Desalination 446 (2018) 70–82

Contents lists available at ScienceDirect

Desalination

journal homepage: www.elsevier.com/locate/desal

Robust superhydrophobic electrospun membrane fabricated by combination of electrospinning and electrospraying techniques for air gap membrane distillation

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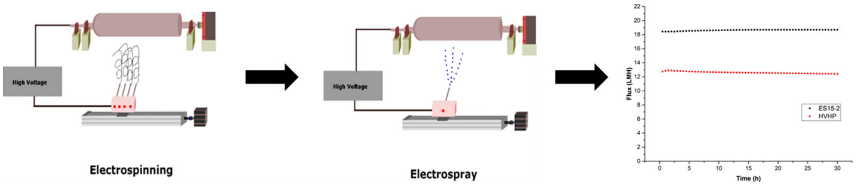
GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Electrospinning
Electrospray
Heavy metal treatment
Air gap membrane distillation
Superhydrophobic
Bead structure
Alumina NPs
Self-cleaning membrane

ABSTRACT

Membrane pore wetting is the main problem hindering long term stability of permeate flux quality in membrane distillation (MD) applications. A superhydrophobic membrane with micro and nanostructured surface features can offer a unique solution to resolve this issue. Thus, a modified electrospun membrane was fabricated using a combination of electrospinning and electrospraying. The membrane surface hydrophobicity was enhanced by constructing a beaded structure from spraying a mixture of non-fluorinated alumina (Al_2O_3) nanoparticles (NPs) mixed with low concentration of PVDF polymer on an electrospun base membrane made from PVDF. The results revealed that a rough surface with a hierarchical structure can be constructed, which could not only enhance the membrane hydrophobicity, but also further enhance the permeate efficiency by improving parameters such as flux and rejection. Additionally, the membrane hydrophobicity could be further tuned by controlling the bead spinning volume. Our study shows that the modified membrane with 7.8 μm beads layer thickness has boosted the liquid entry pressure (LEP) by 61% from 15.5 psi and the water contact angle to 154°. The performance of modified membranes with different spraying volume (1–5 ml) along with the neat electrospun and commercial membranes were examined in an air gap membrane distillation (AGMD) application for 5 h using a 2.5 wt% of synthetic heavy metal solution as a wastewater model. Then, the optimized superhydrophobic membrane with 2 ml spinning volume (ES15–2) was further tested in comparison with the commercial membrane during long-term operations (30 h) using 3.5 wt% of mixed heavy metals. The flux was 18.67 LMH ($l\,m^{-2}\,h^{-1}$) for modified membrane (ES15–2) compare with 12.62 LMH for commercial PVDF membrane during 30 h of long-term operation with feed and coolant temperature at 60 °C, 20 °C, respectively. The present superhydrophobic membrane fabricated by a combined electrospinning/electrospray method shows high potential for MD applications.

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https://doi.org/10.1016/j.desal.2018.09.001
Received 29 June 2018; Received in revised form 30 August 2018; Accepted 2 September 2018

1. Introduction

Membrane distillation (MD) is an emerging separation process which has been applied to different sectors, such as desalination of sea water, brackish water and removal of pollutants from wastewater. MD can play a significant role in treatment of wastewater polluted with heavy metals, which is a major environmental concern threatening public health worldwide. This is due to the unique advantages MD possesses, such as very high rejection of non-volatile compounds, moderate operation conditions such as temperature and pressure, lowered stress on membranes compared with pressure driven separation processes [1–3]. Nevertheless, MD experiences some obstacles to implementation in wastewater treatment, such as membrane durability (pore wetting) and relatively low permeate flux [3,4].

MD is a thermal process (non-isothermal) where the permeate flux is achieved through a driving force created by a difference in a vapour pressure across a porous hydrophobic membrane [5]. Air gap membrane distillation (AGMD), which is one of four MD configurations: direct contact membrane distillation (DCMD), vacuum membrane distillation (VMD) and sweep gas membrane distillation (SGMD), has gained much attention. AGMD configuration functions by the transfer of vapour from the hot feed solution, which is in contact with the hydrophobic membrane surface, to the cold condenser surface via an air gap [5,6]. AGMD offers a unique solution to mitigate the heat lost by conduction in DCMD applications by introducing an insulating air gap between the membrane and the cooling plate [5,7]. However, AGMD suffers from low permeate flux compared with DCMD due to increase mass transfer resistance caused by the separating air gap [8].

To overcome these obstacles, extensive investigations are needed in the membrane fabrication sector to fabricate an adequate membrane. Recently, the electrospinning method, which uses high voltage to fabricate an electrospun membrane, has been increasingly investigated as a unique method for production of membranes with high hydrophobicity and permeate flux. This is due to controllable fibre size, which allows to enhance the membrane hydrophobicity and porosity compared with other fabrication techniques. However, membrane wettability, which is related to pore wetting, is still the greatest challenge to commercialization of MD [9]. This is due to the intrinsic properties of the polymer used in the fabrication process, such as polytetrafluoroethylene (PTFE), poly (vinylidene fluoride) (PVDF) which lacks superhydrophobic properties. Therefore, electrospun membranes fabricated from these polymers need further modification [3].

Generally, two techniques can be utilized to fabricate superhydrophobic membrane, either by increasing the membrane surface roughness of a low surface energy material or by lowering the surface energy of rough surface membrane [10,11]. Many researchers have successfully increased electrospun membrane hydrophobicity by embedding the nanoparticles within the polymer dope solution to increase fibre roughness and lower the surface energy such as: PVDF-PTFE-CNT [12], PVDF-SiO_2 [13], PVDF-PTFE-TiO_2 [14], PVDF-PTFE-GO [15], PVDF-Al_2O_3 [16], PVDF-Clay [17], PSF-Cera flava [18]. Among them, Al_2O_3 NPs possess excellent thermochemical properties, low toxicity and are cost-effective materials with easy chemical surface functionalization by covalent bonds due to abundant OH groups on the NPs surface [19]. Nevertheless, Al_2O_3 has relatively high thermal conductivity around 28 W/m K [19]. This might have slightly negative effect especially in the DCMD application due to increase the membrane thermal conductivity which lead to increase the heat loss by conduction.

Despite all the efforts to embed the NPs in the nanofibres structure, membrane wettability is still one of the main challenges which need to be addressed especially over long-term operation. Inspired by the Lotus effect, a superhydrophobic membrane with WCA above 150 °C and lower sliding angle can be fabricated to overcome pore wetting, in which a hieratical structure of the surface created by micro- and nanostructures can enhance surface hydrophobicity by introduction of air pockets between the rough surface and water drop. In general, different techniques can be used to achieve this goal, such as layer-by-layer [20,21], chemical vapour deposition [22], spray-deposition [3] and electrospray [23]. Among them, electrospray is a simple method due to less steps needed compared with other techniques. Moreover, it can be integrated successfully with the electrospinning method to fabricate membrane with one-step. The advantage of this integration technique is fabricating a superhydrophobic membrane to mitigate pore wetting. However, the biggest hurdles are the stability of the spraying material on the membrane surface and maintaining membrane flux. Few studies have been investigated applying spraying technique for MD application. For example, Zhang et al. [24] explored the effect of NPs concentration in the spraying mixture of SiO_2 NPs and polydimethylsiloxane (PDMS) on water contact angle (WCA) and liquid entry pressure (LEP) using the air brush technique on flat sheet PVDF membrane made by phase inversion. The results revealed that an increase of SiO_2 NPs concentration in the spray mixture from 0 to 1.5 wt% led to an increase in LEP by 19.5%, WCA by 45.8% from 33.3 psi and 107°, respectively. However, the permeate flux suffered a reduction of around 38% from 13 LMH, when coating the neat membrane with 1.89 μm thickness, using DCMD application in which 70 °C and 20 °C was used as a feed and coolant temperature, respectively. In another study, Shaahbadi and his co-authors [23] investigated an electrospray mixture of TiO_2 NPs with poly vinylidene fluoride-*co*-hexafluoropropene (PH) polymer on a PH electrospun membrane. Their results revealed that the modified membrane used in DCMD with a top electrosprayed layer of 25 μm over 100 μm of base membrane had a higher WCA around 162° and water flux 38 LMH. However, the modified membrane had a low LEP (1.1 bar) which they explained was due to possess the membrane high pore size around 0.7 μm. Very recently, Makanjuola et al. [3] fabricated a superhydrophobic electrospun membrane with WCA of 155° and LEP of 22 psi. The electrospun membrane was fabricated by integrating the hydrophobic microparticles (teflon oligomer) with the membrane structure made from poly (vinylidenefluoride-*co*-hexafluoropropylene) nanofibers through pumping the microparticles into the electrospinning chamber every 10 min. This resulted in highly attached microparticles with the nanofibres. However, low permeate flux was recorded about 7 LMH with membrane mean pore size 0.57 μm and membrane thickness 30 μm for DCMD application using 60 °C and 25 °C as feed and coolant temperature, respectively.

In this work, a novel approach was implemented to fabricate a superhydrophobic membrane with beaded surface features through one step production by combining electrospinning and electrospray techniques. Spraying volume of nonfluorinated superhydrophobic Al_2O_3 nanoparticles, which was dispersed in a solvent mixture (DMF: Acetone) and low concentration of PVDF polymer, were investigated in term of membrane morphology and performance. Additionally, membrane morphology and performance were characterized using scanning electron microscopy (SEM); water contact angle (WCA); sliding angle (SA); liquid entry pressure (LEP); mean, minimum and maximum pore size; tensile test; and thermal properties. Moreover, membrane performance for long duration operations (30 h) compared with a commercial membrane was also accomplished.

2. Materials and methods

2.1. Materials

Polyvinylidene fluoride pellets (Mw = 275,000 g/mol), alumina (Al_2O_3) NPs (Mw = 101.96, particle size = 13 nm), hexadecyl trimethyl ammonium bromide (HTAB), dimethylformamide (DMF), acetone, toluene, ethanol, isopropanol were obtained from Sigma-Aldrich, UK. Isostearyl acid was supplied by Nissan Chemical Industries. Cadmium nitrate tetrahydrate, zinc nitrate hexahydrate, lead (II) nitrate, copper nitrate trihydrate, and nickel nitrate hexahydrate were purchased from Fisher Scientific. PVDF commercial