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Desalination across a graphene oxide membrane via direct contact membrane distillation

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HIGHLIGHTS

- Graphene oxide immobilized membrane (GOIM) was synthesized for membrane distillation.
- GOIM showed significant enhancements in flux and mass transfer coefficients.
- GOIM was able to handle high salt concentration and exhibited excellent stability.
- Graphene oxide shows some excellent potential in desalination applications.

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ABSTRACT

We demonstrate the immobilization of graphene oxide on polytetrafluoroethylene (PTFE) membrane surface for desalination via direct contact membrane distillation. The graphene oxide immobilized membrane significantly enhanced the overall permeate flux with complete salt rejection, and the flux reached as high as 97 kg/m^2 h at 80 °C. We attribute this enhancement in flux to multiple factors including selective sorption, nanocapillary effect, reduced temperature polarization as well as the presence of polar functional groups in graphene oxide.

1. Introduction

Global demand for water is expected to grow in the oncoming decades and cost effective alternatives to desalination via conventional thermal distillation and reverse osmosis are of great interest. Membrane distillation (MD) is a membrane based thermal evaporation process that may offer energy efficient water generation at relatively low temperatures (50–90 °C). Therefore, MD can be operated effectively using low grade heat sources and solar power [1–4]. In MD, a hydrophobic porous membrane serves as a barrier between a hot feed and a cool permeate. As the heated brine passes on the feed side of the membrane, it is partially transformed to water vapor. The hydrophobic membrane prevents the passage of the liquid phase while the vapor passes through the pores to be condensed on the permeate side. Here the membrane itself is the key to flux and selectivity, and the development of novel membrane architecture is of great importance to enhance the performance of MD.

There have been significant efforts in the development of nanostructured membranes and of particular interest has been nanocarbons [5–10]. The synthesis of free-standing and silicon-supported vertically aligned CNTs membranes have been reported for reverse osmosis (RO) [11], and self-supporting bucky-paper membranes as well as interfacially polymerized bucky-papers have been used in MD [12]. Recently we have demonstrated the immobilization of nano carbons in different types of polymeric membranes to alter the solute-membrane interactions [13,14]. The physicochemical properties of nanocarbons play important roles. For example the carbon nanotubes (CNTs) provide pathways for mass transport, and the high flux has been attributed to the rapid sorption–desorption as well as atomic-scale smoothness of the CNT walls and the molecular ordering inside the nanopores [15,16]. Nanodiamonds have shown their effectiveness in the enhancement of MD performance [9].

Recently there has been much interest in graphene oxide (GO) as a material with unique electrical and optical properties [17,18]. Potential applications of GO in water desalination and purification has also been explored [19–22]. The unique structural features [23], high mechanical strength [24] and the atomic-level thickness of GO have been exploited

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to fabricate an extremely thin membrane with controlled pore size and high flux [19,20,25,26]. Molecular simulation have shown the impermeability to salt molecules along with high pure water flux [26], and GO nanosheets have demonstrated excellent antifouling properties [27]. Recently graphene oxide (GO) has been used to develop membranes containing photosensitive bacteriorhodopsin [28]. However, real world applications of GO remain a challenge because single (or multiple) graphene sheets are difficult to assemble [19].

Recently, researchers developed the novel concept of hydrophobic/hydrophilic composite membranes for MD and the requirements for enhanced MD flux were also identified based on the physical understanding of the MD process [29–32]. The physical interaction between membrane surface and the water vapor molecules changes the mass transfer resistance as well as the temperature polarization effects [30,33].

GO can be particularly attractive to MD for multiple reasons such as the selective sorption of water vapors, nanocapillary effect for selective sieving of pure water from brine and the reduction in temperature polarization. The pore chemistry of GO where the carbon atoms adjacent to the pores are preferentially hydroxylated or carboxylated are also expected to enhance flux [26]. Therefore, the objective of this research is to immobilize the GO on the surface of the hydrophobic polytetrafluoroethylene (PTFE) membrane to fabricate a high performance desalination membrane for MD. Referred as GOIM, the membrane is used for desalination via direct contact membrane distillation (DCMD).

2. Experimental

2.1. Chemicals, materials and membrane modules

Sodium chloride (NaCl), cyclohexanone and PVDF powder (mol. wt. ~500 K) were obtained from Sigma–Aldrich (St. Louis, MO), and deionized water (Barnstead 5023, Dubuque, Iowa) was used in all experiments. Single atomic layer GO was purchased from TW Nano Materials, CA. Flat 35 μm thick PTFE composite membranes with nonwoven polypropylene support were used in the DCMD experiments. The membrane had 0.2 μm pores and 70% porosity (Advantec MFS, Inc.; Dublin, CA). The DCMD test cell was fabricated from polytetrafluoroethylene (PTFE).

2.2. Experimental procedure

The experimental set up for DCMD is illustrated in Fig. 1. The set up comprised of the membrane cell with an effective membrane area of 14.5 cm^2. The cell was fitted with Viton O-rings, PTFE tubing, and PFA and PTFE connectors. The experimental systems comprised of feed and permeate peristaltic pumps (Cole Parmer, model 7518–60), high temperature water bath (GP-200, NESLAB Instruments Inc., NH) and a chiller (MGW Lauda RM6). The feed used in these experiments contained 3500–34,000 mg/L NaCl and deionized water was used to collect the permeate. The hot feed was recycled to the feed tank and the permeate was collected in the distillate tank. Inlet and outlet temperatures of the feed and distillate were continuously monitored. Viton and different PTFE tubings were used to make connections in the experimental set up. The ionic strength of the original feed solution and permeate were measured using a Jenway Electrode Conductivity Meter 4310. Each experiment was repeated at least three times to ensure reproducibility and the relative standard deviation was found less than 1%.

2.3. Fabrication and characterization of GO immobilized membrane

The fabrication of the membrane utilizes the GO dispersion in cyclohexanone and polyvinylidene fluoride (PVDF) as binder material. The ratio of these materials has been optimized for best MD performances, but not presented in this section for brevity. The preparation of optimized GOIM was as follows. Ten milligram of GO was dispersed in a solution containing 0.2 mg of PVDF powder in 10 mL of cyclohexanone via sonication for six hours of sonication. The PVDF-GO nanoflakes dispersion was then cast drop wise slowly over the PTFE membrane to ensure a uniform distribution throughout the surface. The membrane was then washed with additional acetone to remove extra PVDF from the GOIM surface. The morphology of GOIM was studied using a scanning electron microscopy at an accelerating voltage ranges from 5.00 to 8.00 kV (SEM, Model LEO 1530, Carl Zeiss SMT AG Company, Oberkochen, Germany). This was done by cutting the membranes into 0.5 cm long pieces and coated with carbon films.

Confocal Raman imaging and Raman spectra were measured using a Thermo 135 electron Nicolet Raman spectrometer. The change in hydrophilicity of the membrane surface in presence of GO was determined by contact angle (θ) measurements using an Attension apparatus (model Theta). The measurements were performed at room temperature (22 °C) using the water drop method on dry membranes. The contact angle was measured at least in 5 different locations to get the average value.

The surface roughness of the membranes was measured by atomic force microscopy (Bruker, Dimension ICON AFM) under ambient conditions. The measurements were performed in peak force tapping mode (Scansyst-Air) using a silicon nitride cantilever containing silicon probe with nominal resonant frequency of 70 kHz and nominal tip radius of 2–5 nm. Height and phase contrast data were recorded. The measurement was performed over 100 μm^2 and the average roughness was determined from the entire sample area.

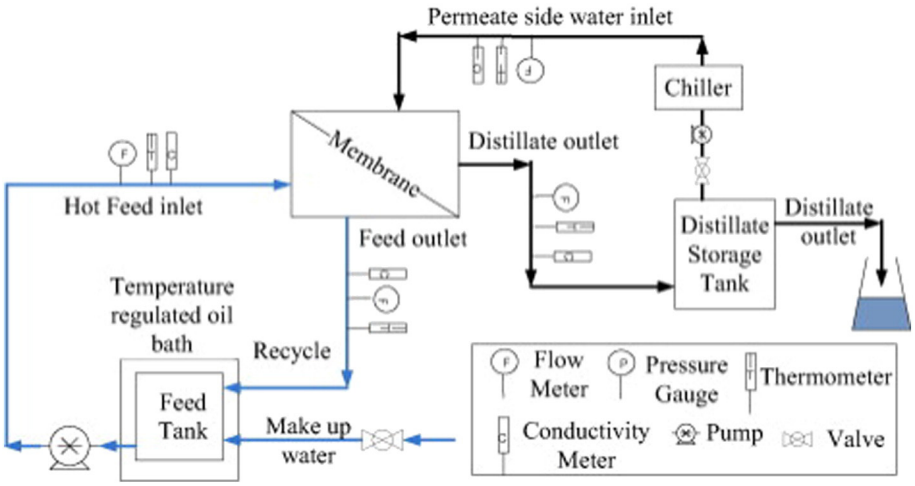

Fig. 1. Schematic diagram of the experimental set up for DCMD.