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CF_4 plasma-modified omniphobic electrospun nanofiber membrane for produced water brine treatment by membrane distillation

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ABSTRACT

This study describes the development and performance of an omniphobic poly(vinylidene fluoride) (PVDF) membrane by electrospinning and CF_4 plasma surface modification for air gap membrane distillation (AGMD). The effect of different duration of plasma treatment on the nanofiber membrane characteristics was investigated. The AGMD performance of the membranes was evaluated using real reverse osmosis (RO) brine produced from coal seam gas (CSG) water that was added with low surface tension liquid (surfactant) as feed solution. Results indicated the formation of new CF_2-CF_2 and CF_3 bonds after plasma treatment, which lowered the surface energy of the membrane, providing omniphobic property, as indicated by its wetting resistance to different low surface tension liquids such as methanol, mineral oil and ethylene glycol. Though no appreciative changes in morphology of the membrane were observed after plasma treatment, optimal treatment condition of 15 min (i.e., P/CF-15 membrane) exhibited lotus effect membrane surface with increased liquid entry pressure of 187 kPa compared to 142 kPa for neat membrane. AGMD performance showed stable normalized flux (initial flux of 15.3 L/m^{2}h) and rejection ratio (100%) for P/CF-15 even with the addition of up to 0.7 mM sodium dodecyl sulfate surfactant to the RO brine from CSG produced water feed, while commercial PVDF membrane suffered membrane wetting after 0.3 mM of surfactant addition. Based on the results, the present omniphobic membrane has good potential for producing clean water from challenging waters containing high salinity and organic contaminants.

1. Introduction

Membrane distillation (MD) is an emerging thermally-driven, membrane-based desalination technology highly suitable to treat hypersaline solutions [1]. In contrast with reverse osmosis (RO) which utilizes very high pressure to separate salts from saline solutions, MD utilizes the partial vapor pressure gradient induced by temperature difference between the feed and the permeate sides as its driving force, hence it can work at significantly lower or negligible pressure [2]. If waste heat or solar energy is available, it presents a viable option for modular-scale desalination process with lower energy requirement and carbon footprint compared to electricity-driven desalination technologies such as RO process [3]. Theoretically, MD can obtain 100% salt rejection as it only allows water vapor to pass through the microporous MD membrane while retaining the salt solution [4]. Thus, the membrane should be highly hydrophobic with adequate liquid entry pressure (LEP) that can prevent the penetration of saline water through the membrane pores, the phenomenon termed as membrane wetting [5]. The presence of some low surface tension components such as oil and surfactants that are usually present in challenging water sources (e.g., coal seam gas produced water) can cause membrane wetting and/or fouling issues which can pollute the permeate water. The membrane characteristics therefore play a very important role in the separation efficiency of the MD process [6]. However, the currently used membranes for research and pilot-scale studies are usually made of polyvinylidene fluoride (PVDF), polypropylene (PP) or polytetrafluor-

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oethylene (PTFE) hydrophobic microfiltration membranes which suffer from low flux and wetting problems as they are not specifically designed for MD operation [7]. Therefore, given the high prospects of MD process for different applications including those for gas and industrial wastewater treatment, there is a need to develop MD membranes with adequate flux without wetting issues for the long-term operation. Membranes with omniphobic properties that provide anti-wetting capability for both water and low surface tension components are particularly attractive for treatment of challenging waters including RO brine from coal seam gas (CSG) produced water.

Recently, increasing number of research has been focused on the development of new MD membranes. The design and fabrication of new hollow fiber and flat-sheet MD membranes using spinning, stretching and phase inversion technique have been recently reported [4,8,9]. Other studies focused on modifying commercial and lab-fabricated membranes to improve their anti-wetting and other membrane properties. Though many of these studies indicated improvement of flux and salt rejection, most of them mainly tested their membranes on relatively "clean" water or at seawater quality, while a few considered higher salt concentrations without the presence of organics and low surface tension contaminants like oil and surfactants. CSG, also known as coal bed methane (CBM), is a natural gas located in the coal seams underground (300~1000 m) [9,10]. The CSG exploration involves the treatment and management of huge volume of produced water most of which are highly saline. In many cases, this CSG produced water is treated by RO process before reuse or environmental discharge. The RO brine from CSG produced water usually contains varying amounts of low surface tension contaminants, which need to be removed from the RO brine. MD membranes possessing high hydrophobicity, adequate pore size, narrow pore size distribution and high liquid entry pressure [9] are ideal for treating any saline water. However, for highly challenging water such as CSG produced water containing low surface tension contaminants, MD membrane with omniphobic properties are more suitable. Therefore, different groups have tried various approaches for developing new MD membranes [6,11,12].

In recent years, membranes fabricated by electrospinning have gained attention as a promising membrane for MD application [13]. Electrospinning works via the application of high voltage on a polymer solution that emits ultrafine fibers directed on an oppositely-charged collector. Electrospun membranes boast high surface area to volume ratio, controllable pore sizes and membrane thickness, high porosity and adequate mechanical strength [14]. Most polymers that are able to be dissolved in a solvent and possess adequate solution viscosity and conductivity can be electrospun into membranes. This makes electrospinning an attractive technique due to its versatility and ease of operation. Among the many applications, electrospun membranes have recently been utilized as a potential stand-alone or as a support-membrane material for desalination, water and wastewater treatment processes. Reports in literature signify the potential of nanofiber membranes for MD application.

Providing omniphobicity to the electrospun nanofiber membrane is an attractive strategy to exploit its highly porous and multi-layered structure with relatively rough surface. Among the many surface modification methods, plasma treatment is a scalable approach to provide resistant coatings on the membrane surface [15,16]. In particular, tetrafluoromethane (CF_4) plasma modification enables etching, replacement or polymer modification of the membrane, enhancing its anti-wetting properties. Several previous studies noted that CF_4 plasma was able to make fluorinated polymer surfaces exhibiting desirable properties of low surface free energy and low coefficient of friction, hence improving surface wettability [15,17–22]. Wei et al. [22] reported that fluorination and deposition layer formation on the membrane surface were the main reasons for the wettability change of the membrane surface. Recently, few research groups reported CF_4 plasma modification of phase inversion [23] and commercial [15,22,24] membranes and detailed their improved membrane characteristics and desalination performance via direct contact MD (DCMD) process. However, no study has been reported on the potential of CF_4 plasma modified nanofiber membranes. The overlapping nanofiber structure already provides relatively rough surface that gives increased hydrophobicity to the membrane. When this membrane is further exposed to CF_4 plasma treatment, the fluorination and modifying the surface into having much lower surface energy further improves the anti-wetting properties of the membrane probably by making the membrane omniphobic. This could be interesting and worth investigating for its application to challenging waters containing organic contaminants. In this study, we investigated the modification of the nanofiber membranes by CF_4 plasma treatment to improve its hydrophobic and omniphobic properties, and evaluated their performance via air gap MD (AGMD). The morphology, wetting properties for water and low surface tension liquids, and AGMD performance using real RO brine from CSG produced water with the addition of surfactant as feed of the neat and plasma modified nanofiber membranes were evaluated and compared.

2. Experimental methods

2.1. Materials

Poly(vinylidene fluoride) (PVDF, Kynar® 761, Mw =441,000 g/mol) was purchased from Arkema Inc., Australia. N, N-dimethylformamide (DMF), sodium dodecyl sulfate (SDS), diiodomethane, ethylene glycol, methanol, and lithium chloride (LiCl) were all purchased from Sigma-Aldrich. Deionized (DI) water from a Millipore Milli-Q water system was used. A commercial PVDF membrane herein referred to as C-PVDF (Durapore® - GVHP, pore size of 0.22 μm) was purchased from Millipore. All chemicals were used as received.

2.2. Dope preparation and electrospinning conditions

Homogenous PVDF solution with a concentration of 15 wt% was prepared by overnight stirring in a mixed solvent composed of DMF and acetone (4:1 by wt%). A small amount of LiCl (0.004 wt%) was added to the PVDF solution to improve its electrospinnability. Details of the electrospinning system are reported previously [13,14]. PVDF solution placed in a syringe was pushed at a flow rate of 1.5 mL/h. Continuous flow of nanofibers was obtained at an applied voltage of 18 kV and a tip-to-collector distance (TCD) of 15 cm. The nanofibers were directly collected on a grounded rotating drum collector covered with aluminum foil. The chamber humidity and temperature were maintained at 40–45% and 20–25 °C, respectively for all tests. After electrospinning, the fabricated electrospun nanofiber membranes (ENMs) were dried in an oven at 60 °C for 2 days to remove the residual solvents. After that, the electrospun membranes were subjected to hot-press post treatment to improve its stability.

2.3. CF_4 plasma modification

For plasma treatment, an IoN 40 plasma system (PVA TePla Co. Ltd.) equipped with parallel plate electrodes coupled with a radio frequency (RF) glow discharge system was utilized [23]. The electrospun membranes were first placed on the plates, then, CF_4 gas was introduced to the chamber at a flow rate of 250 standard cubic centimeter per minute (SCCM) [15]. RF glow discharge power was set at 150 W, and the treatment time was varied at 5, 10, 15, 20, 30, and 60 min (herein referred to as P/CF-5, P/CF-10, P/CF-15, P/CF-20, P/CF-30, and P/CF-60, respectively) to find the optimum treatment time [22]. After the treatment, the chamber was purged with N_2 for around 10 min at atmospheric pressure to reduce the physical adsorption of CF_4 gas on the surfaces. Thereafter, the treated electrospun membrane was taken out from the chamber and was kept in a clean