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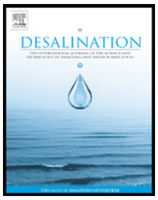


Effects of hydrophilic CuO nanoparticles on properties and performance of PVDF VMD membranes

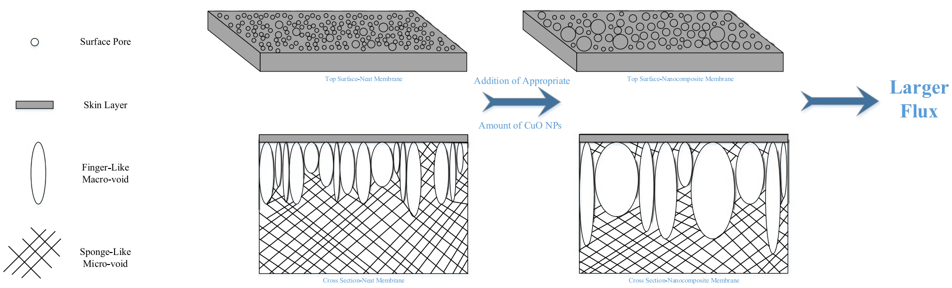
Mohammadali Baghbanzadeh, Dipak Rana, Takeshi Matsuura, Christopher Q. Lan *

Department of Chemical and Biological Engineering, University of Ottawa, 161 Louis Pasteur Private, Ottawa, Ontario K1N 6N5, Canada

HIGHLIGHTS

- Addition of 2.0 wt.% CuO NPs to PVDF membrane resulted in 153.4% increase in VMD flux.
- Salt rejection was not compromised (99.9% or higher).
- Membrane pore size increased from 82.2 to 110.4 nm.
- Contact angle increased from 78.1° to 91.6°.
- LEP_w was in the range of 3.0 to 4.9 bar, suitable for VMD operations.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, composite membranes of hydrophilic CuO and $CaCO_3$ nanoparticles and polyvinylidene fluoride (PVDF) were developed by phase inversion method. The fabricated membranes were subjected to different characterizations including morphology study, pore size, porosity, and thickness measurement, wettability and surface roughness analysis. The membrane performance was examined in terms of pure water flux in vacuum membrane distillation (VMD), salt rejection, and liquid entry pressure of water (LEP_w). It was found that the membrane performance was optimized when 1.0 to 2.0 wt.% of CuO nanoparticles were embedded into the PVDF matrix via enhancing the membrane structure through enlarging surface pores and thickening the finger-like layer (in other words, thinning of the sponge-like layer). As a result, flux increased by 153.4% at the feed temperature of 27.5 °C and vacuum pressure of 1.2 kPa, when 2.0 wt.% of the CuO nanoparticles were embedded in PVDF. Membrane selectivity did not drop as a result of the CuO nanoparticles incorporation and was more than 99.99%. All the nanocomposite membranes showed reasonable contact angle and $LEP_{w,}$ which proved appropriateness of the fabricated membranes for VMD application. Regarding the type of hydrophilic nanomaterials, CuO demonstrated better performance than $CaCO_3$ in terms of membrane permeability improvement.

1. Introduction

The increase in water demand for domestic, agricultural and industrial uses and a remarkable reduction in desalination costs due to the technological improvements resulted in much attention toward saline water desalination technologies during the last few decades. Generally, desalination technologies could be divided into three different categories including: 1) Thermal processes such as Multi-stage Flash Distillation (MSF), Multiple Effect Distillation (MED), and Mechanical Vapor

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Abbreviations: EDX, electron dispersion spectroscopy; FO, forward osmosis; LEP, liquid entry pressure; MD, membrane distillation; MED, multiple effect distillation; MF, microfiltration; MSF, multi-stage flash distillation; NF, nanofiltration; NP, nanoparticle; PP, polypropylene; PVDF, polyvinylidene fluoride; RO, reverse osmosis; SEM, scanning electron microscopy; UF, ultrafiltration; VC, mechanical vapor compression.

* Corresponding author.

E-mail address: Christopher.Lan@uottawa.ca (C.Q. Lan).

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Compression (VC), 2) Membrane processes including Reverse Osmosis (RO), Forward Osmosis (FO), Ultrafiltration (UF), Microfiltration (MF), Nanofiltration (NF), and Membrane Distillation (MD), and 3) Hybrid processes combining different individual processes to enhance the total efficiency and to mitigate environmental liabilities.

It has been reported that around 63.7% of the produced pure water from desalination technologies is generated through membrane-based technologies while the remaining is achieved by thermal processes [1]. RO is now considered as the world's leading process desalination [1,2], due to its relatively low specific energy consumption which would result in a lower pure water production cost.

MD is considered as an emerging technology which is claimed to become competitive with RO soon [2]. Table 1 presents a comparison between the RO and MD technologies in terms of process characteristics. It seems to be evident that MD has potential to compete in the desalination market provided that a high performance membrane is fabricated and the entire MD process is appropriately designed to minimize the thermal energy consumption.

Nanocomposite membranes demonstrated to have great potential in improving the membrane performance in terms of flux, rejection, antifouling characteristics, thermal, mechanical, and chemical stability in membrane water treatment including ultrafiltration [3–5], microfiltration [6–8], nanofiltration [9–11], reverse osmosis [12–14], and forward osmosis [15–17]. To this end, different nanomaterials such as SiO_2, carbon nanotubes (CNTs), TiO_2, Al_2O_3, $CaCO_3$, Ag, and nanozeolites have been used [5,16,18–23]. Nonetheless, very little information is available on the effects of different nanoparticles on the properties and performance of MD membranes even though some of the pioneering works have shown great potential of nanocomposite membranes for MD [23–25]. For instance, Gethard et al. [24] used carbon nanotubes in a polypropylene (PP) hollow fiber membrane and applied the prepared membranes in a Sweep Gas Membrane Distillation (SGMD) process and obtained almost 83.3% increase in the flux when a solution of NaCl and $MgSO_4$ was used at 80 °C as the feed. Hou et al. [23,25] used hydrophobic modified $CaCO_3$ as the nano-additive to prepare a nanocomposite membrane of PVDF and $CaCO_3$ and employed those membranes in a Direct Contact Membrane Distillation (DCMD) configuration. According to their results and for a NaCl solution of 35 g/L, around 14.9% increase in the flux was observed when hollow fiber membranes were used at a feed temperature of 80.5 °C [23], while almost 30.8% increase in the flux was obtained for the flat sheet membranes at 83 °C [25].

To improve the performance of MD membranes via the incorporation of nanomaterials, appropriate selection of nanoparticles seems to be a key factor. Typically, nanoparticles can be divided into two different categories, hydrophobic and hydrophilic nanoparticles. It is usually assumed that the incorporation of hydrophobic particles into the membrane matrix results in a more hydrophobic membrane surface while the effect will be reversed by the incorporation of the hydrophilic ones. On the other hand, it has been demonstrated that hydrophilic nanoparticles are able to change the solvent/non-solvent exchange rate in the phase inversion process, which may result in a membrane of improved morphology. [10,11,26–28].

Table 1
The different features of reverse osmosis and membrane distillation in a desalination process.

Desalination process	RO	MD
Fouling & scaling potential	High	Low
Feed pre-treatment	Necessary	Could be ignored
Handling the high concentration feed	Sometimes fails	Able
Recovery ratio	Limited (increase in osmotic pressure with concentration)	Depends on feed temperature and complexity of the process
Brine disposal	Depends on the recovery ratio	Depends on the recovery ratio
Electrical energy consumption	High	Negligible
Thermal energy consumption	Negligible	High
Operating conditions	Harsh	Mild

In this work, an attempt is made for the first time to develop mixed-matrix membranes by incorporating a hydrophilic nanoparticle, i.e., CuO nanoparticle, with polyvinylidene fluoride (PVDF). In a previous study, we have demonstrated that the PVDF membranes are appropriate for MD [29] even though PVDF's contact angle is less than 90° and it is commonly accepted view that MD requires a contact angle of 90° [30]. In this study, we further demonstrated that incorporating hydrophilic CuO nanoparticles with PVDF could result in membrane of sufficient liquid entry pressure of water (LEP_w) for Vacuum Membrane Distillation (VMD) with improved flux and satisfactory rejection.

Among the MD configurations which have been universally accepted, such as Direct Contact Membrane Distillation (DCMD), Air Gap Membrane Distillation (AGMD), Sweep Gas Membrane Distillation (SGMD), and Vacuum Membrane Distillation (VMD), the last one is selected in this study, since VMD is able to generate the highest achievable driving force for a given feed temperature. Moreover, VMD seems to be more economical from the view point of energy consumption for a given driving force. As an illustrative example, according to Cabassud et al. [30], 1.3 kWh/m^3 of electrical energy is required to generate a vacuum pressure of 100 Pa at the permeate side. If water at an ambient temperature of 25 °C, which has a saturation pressure of 3.166 kPa, is used as the feed for VMD at a vacuum pressure of 100 Pa, the driving force would be 3.066 kPa. However, according to Al-Obaidani et al. [31], for every 1 °C temperature increase in feed temperature, around 1.82 kWh/m^3 thermal energy is required. Therefore, to obtain the same driving force in a DCMD configuration using the same water at ambient temperature of 25 °C as both the coolant and the source of feed water, the feed needs to be heated up to 36.9 °C (saturation pressure 6.232 kPa), which means around 21.7 kWh/m^3 thermal energy needs to be consumed. In other words, the thermal energy required to obtain the same driving force is almost 1600.0% that of the electrical energy required for each cubic meter of the permeate product in a VMD process in this particular case.

2. Experimental methods

2.1. Materials

Polyvinylidene fluoride (PVDF) of different molecular weights, Kynar® 740, (Pellet, melt viscosity: 1850 ± 250 Pa.s; melting temperature: 160.1 °C) and Kynar® HSV900 (Powder, melt viscosity: 4930 Pa.s; melting temperature: 165.1 °C) were supplied as the host polymer by Arkema Inc. (Philadelphia, PA). To measure the melt viscosity, ASTM D3835 at 232 °C was employed. Anhydrous N, N-dimethylacetamide (DMAc) as the solvent was purchased from Sigma-Aldrich with the purity of 99.9%. Hydrophilic spherical CuO and $CaCO_3$ nanoparticles were purchased from Skyspring Nanomaterials Inc. CuO nanoparticles had a purity of 99+% with the size of 40 nm, and $CaCO_3$ nanomaterials 97.5% and 15–40 nm. NaCl and n-butanol were supplied by Fisher Scientific and used as received.

2.2. Membrane fabrication

To fabricate the membranes, phase inversion method was employed, and the casting solution and suspensions were prepared as follows: