treat brackish water or sea water) must be precisely controlled to effectively remove salt ions (e.g. monovalent salt—sodium chloride) without substantially compromising the permeate flux rate. When the selectivity of the barrier layer is reduced, the membranes can be used for nanofiltration (NF), such as water softening, removal of color, taste, odor and other small contaminants, at higher flux [3]. The thin film composite (TFC) structure (i.e., an ultra-thin, very dense barrier layer on top of the porous support) is the most common format in NF and RO membranes [4]. In the following, we provide a detailed discussion on the present status of TFC membranes in order to set the proper stage for our development of a new type of high flux TFC membranes based on the nanofiber mid-layer support.

The most widely used method to prepare the barrier layer on the porous support for fabrication of TFC membranes in NF and RO applications is interfacial polymerization [5]. Typically, monomeric or polymeric amine-impregnated porous support (itself is usually an ultrafiltration (UF) membrane made by the phase inversion method) is brought in contact with the organic acyl halide solution for a short time (up to a few minutes) to produce a highly cross-linked, network-structured, ultra-thin (about a couple of 1000 Å) barrier layer. Various parameters in the interfacial polymerization (such as the reactant concentration, the partition coefficient of the reactant, the reactivity ratio of reactant blends, and overall kinetics and diffusion rate of each reactant) as well as processing procedures (such as by-products removal, hydrolysis or competitive by-reactions, and post-reaction or treatments) determine the performance of TFC membranes [4]. Most state-of-the-art NF membranes employ interfacially polymerized polyamide thin film as the barrier layer and UF membrane as the support [6,7]. The performance of interfacially polymerized polyamide barrier layer is also dependent on the additives used during polymerization, post-treatments (e.g. the by-product removal) and pre-conditioning of the support scaffold (e.g. minimizing the pore blocking during polymerization). Typically, without the proper selection of additives and pre- and post-treatments, the reported flux and selectivity (or rejection) of laboratory-made membranes are always low (e.g. 0.11–0.52 l/m² hpsi with 93–98% rejection of MgSO_4 at 1000–3000 ppm) when compared with those of commercially

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available NF membranes (e.g. 0.66–0.76 l/m² h psi with 97–98% rejection of MgSO₄ at 2000 ppm) [6,8–14]. The support materials (e.g. UF membranes with several tenths of thousands of molecular weight cutoffs, MWCs) usually have only a relatively small fraction of pores on the surface (7–12% with pore sizes ranging from 1 nm to 30 nm) [15] so that the structure can support a very thin barrier layer (with thickness down to 50 nm). The network structure of the barrier layer has to be sufficiently tight to differentiate the diffusive motions of water molecules and salt ion–water aggregates. A small increase in the barrier layer thickness can drastically increase the hydraulic resistance by several times [16].

Besides the barrier layer composition and pre-/post-treatments, the properties of the supporting mid-layer would also need to be fine-tuned in order to get the high flux performance. Various support layers (e.g. UF membranes with different performances) were tested to maximize the productivity of thin film composite membrane. For example, microfiltration (MF) membranes have been used for laminating ultra-thin cellulose acetate films [17]. Only the microfilter with pore sizes of 100–1000 Å showed 93–95% rejection of sodium chloride solution (3500 ppm) at 1500 psi. The microfilter with an average pore size of 4500 Å resulted in failure of coating. The microfilter with a pore size of 500 Å showed about 2 times higher permeate flux than that of the Loeb–Sourirajan asymmetric membrane when they were laminated with the cellulose acetate film (thickness ~2000 Å). Multiple polyelectrolyte layers (e.g. poly(styrene sulfonic acid) sodium salt (PSS)/poly(allylamine hydrochloride) (PAH) layers) deposited on the polyethersulfone (PES) UF membrane support was also examined for NF applications [18]. When PSS-capped 4-layered coating of [PSS/PAH] was deposited on the PES UF support with MWCO of 10 kDa, the composite membrane showed 96.1% of sulfate ion rejection (the feed concentration was 1000 ppm), but the sulfate ion rejection was only 63% when the PES UF support with MWCO of 500 kDa was used. Meanwhile, the permeate flux increased from 26.7 l/m² h (for 10 kDa PES UF support) to 33.8 l/m² h (for 500 kDa PES UF support) at 72 psi. In another study, interfacially polymerized (IFP) aromatic polyamide layer was applied on two different pore sized membrane supports (type 1: 70 nm, type 2: 150 nm). Type I supported IFP composite membrane showed a lower permeate flux (35.7–45.9 l/m² h) but higher rejection (95–96%) than those (76.5–83.3 l/m² h with 70–65%) based on Type II supported IFP composite membrane at 250 psi using 2000 ppm of sodium chloride solution [19].

Electrospinning is a technique that can make nonwoven nanofibrous scaffolds with highly porous, inter-connected void network structures [20,21]. A variety of polymers, including those routinely used in membrane filtration (e.g. polyacrylonitrile, PAN, polyvinylidene fluoride, PVDF, polysulfone and polyethersulfone), can be processed via electrospinning. There are several unique features of electrospun nanofibrous scaffolds, which could be differentiated from conventional filter media such as MF, UF, NF and RO membranes based on porous membrane supports. (1) The surface porosity of electrospun nanofibrous scaffolds is similar to the bulk porosity, which is close to 80% or higher. (2) The surface pore structures (created by nonwoven nanofiber deposition) are all inter-connected throughout the membrane (horizontally and vertically), so there are no dead-end pores in electrospun nanofibrous scaffolds. (3) The surface of electrospun nanofibrous scaffolds is smooth enough to support the barrier layer (in micron² or less area) as long as the nanofiber deposition is uniform. (4) Typical open pore MF membranes (e.g. the depth filter type) made by solution precipitation from solvent evaporation and water absorption possess a rough surface morphology (for an area range similar to that of the electrospun membrane), which are not suitable to support the ultra-thin barrier layer coating.

Recently, a new kind of thin film composite membranes based on the electrospun nanofibrous scaffold as the support layer has been reported (we term them thin film nanofibrous composite, TFNC, membranes) [22–24]. For the UF application, TFNC membranes containing a thin hydrogel top coating and a nanofibrous mid-layer scaffold showed very high flux and low-fouling behavior over those of commercial UF membranes. In the current study, an interfacially polymerized polyamide barrier layer composed of different ratios of piperazine and bipiperidine was fabricated on both PAN electrospun nanofibrous scaffold and PAN UF membrane as the mid-layer supports. The performance of the resulting membranes was compared with each other as well as with those of commercial NF membranes.

2. Experimental

2.1. Materials

Polyacrylonitrile (PAN, with weight average molecular weight of 1.5×10^5 g/mol), dimethylformamide (DMF), piperazine (PIP), bipiperidine (BP), dihydrochloride, trimesoyl chloride, and triethylamine were purchased directly from Sigma–Aldrich. Nonwoven poly(ethylene terephthalate) (PET) substrate (Hollytex 3242) was provided by Ahlstrom Mount Holly Springs. PAN400 ultrafiltration membrane was purchased from Sepro Inc. (CA). NF270 and NF90 nanofiltration membranes were provided by Dow Filmtec. Magnesium sulfate heptahydrate, D-(+)-raffinose pentahydrate, and D-(+)-glucose were purchased from Sigma–Aldrich. Sucrose was purchased from Fluka. Milli-Q water purification system was used to generate purified water. All chemicals were used as received unless noted.

2.2. Preparation of PAN nanofibrous scaffolds by electrospinning

The procedure for electrospinning of PAN nanofibrous scaffolds was as follows. PAN was dissolved in DMF at 60 °C for 2 days until it became a homogeneous solution (solution concentration 8 wt%). The PAN solution was electrospun onto an aluminum foil or a nonwoven PET support at 15 kV. The flow rate was 20 μl/min and the spinneret diameter was 0.7 mm. The distance between the collector and the spinneret was 10 cm. In the electrospinning setup, a rotating metal drum (diameter: 9 cm, rotating speed: 300 rpm) was used to collect the deposited nanofibers. A stepping motor was used to control the oscillatory translational motion perpendicular to the drum rotation direction (the oscillation distance was about 12 cm) to ensure the production of uniform electrospun scaffolds with a sufficiently large membrane area (i.e., larger than 7.6 cm × 10.2 cm). The porosity ($= (1 - \rho_{\text{electrospun}} / \rho_{\text{powder}}) \times 100$ (%)) of the electrospun membrane was determined by using bulk density ($\rho_{\text{powder}} = 1.184$ g/cm³) of PAN powder and electrospun membrane density (by measuring known size and dimension of membrane).

2.3. Fabricate polyamide barrier layer by interfacial polymerization

TFNC and TFC membranes containing a polyamide barrier layer were prepared by interfacial polymerization on the PAN electrospun nanofibrous scaffold and PAN400 UF membrane, respectively. The procedures for interfacial polymerization were as follows. Piperazine, bipiperidine and dihydrochloride were dissolved in Milli-Q water at varying concentrations and mixture compositions (the total amine concentrations ranged from 0.125% to 1% (w/v), where bipiperidine/dihydrochloride ranged from 0% to 60% (w/w) with respect to the amount of piperazine). An area of 3.5 in. × 4.5 in.

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