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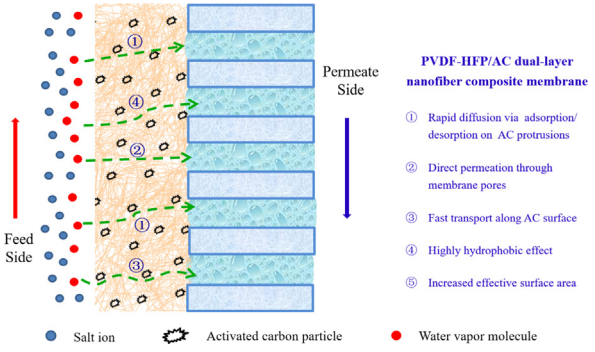
Activated carbon enhanced hydrophobic/hydrophilic dual-layer nanofiber composite membranes for high-performance direct contact membrane distillation

Lihua Zhao[a,b], Chunrui Wu[a], Xiaolong Lu[a,*], Derrick Ng[b], Yen Bach Truong[b], Zongli Xie[b,*]

[a] State Key Laboratory of Separation Membranes and Membrane Processes/ National Center for International Joint Research on Separation Membranes, Institute of Biological and Chemical Engineering, School of Material Science and Engineering, Tianjin Polytechnic University, Tianjin 300387, PR China
[b] CSIRO Manufacturing, Private bag 10, Clayton South MDC, VIC 3169, Australia

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, activated carbon (AC) enhanced hydrophobic/hydrophilic dual-layer nanofiber composite membranes were prepared for direct contact membrane distillation (DCMD) by incorporating different concentrations (0–3.0 wt%) of AC nanoparticles into the polyvinylidene fluoride-*co*-hexafluoropropylene (PVDF-HFP) hydrophobic active layer. The membranes were composed of two layers, a thin hydrophobic PVDF-HFP/AC electrospun active layer and a thick hydrophilic support layer. Results indicated that the incorporation of AC nanoparticles have greatly increased the membrane properties and performance. The membrane containing 1.5 wt % AC nanoparticles (M3) showed the best flux performance (45.6 L/m^2 h) compared to other membranes fabricated in this study and a commercial PTFE benchmark membrane (41.8 L/m^2 h) without compromising the salt rejection. A two-dimensional model was developed to investigate the flux profile of the PVDF-HFP/AC membranes. The present study suggests that the incorporation of AC nanoparticles into PVDF-HFP active layer can impart additional functionalities to the composite membranes that would enhance the membranes DCMD performance. The fabricated PVDF-HFP/AC composite membranes present great potential in the application of DCMD desalination.

* Corresponding authors.
E-mail addresses: 13920286131@163.com (X. Lu), zongli.xie@csiro.au (Z. Xie).

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1. Introduction

Membrane distillation (MD) is a thermally-driven membrane separation process that allows only water vapor and other volatile molecules to pass through a hydrophobic, microporous membrane [1–5]. This process is considered to be a promising next-generation seawater desalination and water purification technique. As an emerging membrane technology, MD possesses some unique advantages over the conventional membrane processes, being its theoretically complete rejection of non-volatile species, the potential usage of low-grade waste heat and/or alternative energy sources, and operations can be carried out at ambient pressures and less strict requirements in terms of mechanical strength of the membranes used [6]. Despite these advantages, however, this process is also attended by some drawbacks, such as relatively low flux, lack of appropriate membranes, intensive energy consumption (if solar, waste heat or other alternative energy source is not used), and membrane wetting and fouling problems, that hinder the MD from full-scale commercializing. The present study addresses the first issue, i.e., relatively low flux with respect to commercially available reverse osmosis (RO) process. Development of MD membranes with higher flux is the primary goal of this research.

The ideal MD membranes should have (1) superior hydrophobicity, (2) highly porous structure, and (3) appropriate pore size distribution [7]. The currently-used MD membranes are not specifically designed for MD operation. Most of the commercially available membranes that made by non-solvent induced phase separation (NIPS) [8], thermally-induced phase separation (TIPS) [9], stretching [10], or sintering [11] methods are initially fabricated for microfiltration (MF) purpose. Normally, those MF membranes are not exactly suitable for MD applications and prone to encounter low permeability and wetting problems that showing unsatisfactory performance in MD process. Thus, there is an imperative demand to explore an appropriate membrane specifically designed for MD process for a better MD performance.

In recent years, electrospinning technique has attracted considerable interest for its applications in membrane-based desalination and water reuse applications [12–16]. Compared with membranes fabricated via conventional methods, electrospun nanofiber membranes (ENMs) exhibit many outstanding characteristics such as higher hydrophobicity, higher porosity with interconnected pore structure, tunable pore size and membrane thickness, which have attracted enormous attention in the field of MD [17]. Moreover, compared to NIPS and TIPS techniques, electrospinning is a simpler method to fabricate membranes.

Recently, electrospun membranes have been extensively used in MD desalination applications [18–21]. Some of the membranes or composites that incorporated with carbon-based nanoparticles such as carbon nanotube (CNT) [22,23] and graphene [24] have demonstrated superior flux performance. Other studies [25–27] fabricated dual-layer or triple-layer nanofiber membranes and found that using hydrophobic/hydrophilic dual-layer membrane could achieve higher MD flux than the single-layer hydrophobic membrane. If someone can combine these two advantages into one membrane, the membrane properties and performance will be drastically improved.

In this work, activated carbon (AC) enhanced hydrophobic/hydrophilic dual-layer nanofiber composite membranes were fabricated by electrospinning technique and investigated their DCMD performance. The fabricated membranes have been designed to encompass two distinctive layers: a hydrophobic nanofiber active layer and a bottom (support) layer which is made of a hydrophilic commercial membrane. Polyvinylidene fluoride-*co*-hexafluoropropylene (PVDF-HFP) was used as the hydrophobic material for nanofibers fabrication as PVDF-based membranes are usually used for commercial membrane separation applications due to their good mechanical, thermal and chemical stability. Furthermore, PVDF-HFP was chosen due to its higher hydrophobicity and free volume properties than that of a PVDF alone due to its excellent hydrophobicity [27]. AC nanoparticles were selected as the nanofiller material that could provide additional functionalities to the PVDF-HFP nanofibers due to its inherently hydrophobic nature and strong adsorption/desorption properties like other carbon-based materials such as CNT and graphene.

2. Experimental

2.1. Materials

Polyvinylidene fluoride-*co*-hexafluoropropylene (PVDF-HFP, Mw = 400,000 g/mol), activated carbon (AC, particle size < 500 nm), *N*, *N*-dimethylformamide (DMF), acetone, sodium chloride (NaCl), and lithium chloride (LiCl) were all purchased from Sigma-Aldrich. Commercial hydrophilic Biodyne-A Nylon 6,6 membrane (thickness = 160 μm and water contact angle less than 40°) was sourced from Pall corporation and used as the hydrophilic substrate (support layer) of the dual-layer membrane. In addition, a commercialized polytetrafluoroethylene (PTFE) flat-sheet membrane from Porous Membrane Technology (Ningbo, China) was used as a comparison.

2.2. Membrane preparation

Electrospinning dope solutions were prepared by dissolving 15 wt% PVDF-HFP and a certain amount of AC nanoparticles (0, 0.5, 1.0, 1.5, 2.0, 3.0 wt% to PVDF-HFP) in a DMF/acetone mixed solvent via overnight stirring. In addition, 0.005 wt% LiCl was added into above solutions to improve the dope electrospinning ability. Table 1 shows the compositions of the dope solution used in this study.

Electrospinning set-up is shown in Fig. 1 and more details of the electrospinning equipment are described in a previous published paper [28]. To fabricate dual-layer hydrophobic/hydrophilic membrane, the commercial hydrophilic Nylon 6,6 membrane was first fixed onto the surface of rotating drum collector, followed by electrospinning the hydrophobic PVDF-HFP nanofibers on top of the Nylon 6,6 substrate. Six kinds of membranes with different AC contents were fabricated. The fabricated fresh membranes were then placed in a vacuum oven at 60 °C for 24 h to evaporate all the redundant solvent. The electrospinning operating conditions are summarized in Table 2.

2.3. Membrane characterization

2.3.1. Membrane morphology

Membrane surface and cross-section morphologies were investigated using a scanning electron microscopy (SEM, Zeiss Merlin Gemini 2). The samples were sputtered with Ir for 30 s before SEM analysis. Cross-section samples were prepared by immersing the membrane into liquid nitrogen and fracturing carefully. The specimens were attached to an aluminum sample holder and dried under vacuum for at least 24 h.

2.3.2. Membrane pore size & pore size distribution

The pore size and pore size distribution of the fabricated nanofibers

Table 1
Compositions of the dope solution used in this study.

Membrane code	PVDF-HFP (wt%)	DMF (wt %)	Acetone (wt %)	LiCl (wt %)	AC (wt %)[a]
M0	15	68	17	0.005	0
M1	15	68	17	0.005	0.5
M2	15	68	17	0.005	1.0
M3	15	68	17	0.005	1.5
M4	15	68	17	0.005	2.0
M5	15	68	17	0.005	3.0

Note:
[a] The AC content was on the basis of the PVDF-HFP weight.