Selective hydrophilization of the permeate surface to enhance flux in membrane distillation

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ABSTRACT

This paper reports the development of novel hydrophilized membrane for water desalination using direct contact membrane distillation (DCMD). The permeate side of a porous polytetrafluoroethylene (PTFE) membrane on polypropylene (PP) support was hydrophilized by chemical treatment with oxidizing agents to enhance the rapid condensation and removal of permeated vapors. Depending upon the process conditions, permeate flux was as high as 61 L/m^2 h, and as much 73% higher than an unmodified membrane. 58% increase in overall mass transfer coefficient was also observed with the hydrophilized membrane. In short, hydrophilization of membrane surface showed enhanced flux at lower temperature, making this a more energy efficient process.

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1. Introduction

Desalination of sea and brackish water is commercially carried out by methods such as multi stage flash distillation (MSF), multiple effect desalination (MED), and reverse osmosis (RO). These techniques have their limitations such as high energy consumption and equipment cost [1,2]. At this point there is a need to develop cost effective low temperature processes that can utilize industrial waste heat and solar energy to desalinate water.

Recent studies [3] show that membrane distillation (MD) as a promising alternative that involves the transport of vapors through a micro porous, hydrophobic membranes [4,5]. The driving force is provided by the vapor pressure gradient across the membrane [6,7]. The advantage of MD is that it can be operated at relatively lower temperatures, does not require large vapor space as in MSF, is less prone to fouling than RO, can generate high purity water and can handle water with high salt concentrations. All of these advantages make it attractive for the production of high purity water where low quality industrial heat is available in the form of boiler blow downs, flue gasses, or low pressure steam [8–10]. MD has also been used with thermally sensitive food and pharmaceutical products [11]. Various modes of MD have been developed where the condensing medium varies from cold distillate to a sweep gas or vacuum [6].

MD is carried out using hydrophobic micro porous membranes to facilitate selective water vapor transport. Different membranes in flat-sheet or hollow fiber forms, made of polytetrafluoroethylene (PTFE), polypropylene (PP), and polyvinylidene-di-fluoride (PVDF) have been used in MD [12,13]. Several techniques such as phase inversion and stretching of dense films have been used to make MD membranes, and hydrophilic membranes have been surface treated to enhance hydrophobicity [14]. Composite membranes consisting sandwiched hydrophobic/hydrophilic layers has also been reported [15–21].

Despite various advantages, the potential of MD is yet to be fully realized. MD performance can be negatively affected by increased heat loss, mass transfer resistance, trapped air within membrane pores, pore wetting and temperature polarization [22,23]. Much effort has gone into developing methods for enhancing the performance of the membranes by modifying membrane surface including immobilization of nanoparticles and nano carbons [24–28]. An important consideration is the fast removal of water vapors in the permeate side of the membrane to increase the concentration gradient for mass transfer. This is applicable for all types of MD [6]. As the water vapor comes through, it needs to be rapidly condensed and removed. While the feed side of the membrane needs to be highly hydrophobic to prevent pore wetting, it is feasible to have a more hydrophilic permeate surface so that it would have higher affinity to the water vapor, and consequently facilitate its rapid removal. The objective of this research is to enhance MD flux by selective hydrophilization of the permeate side of the membrane. A more specific objective is to study this phenomenon in direct contact membrane distillation (DCMD) where pure water is used to collect the permeated water vapors.

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2. Experimental

2.1. Materials and methods

MD experiments were carried out in the DCMD mode [29]. The schematic diagram of the experimental setup is shown in Fig. 1. Typical setup consists of a PTFE membrane cell having an effective membrane area of 14.5 cm². The membrane holder had Viton O-rings, PTFE tubing, PFA and PTFE connectors, as well as pumps for feed and permeate flow. The system has been described before [30]. Constant temperature water bath (Neslab Waterbath Model GP 200, NESLAB Instruments, Inc, Newington, NH, USA) was used to maintain steady feed temperature and a bench top chiller (Poly-science LS5, Cole-Parmer, USA) was used to maintain the permeate temperature around 15–20 °C. Feed and permeate solutions were contacted in the membrane module in a counter current flow. Both the feed and permeate were recycled from their respective reservoirs using Master Flex Easy Load peristaltic pumps (Cole-Parmer, USA). The inlet and outlet membrane temperatures were monitored using temperature sensors (Four-channel Data Logging Thermometer, RS-232, Cole-Parmer, USA). Hydrophobic PTFE membrane of 0.2 µm pore size and 130 µm overall thickness with polypropylene support was obtained from Advantec (Toyo Roshi Kaish, Ltd, Japan).

2.2. Membrane hydrophilization

The membrane under study was a highly hydrophobic Teflon membrane with polypropylene support. Surface modification via chemical treatment of the polypropylene backing was carried out to enhance the hydrophilicity of the permeate side. The process was initiated with treatment with chromic acid solution which was prepared by mixing potassium dichromate ($K_2Cr_2O_7$), sulfuric acid and water in a ratio of 1:20:30 [31]. After preliminary wetting in acetone, the membrane was treated with the chromic acid solution for 1 min in an oven maintained at 60 °C. The membrane was then washed with distilled water.

The hydrophilization was characterized by measuring the contact angle of water droplet on membrane surface, Fourier trans-form infrared (FTIR) spectroscopy (Magna IR System 560, Nicolet Instrument Corporation, Wisconsin, USA) and Scanning Electron Microscope with Energy Dispersive X-ray (SEM-EDX) Spectroscopy (Leo 1530 VP, Carl Zeiss SMT AG Company, Oberkochen, Germany). All characterization was performed three times and average was reported. Performance of the hydrophilized membrane was com-pared with that of the unmodified membrane by determining the flux at different flow rates, temperature and salt concentration. After attaining equilibrium, the MD experiments were performed for a duration of 3 h, the flux was monitored every 30 min. All experiments were repeated three times and the relative standard deviation for the experiments was estimated to be within 1%.

2.3. Gas permeation test

The effective surface porosity over the effective pore length was measured by gas permeation tests reported in the literature [32]. The total molar flux per unit trans membrane pressure difference across the porous PTFE membrane can be described as

$$\frac{J_w}{\Delta p} = \frac{2}{3}\left(\frac{8RT}{\pi M}\right)^{0.5}\frac{1}{RT}\frac{r\varepsilon}{L_p} + \frac{\bar{p}}{8\mu RT}\frac{r^2\varepsilon}{L_p} \tag{1}$$

where ε is surface porosity, r is mean pore radius of the membrane, μ is gas viscosity, R is gas constant, $\bar{p}$ is the average feed and perme-ate pressure, M is molecular weight of gas, L_p is effective pore length and T is temperature (k). The first term of the equation represents the Knudsen flow and the second term the Poiseuille flow. The gas permeation flux per unit of driving force $\left(\frac{J_w}{\Delta p}\right)$ can be calculated as,

$$\frac{J_w}{\Delta p} = \frac{N_{t,w}}{A} \tag{2}$$

where $N_{t,w}$ is total molar gas permeation rate (mol s^{-1}), p is the trans membrane pressure difference across the membrane area A. The total gas permeation rate through the membrane at difference pressure was measured using a bubble flow meter. By plotting nitrogen flux $\left(\frac{J_w}{\Delta p}\right)$ as a function of mean pressure $\bar{p}$, the effective
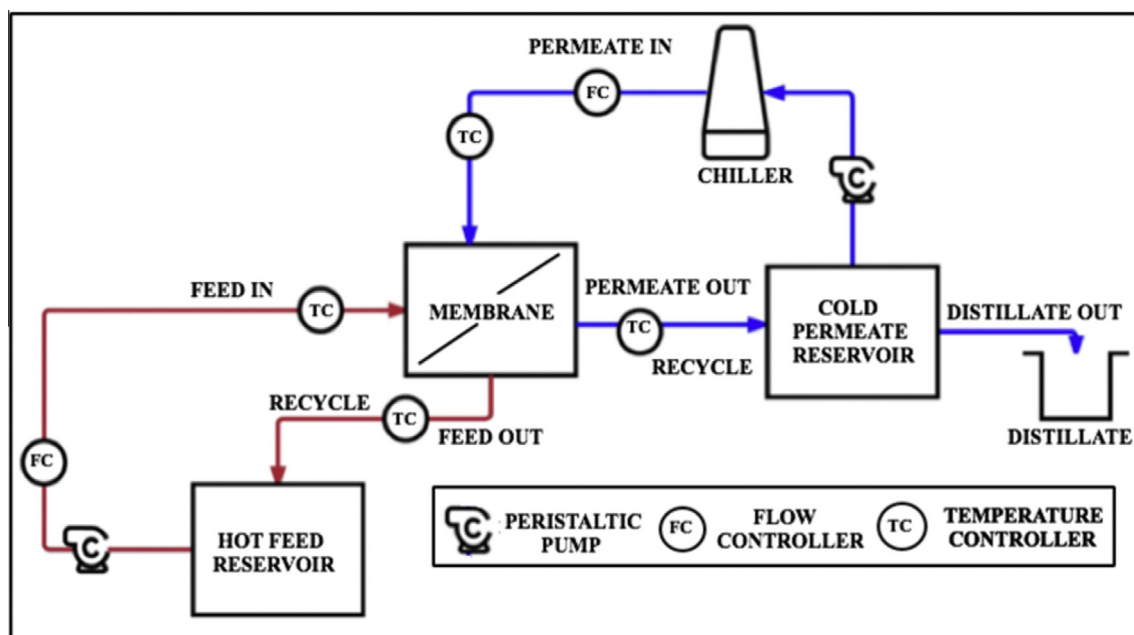

Fig. 1. Experimental setup for direct contact membrane distillation using hydrophilized membrane.