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Water desalination using graphene-enhanced electrospun nanofiber membrane via air gap membrane distillation

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ABSTRACT

This study demonstrates the preparation and desalination performance via air gap membrane distillation (AGMD) of a graphene-loaded electrospun nanofiber membrane. Different concentrations of graphene (0–10 wt%) were incorporated in/on electrospun polyvinylidene fluoride-co-hexafluoropropylene (PH) membrane to obtain a robust, and superhydrophobic nanocomposite membrane. The results showed that graphene incorporation has significantly enhanced the membrane structure and properties with an optimal concentration of 5 wt% (i.e., G5PH). Characterization of G5PH revealed membrane porosity of $> 88\%$, contact angle of $> 162°$ (superhydrophobic), and high liquid entry pressure (LEP) of > 186 kPa. These favourable properties led to a high and stable AGMD flux of 22.9 L/m^2 h or LMH (compared with ~ 4.8 LMH for the commercial PVDF flat-sheet membrane) and excellent salt rejection (100%) for 60 h of operation using 3.5 wt% NaCl solution as feed (feed and coolant inlet temperatures of 60 and 20 °C, respectively). A two-dimensional dynamic model to investigate the flux profile of the graphene/PH membrane is also introduced. The present study suggests that exploiting the interesting properties of nanofibers and graphene nanofillers through a facile electrospinning technique provides high potential towards the fabrication of a robust and high-performance AGMD membrane.

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1. Introduction

Membrane distillation (MD) is an emerging non-isothermal membrane separation technology for treating saline and hyper saline solutions such as seawater or reverse osmosis (RO) brine [1–3]. Unlike pressure-driven processes, the driving force in MD is the partial vapour pressure difference brought about by the temperature difference between the feed and permeate streams [4–7]. Since MD does not require high pressure, its fouling and scaling propensity is not as problematic as other processes, thus less pre-treatment is required. So MD can be made into compact systems and can even use non-corrosive and cheap plastic materials as

hydraulic pressure is low. So far, it presents a very promising prospect for portable and stand-alone desalination process. However, full-scale commercialisation of MD still faces three major issues: the lack of appropriate membranes, proper and efficient module design, and intensive energy consumption (if solar, waste heat or other alternative energy source is not used). The present study addresses the first issue, i.e., the lack of appropriate membranes for MD.

MD requires a hydrophobic and porous membrane to proceed with its separation process, i.e. only allowing water vapour to pass through and not the liquid water. In most MD studies including bench-scale and pilot experiments, commercially-available flat-sheet or hollow fibre microfiltration membranes are usually employed due to their hydrophobic property, adequate pore sizes, and decent porosity. However, these microfiltration membranes are not ideally-designed for MD, thus they suffer from low permeability and wetting problem in long term performance. Hence,

there is a need to design and manufacture new membranes for MD application [8–12].

Among the different membrane designs fabricated by various techniques, electrospun membranes have garnered wide interest in the recent years as potential membranes for MD due to their unique characteristics. These membranes are fabricated through an electrospinning process, wherein a high voltage is applied to a polymer solution, which is emitted into jets and form into sub-micron-sized fibres and collected as a non-woven flat-sheet membrane [13]. Electrospun membranes possess high hydro-phobicity, high porosity, high surface area-to-volume ratio and interconnected pore structure. The overlapping structure of the nanofiber provides rough nano-scale surface which leads to in-creased hydrophobicity that is ideal for the MD process. In recent years, a number of research studies are reported using electro-spinning for MD application [14–17]. Several polymers have been electrospun including polyvinylidene fluoride (PVDF), poly-vinylidene fluoride-co-hexafluoropropylene (PVDF-co-HFP), and polystyrene (PS) [14,16–19]. However, to date, continuous research efforts are still being undertaken to manufacture a robust elec-trospun membrane for long term efficient MD performance. Su-perhydrophobic membranes are being sought out as an appro-priate membrane for MD [20–23]. At having superhydrophobicity, it can lead to less wetting problem, enhanced liquid entry pressure (LEP), improved water vapour flux and high salt rejection [8,24]. Incorporation of nanofillers such as silica and carbon nanotubes (CNTs) in/on nanofibers is reported to lead to superhydrophobic electrospun membranes.

Recently, increasing interest is given to graphene as a unique nanofiller material that has interesting properties that could pro-vide additional functionalities to the host material. Graphene is two-dimensional (2D), single carbon atom composed of sp^2 ar-ranged in a honeycomb structure, and is an emerging new mate-rial used in various research fields including water treatment and purification processes [25–27]. It has high thermal stability and electrical conductivity, high mechanical stiffness, low permeability to water, and is low cost [28,29]. The very high aspect ratio and high specific surface area make graphene ideal filler that could promote better interaction with the host polymer. Water and va-pour molecules cannot penetrate via pure graphene pore due to its unique nature [30]. Graphene is particularly attractive for MD application due to its hydrophobic nature, selective sorption of water vapours, and anti-fouling properties [30–32]. Recent pro-gress on the much cheaper synthesis of graphene provides better potential for its wider use [33].

Together with the attractive properties of nanofibers, the in-corporation of graphene provides additional properties to the composite membrane such as added roughness and hydro-phobicity that leads to robust and highly efficient MD membrane. In the present study, we exploited the unique properties of gra-phene to enhance the overall properties of a polymeric nanofiber membrane towards the production of a robust superhydrophobic membrane for long-term air gap membrane distillation (AGMD) application. To the best of our knowledge, no one has reported yet on the use of graphene-incorporated electrospun nanofiber membrane for AGMD desalination. Realizing the excellent prop-erties of graphene and electrospun nanofiber membranes, their combination as MD membrane is worth exploring. Hence, the objective of this study was to determine the optimal concentration of graphene in/on the electrospun nanocomposite membrane to lead to a robust and high AGMD performance desalination mem-brane. A series of measurements, characterization and AGMD tests were performed to determine the most suitable graphene loading and membrane composition for AGMD desalination.

2. Materials and methods

2.1. Materials

PVDF-co-HFP (Mw=450,000 g/mol, Kynar Powerflex®LBG) (referred herein as PH) and N, N-dimethylformamide (DMF) solvent were purchased from Arkema Inc., Australia and Sigma-Aldrich, re-spectively. The graphene used in the present study was xGNP-C500-grade material from XG-Science, USA, which has a particle diameter of 1–2 μm, an average thickness of 2 nm and an average surface area of 500 m²/g. Ethanol was purchased from Ajax Finechem Pty Ltd. For AGMD performance test, sodium chloride (NaCl, Chem-supply) and deionized (DI) water were used. All chemicals were used as received. Commercial PVDF membrane (Durapore®-GVHP, pore size=0.22 μm) received from Merck Millipore was used as a reference for AGMD flux and salt rejection performance comparison.

2.2. Dope preparation

Neat PH solution (referred herein as PH18) was prepared by dissolving 18 wt% PH in DMF/acetone solvent (4:1 ratio) via magnetic stirring overnight. For graphene/PH solutions, a given amount of graphene (1, 3, 5, 7, and 10 wt% relative to PH; referred herein as G1PH, G3PH, G5PH, G7PH and G10PH, respectively) was first dispersed in a certain amount of DMF/acetone solution by bath sonication (Thermoline Scientific) for 1 h and then mixed with 18 wt% PH solution by magnetic stirring at 80 °C for another hour followed by stirring at room temperature for 24 h.

2.3. Electrospinning of superhydrophobic G/PH nanofiber membranes

The electrospinning set-up is explained in detail in our previous work [14]. All of the fabricated membranes were electrospun at an employed voltage, tip-to-collector distance, and feed flow rate of 10 kV, 100 mm, and 1.0 ml/h, respectively (Table S1). All nanofibers were di-rectly fabricated onto a rotating drum collector covered with aluminium foil. The polymer solution was supplied in a 10 ml syringe attached with a needle (21 G, inner diameter=510 μm) that was mounted on an adaptor. The needle kept on oscillating sideways during electrospinning and was controlled by LabView software (National Instrument). The chamber humidity (40–50%) and temperature (18–23 °C) were main-tained constant throughout the electrospinning process. After electro-spinning, the as-spun membranes were peeled off from the aluminium foil and transferred onto a baking paper and kept in a dry oven (OTWMHD24, LABEC) at 50 °C for 1 day to remove the residual solvents.

2.4. AGMD performance test

The commercial PVDF, and neat and G/PH electrospun nanofi-ber membranes were operated in a home-made AGMD set-up (Fig. 1) with a feed channel dimension of 60×35×1 mm (L×W×H), an effective membrane area of 21 cm² and an air gap thickness of 3 mm. The coolant plate was made of a stainless steel to condense the water vapour. The AGMD in a co-current flow set-up was carried out with constant inlet temperatures at the feed and the coolant sides of 60 ±1.5 °C and 20 ±1.5 °C, respectively. The feed solution was 3.5 wt% NaCl solution (conductivity of 62.0 ± 0.5 mS/cm) and the coolant fluid was tap water. The feed and coolant circulation rates were both maintained at 12 L/h.

2.5. Characterizations of the G/PH and neat PH electrospun nanofi-ber membranes

The surface and cross-sectional morphologies of graphene/PVDF-co-HFP (G/PH) nanofiber samples were observed by