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New insights into fabrication of hydrophobic/hydrophilic composite hollow fibers for direct contact membrane distillation

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HIGHLIGHTS

- Hydrophobic/hydrophilic dual-layer hollow fibers were fabricated for DCMD.
- Outer surface of the outer layer was independent of the additive types.
- Hydrophilicity of the inner layer affected the DCMD performance.
- Pore wetting status was tentatively correlated with the membrane performance.

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ABSTRACT

Dual-layer composite membrane is a new design for direct contact membrane distillation (DCMD) with membrane performance potentially superior to that of single layer porous membranes. Using dry–wet phase inversion technology, novel dual-layer hollow fiber membranes were fabricated in current research. The outer layer was made from polyvinylidene fluoride (PVDF) with polyvinylpyrolidone (PVP) or glycerol as non-solvent additive, while the inner layer consists of PVDF and polyvinyl alcohol (PVA) blend. The effect of the nonsolvent additive type in the outer layer and that of PVA/PVDF blending ratio in the inner layer on the morphological, mechanical and separation characteristics of the composite membranes was investigated. Membrane performance was further correlated to the physicochemical and morphological characteristics of the membranes. In particular, a thorough investigation of pore wetting in DCMD was attempted for the first time in this work, observing the cross-sectional distribution of EDX chlorine signals as an indication of the penetration of sodium chloride solution into the pore from the feed.

1. Introduction

Freshwater resource scarcity is a common problem for many countries. With growth in population and expansion of human activities, the problem of water contamination becomes more and more serious due to the huge volume of wastewater discharged and the complicated pollutants. Keeping the balance between freshwater supply and wastewater generation, which is essential to the conservation of water, is already beyond the capability of hydrological cycle involving only natural processes. Environmentally sound measures must be taken to prevent the situation from further deterioration.

Seawater desalination and wastewater reclamation have been incorporated into the memorandum of maintaining global water sustainability. Among the various separation technologies actually utilized or potentially applicable in the above systems, membrane distillation (MD) is commented positively by many researchers dealing with the tasks of removing inorganic salts from water stream (Alkhudhiri et al., 2012; Curcio and Drioli, 2005). Compared with non-membrane separations, the benefits of MD lie in the small foot-print and continuous operation. Relative to other membrane separations (i.e. reverse osmosis) it has the advantages of theoretically 100% ions rejection, high concentration factor, and mild operation temperature and/or pressures (Lawson and Lloyd, 1997).

MD is classified into direct contact membrane distillation (DCMD), air gap membrane distillation (AGMD), sweeping gas membrane distillation (SGMD) and vacuum membrane distillation (VMD). DCMD using cold liquid to collect water vapor is the

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simplest configuration. Like other membrane separations, DCMD relies on high flux and efficient rejection as important variables for reducing system investment and operation cost (Criscuoli et al., 2008). Due to the constraint by heat transfer, further improvement in flux might resort to using materials with higher thermal resistance. However, the hydrophobic materials, such as polyvinylidene fluoride (PVDF) and polypropylene (PP), which are already high in ranking of heat resistance, have been widely used in DCMD and the further breakthrough seems difficult (Han and Fina, 2011). On the other hand, fabrication of more porous or thinner membranes is desirable to increase the flux (Bonyadi et al., 2009; Lawson and Lloyd, 1997). Those membranes are, however, not mechanically strong enough for practical applications. Thus, in order to satisfy both requirements of high heat transfer resistance and high mass transport, the concept of hydrophilic/hydrophobic dual-layer membranes was proposed for DCMD (Bonyadi and Chung, 2007; Edwie et al., 2012; Khayet et al., 2006, 2005; Peng and May, 2011; Su et al., 2010). The thin hydrophobic layer facing the feed is not wetted by liquid water, while allowing the transport of vapor through the pores. The relatively thick porous hydrophilic layer is filled with water from the cold permeate side and does not contribute to vapor transfer resistance. At the same time, the hydrophilic layer serves as the mechanical support for the thin hydrophobic layer as well as can provide additional resistance for heat conduction through the membrane. One of the methods to fabricate such dual-layer membranes is the casting of polymer solutions which consists of a surface modifying macromolecule (SMM) and a host polymer, e.g. SMM was incorporated in hydrophilic polyetherimide (PEI) in Khayet et al.'s work for DCMD (Khayet et al., 2005). Khayet's dual-layer membranes showed fluxes at least as high as those of the commercial polytetrafluoroethylene (PTFE) membranes. Another method is relying on addition of the hydrophobic and hydrophilic additives into the outer and inner layers to modify or promote the hydrophobicity and hydrophility respectively. Su et al. fabricated the dual-layer membrane using the co-extrusion/phase inversion method and investigated the influence of changing the thermal conductivity of inner hydrophilic layer on the flux in DCMD (Su et al., 2010). Graphite particles and multiwall carbon nanotubes were used as the filler to make the inner layer more hydrophilic. It was found that the synergistic effect of graphite and multiwall carbon nanotubes has substantially enhanced the thermal conductivity of hydrophilic layer, and consequently the vapor flux.

The most ideal design of the dual-layer membrane is such that the hydrophobic outer layer is kept dry to enable desalination, while the inner layer is fully wetted to enhance the flux. These twin requirements are satisfied when the materials for the inner and outer layers are properly chosen and their morphologies in terms of pore size, porosity, tortuosity etc. are properly adjusted (Curcio and Drioli, 2005; Song and Jiang, 2013). However, few researches have been so far performed to reveal material selection and structural design criteria of the dual-layer membrane for DCMD. In light of this, the current work will investigate: (1) the effect of spinning conditions, particularly the composition of the polymer and the additive in the spinning dope on the morphological and physiochemical characteristics of the dual-layer hollow fiber membranes, and (2) the relationship between the DCMD performance (flux and rejection) and above physicochemical and structural properties of the hollow fiber membranes. Hollow fibers are fabricated in the current work making the outer (shell side) and inner (lumen side) layers hydrophobic and hydrophilic, respectively. As the base polymer for both layers, PVDF is used to ensure good adhesion between the two dopes, one for the outer layer and the other for the inner layer to prevent delamination of two layers (Bonyadi and Chung, 2007). PVDF is widely used in the preparation of MD membranes due to its sufficiently high hydrophobicity, acid resistance and other suitable chemical and physical properties (Drioli et al., 2011; Lovinger, 1982). Polyvinyl alcohol (PVA) was blended into PVDF to form an inner hydrophilic layer. It is reported that PVA has good dynamic miscibility with PVDF (Li et al., 2010). Glycerol and polyvinyl pyrrolidone (PVP) are the non-solvent additives for improving the porosity of the hydrophobic outer layer (Simone et al., 2010; Song and Jiang, 2013; Wang et al., 2000).

2. Experimental

2.1. Materials

Poly (vinylidene fluoride) (PVDF 1300, Mw 350,000) was purchased from Kureha (Japan). Polyvinylalcohol (PVA T-350 Mw 800,000) supplied by Nippon Gohsei (Japan) was rinsed using pure water and dried at either 60 °C or 100 °C for 2 h prior to use. Polyvinyl pyrrolidone (PVP Mw 8000) was purchased from Aladdin Industrial Corporation (Shanghai, China). PVDF and PVP were dried at 100 °C in vacuum for 24 h before being used for dope preparation. N-methyl-2-pyrrolidone (NMP), methanol and hexane were purchased from Sinopharm Chemical Reagent (Shanghai, China) and used as received.

2.2. Preparation of spinning dopes

To prepare the outer layer spinning dope, predetermined amounts of PVDF and PVP were added into NMP under vigorous stirring. The resultant mixture was heated to 80 °C and kept stirred for 12 h to form a homogenous solution. When glycerol was used as an additive instead of PVP, a predetermined amount of glycerol was added into NMP first, followed by addition of PVDF.

To prepare the inner layer spinning dope, a predetermined amount of PVA was first dissolved in NMP at 95 °C. After complete dissolution of PVA, the temperature was lowered to 80 °C and the predetermined amount of PVDF powder was added into the PVA solution. After 12 h of continuous stirring, a clear tri-component solution was obtained. The dope compositions are summarized in Table 1. The solutions were stored in containers at 60 °C and degassed for 12 h before being subjected to hollow fiber spinning.

2.3. Hollow fiber spinning and module fabrication

A triple-orifice-spinneret was used for dual-layer hollow fiber spinning. The polymer solutions were transferred to the spinneret by two gear pumps while the bore fluid was supplied to the center of the spinneret by a syringe pump from their respective storage

Table 1
Compositions of dopes and coagulants for the dual-layer hollow fiber membranes preparation.

ID	*Outer layer dope Composition (wt%)*	*Inner layer dope PVDF/PVA ratio (total polymer wt% 15, NMP wt% 85)*	*Bore fluid Composition (wt%)*	*External coagulant (wt%)*
P5	PVDF: 12	95/5	Water:80	Water:100
P10	PVP: 10	90/10	Ethanol:20	
P15	NMP: 78	85/15		
P20		80/20		
G5	PVDF:12	95/5	Water: 80	Water:100
G10	Glycerol:10	90/10	Ethanol:20	
G15	NMP:78	85/15		
G20		80/10		