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Surface treatment of polyethersulfone membranes for applying in desalination by direct contact membrane distillation

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1. Introduction

Desalination of water resources has essential importance for not only preserving human life but also providing industrial consumptions. Various thermal and membrane technologies with different mechanisms have been used for desalination [\[1\]](#page--1-0). More than 60% of the world desalinated water is produced from sea water by thermal methods such as multi-stage flash (MSF) and multiple effect distillation (MED), which simulate the water cycle by converting the heated sea water to fresh water via condensation. Desalination can also be performed by membrane processes such as reverse osmosis (RO) and membrane distillation (MD) [\[2\]](#page--1-0). The pressure difference across the membrane supplies the driving force in the reverse osmosis process. However, in membrane distillation, the driving force is the difference between the vapor pressure on both sides of the membrane [\[3,4\].](#page--1-0) The main advantages of MD compared to other desalination processes are its high selectivity for nonvolatile compounds (almost total retention of ions, macromolecules, colloids, etc.), working at low temperatures and pressures, and possibility to be coupled with low-grade waste energy resources. Various configurations of this process such as direct contact (DCMD), air gap (AGMD), sweeping gas (SGMD), vacuum (VMD), permeate gap membrane distillation (PGMD), and material gap membrane distillation (MGMD) have been the subjects of many researches [4–[11\].](#page--1-0) The process has not been fully commercialized yet mainly due to the high membrane price as well as relatively lower

In the present work, the surface of polyethersulfone (PES) membrane is treated by using tetraethylorthosilicate (TEOS) and trimethylchlorosilane (TMSCl) as grafting agents. Attenuated total reflection infrared spectroscopy (ATR-IR), scanning electron microscopy (SEM) coupled to an energy-dispersive X-ray spectrometer (EDX), atomic force microscopy (AFM), and optical contact angle measurement (OCA) are applied to identify and characterize the membranes. The water contact angle of as high as 150° is obtained for the treated membranes. The modified membranes are examined for desalination using a direct contact membrane distillation setup. Effects of different conditions in membrane preparation as well as operating parameters are investigated. A separation factor of 99.7% and comparable permeate fluxes to those of a commercial polytetrafluoroethylene (PTFE) membrane are obtained.

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fluxes compared to those of the well-established commercialized desalination processes such as reverse osmosis [\[12,13\]](#page--1-0).

Because of the significant role of membrane in the operation costs, efforts are made to obtain economical membranes. In general, membranes used in MD process should have low resistance against mass transfer and low thermal conductivity to avoid heat losses. Moreover, the membranes must exhibit good thermal stabilities at high temperatures and proper resistance against acidic and basic chemicals.

One of the advantages of DCMD process is that it is not restricted by precipitating of organic and inorganic materials as the membrane works at atmospheric pressure and does not require elevated temperatures. Compared to high pressure driven processes such as RO, the membrane fouling and scaling effects are less important problems in DCMD when the NaCl concentration is lower than 4.5 wt.% [\[2,14](#page--1-0)–16].

Ohta et al. [\[17\]](#page--1-0) found higher permeabilities and thermal efficiencies for a partially hydrophilic fluorocarbon compared to those of a partially hydrophilic silicon membrane. Khayet et al. [18–[21\]](#page--1-0) proposed a porous type hydrophobic/hydrophilic composite membrane for applying in DCMD by a phase inversion method using surface modifying macromolecules (SMMs). In a similar study, Essalhi et al. [\[22\]](#page--1-0) used a composite hydrophobic/hydrophilic membrane fabricated by a fluorinated SMM and a hydrophilic host polyetherimide polymer. Zhang et al. [\[23\]](#page--1-0) developed a modification method for hydrophobizing Torlon® polyamide-imide (PAI) membranes by surface modifying of PAI with a silane coupling agent, 3-aminopropyltrimethoxysilane (APTMS), and a perfluro-compound (Fluorolink S10). Wu et al. [\[24\]](#page--1-0) in their study provided a composite hydrophobic membrane of cellulose acetate and cellulose nitrate by radiation grafting polymerization and plasma

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Fig. 1. Schematic diagram of experimental DCMD setup; 1) feed compartment, 2) permeate compartment, 3) membrane module, 4) feed vessel, 5) permeate (cooling) vessel, 6) water bath, 7) heater, 8) cooling jacket, 9) peristaltic pumps, 10) thermometers, 11) sampling valves.

polymerization to enhance the permeability. Each of these treatment procedures has its own advantages and limitations. However, because of demanding costly polymeric membranes and/or pretreatment steps, the high price of prepared membranes is still an impediment against their mass production.

Polyethersulfone (PES) is a low-price commercial membrane, which is widely used in separation processes due to its excellent chemical stability, mechanical strength and ease of fabrication by phase inversion methods [\[25\].](#page--1-0) However, owing to the presence of etheric bonds in the PES chains, this membrane demonstrates partial hydrophilic characteristics and cannot be applied directly in the membrane distillation. Therefore, some surface treatments are required to modify the PES membranes for using in such an application. In a work by Wei et al. [\[26\]](#page--1-0), the surface of asymmetric PES membranes were modified by CF_4 plasma treatment. DCMD tests of both flat and hollow fiber treated membranes demonstrated high water flux and salt rejection for desalination purposes.

In the present study, in order to improve the performance of the PES membrane in desalination process, a technique is applied to graft trimethylchlorosilane (TMSCl) on the membrane surface. The treated membranes are characterized and the effects of various treatment parameters on their physical and chemical properties of the treated membranes are examined. The performance tests are performed on a direct contact membrane distillation setup, and the results are compared with those of a commercial PTFE membrane.

2. Experimental

2.1. Materials

Polyethersulfone (PES) (Ultrason E6020, Mw $= 58,000$) was supplied from BASF, Germany. Polyvinylpyrrolidone (PVP) (K90, Mw = 360,000), anhydrous N, N-Dimethylacetamide (DMAc), anhydrous ethanol, solution of 32 wt.% ammonium hydroxide (NH4OH), isopentane, and chloride sodium (NaCl) were purchased from Merck, Germany. Commercial PTFE membrane was supplied from Sartorius Stedim Biotech, UK. Trimethylchlorosilane (TMSCl) was purchased from Fluka, Switzerland. Tetraethylorthosilicate (TEOS) was purchased from Aldrich, USA. All materials were used as they received without further treatments.

2.2. Experimental setup

The applied DCMD setup consists of a round-shape module with two cylindrical compartments for the feed and permeate streams. Each compartment (volume $= 110$ cm³, inside diameter $= 3.7$ cm) has an inlet on the side wall and an outlet near the junction plane for circulating

Fig. 2. Schematic of surface treatment reactions.

Fig. 3. ATR spectra of treated membrane surface.

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