Electrospun PVDF nanofibre membranes for desalination of brackish water in membrane distillation

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ABSTRACT

Membrane distillation has emerged as a highly efficient process in desalination of saline water. However, this process is affected by wetting of membrane pores and the low porous nature of membranes, causing low rate of water recovery. This study sought to mitigate these challenges by synthesizing highly porous and super-hydrophobic polyvinylidene fluoride (PVDF) nanofibre membranes modified with organically functionalized silica (SiO_2) nanoparticles (NPs). The highly porous nanofibre membranes were synthesized using an electrospinning technique. The membranes were found to be mechanically strong and porous. Addition of the organically modified SiO_2 NPs to the electrospinning solution resulted in the formation of super-hydrophobic membranes. These membranes were tested for their salt rejection capacity and water fluxes. They were found to reject the salt ions from water at high efficiencies (> 99%) with water fluxes ≈ 64 litres per hour indicating their capacity to produce high purity water in large quantities.

Keywords: Membrane distillation, porous, PVDF nanofibre membranes, silica nanoparticles, super-hydrophobic

1 INTRODUCTION

While 70% of the earth is covered with water, only 0.03% is available as fresh water. The rest is saline/seawater [1]. As such, the sustainable purification of saline water has become critical in order to produce abundant water that could be supplied for consumption in adequate amounts. Such purification systems include membrane distillation (MD), which is a cost-effective and highly efficient process of water desalination [2].

The membrane distillation (MD) process has received remarkable attention in membrane technology developments [3]. In the MD process, water is transferred through the membrane in the form of the water vapour induced by the temperature difference across the hydrophobic membrane. Therefore in MD, the membrane should be highly porous for enhanced water recovery [4], hydrophobic to prevent membrane wetting [4] and water passes through the membrane as water vapour for a successful separation [5].

Although, such conditions are a key solution to MD, wetting and porosity are the critical challenges in MD [6]. The membrane wetting in MD occurs when the membrane used is hydrophilic or when the applied pressure is greater than the liquid entry pressure (LEP) due to the less porous membrane [7]. Munirasu et al, demonstrated that PVDF membrane coagulated in an alcohol bath as a non-solvent, produced a super-hydrophobic membrane with contact angle (CA) >150°, which is a key solution in prevention of membrane wetting [8]. However, this preparatory method compromises the mechanical strength of the membrane.

There are no scientific findings on MB membranes with combined super-hydrophobicity and good mechanical stability that are super-porous to prevent the occurrence of membrane wetting while maintaining high rejection and high water flux. This study sort to concurrently address wetting, porosity and mechanical properties of the membranes used in MD. This was achieved through the synthesis of the electrospun super-hydrophobic PVDF nanofibre membrane decorated with organically modified silica (SiO_2) nanoparticles (NPs).

2 EXPERIMENTAL

2.1 Synthesis of membranes

The membranes were synthesized using the electrospinning technique. The PVDF nanofibres were prepared at the following conditions: 15% (w/v) polymer concentration,, the syringe injection flow rate of 1.0 mL/h,

a distance of 14 cm between the aluminium foil and the tip of the needle, and a voltage of 23 kV at room temperature. To modify the properties of the membranes, they were embedded with the 1.0% (w/v) organically functionalized SiO_2 NPs to enhance their super-hydrophobicity in an in-situ electrospinning of the polymer containing the NPs.

2.2 Characterization

The surface morphology, contact angle, mechanical strength and pore sizes of the membranes were analysed using a scanning electron microscope (SEM), a drop shape analyser and X-ray scattering equipped with the universal extensional fixture and liquid expulsion Capillary Flow respectively.

2.3 Membrane performance

The performance of the PVDF nanofiber membranes modified with organically functionalized SiO_2 NPs was tested on a direct contact membrane distillation (DCMD) lab-scale set-up using NaCl solution (concentration ≈ 30 x 10^3 mg/L) which is slightly above the total concentration of dissolved salts in brackish water. The feed temperature was varied from 20 °C to 80 °C while the permeate temperature was kept at 20 °C in a counter mode. The feed and the coolant solutions were used at the flow rate of 0.75 L/min. The water conductivities were measured using a Shimadzu conductivity meter to determine the salt rejection efficiencies. The water flux was measured by measuring the amount of water permeated through the membrane in the form of vapour. The following equation was thus used to calculate the water flux (J_{water}):

$$J_{water} = \frac{\Delta V}{\Delta t A_m} \quad (1)$$

3 RESULTS AND DISCUSSION

3.1 Scanning electron microscopy analysis of the membranes

SEM was used to determine the surface morphology and cross-sectional view of the PVDF nanofiber membranes (**Fig. 1**). Uniform non-beaded nanofibres were observed at the following optimized electrospinning conditions: (a) 15% (w/v) polymer concentration in a mixed solvent system of acetone:DMAc with a ratio of 56:44, (b) a voltage of 23 kV, (c) a flow rate of 1.0 mL/h, and (d) a distance of 14 cm between the tip of the needle and the rotating collector (**Fig. 1**). 15% (w/v) was found to be the characteristics concentration where electrospinning of PVDF was possible. At the voltage of 23 kV and distance of 14 cm, a sufficient electric field which was generated to overcome the surface tension of the PVDF, hence produce uniform nanofibres. The addition of 1.0% SiO_2NPs relative to PVDF affected the mophology of the resulatnt nanofibres, hence produced slightly beaded PVDF nanofibre membranes. The change in morphology was due to the polymer stream breakdown and failure to stabilize the polymer jet bending which affects the molecular entanglement [9]. These effects were caused by the SiO_2 NPs that affected the viscosity and the overall concentration of the electrospinning solution. The corresponding intertwined structures that were observed at the cross-sectional SEM images indicated that the nanofibres were highlyporous.

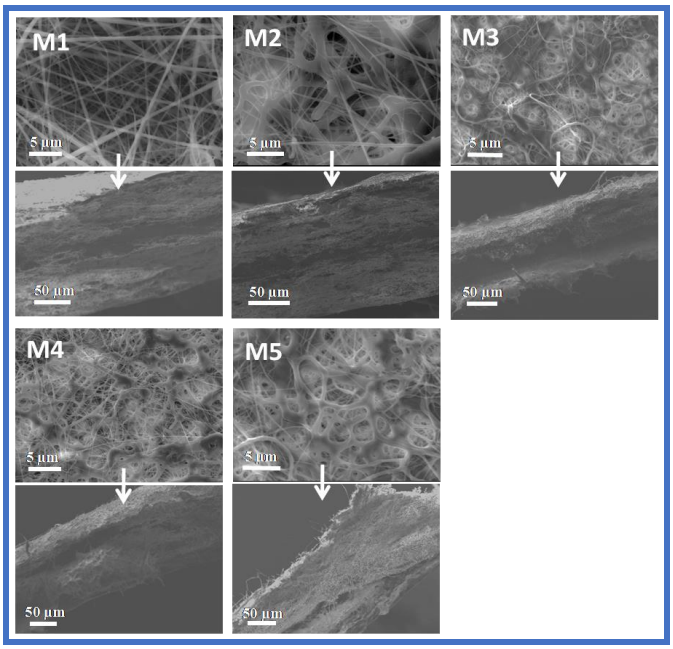

Fig. 1: SEM images of the PVDF electrospun nanofiber membranes with SiO_2 NPs. (M1) Unmodified membrane, (M2), (M3), (M4), and (M5) membrane modified with pristine SiO_2 NPs, ODTS functionalized SiO_2 NPs, OTMS functionalized SiO_2 NPs, and Cl-DMOS functionalized SiO_2 NPs respectively.

3.3 Contact angle and tensile strength measurements

The contact angle and tensile strength measurements of the membranes are presented on (**Fig. 2**) The pristine PVDF membranes were slightly hydrophobic to super-hydrophobic due to addition of SiO_2 NPs (**Fig. 2**). The advantage of a super-hydrophobic process is that it does not

only possess anti-wetting behaviour but also assist in the self-cleaning of the membrane by a process called "lotus effect", which is known to prevent membrane fouling by self-cleaning mechanisms [10]**.** The membranes with high contact angles were reported in other recent findings where alcohols were used as non-solvents during phase inversion [8]. However, their critical challenges are compromised mechanical strength and less porous membranes prepared in phase inversion process.

The Young's modulus of the nanofibre membrane was calculated from the elastic region of the plots of the stress-strain graphs. The Young's modulus of M1, M2, M3, M4, and M5 were found to be 377 ± 12 MPa, 358 ± 10, 331 ± 5 MPa, 338 ± 8 MPa and 341 ± 6 MPa respectively. The reduction of the mechanical strength of the PVDF membrane upon addition of the SiO_2 NPs was associated with the formation of the beaded nanofibres that were accompanied by spraying, thus weakening the resultant nanofibres.

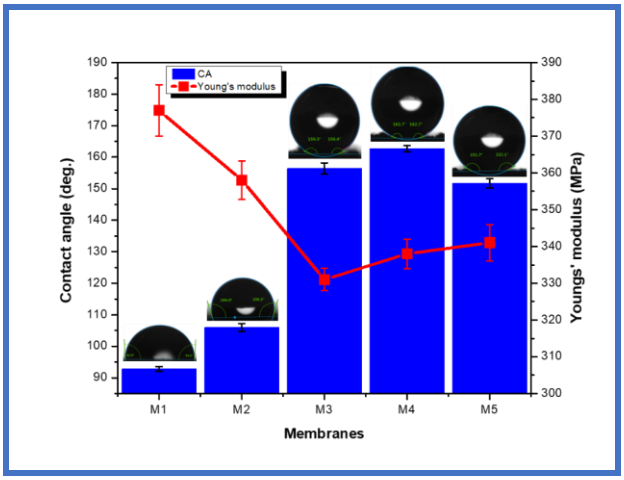

Fig. 2: Contact angle measurements and the tensile strengths of the nanofibre membranes.

3.2 Porosity measurements

The nanofibre membrane pore size measurements were carried out using liquid expulsion Capillary Flow Porometer. The wet-to-dry method showed the poor distribution of the membrane pore sizes while the dry-to-wet method demonstrated a good distribution of the membrane pores. The pore distribution plots of the membranes are presented in **Fig. 3.** The average pore sizes of M1, M2, M3, M4, and M5 were found to be 1.89 µm, 1.48 µm, 1.24 µm, 1.41 µm, and 1.27 µm respectively. The decline in pore structure from unmodified to modified membranes using SiO_2 NPs was associated with the induction of the formation of beaded nanofibres which were accompanied by spraying. Spraying blocks the pores of the sub-micron structures of the nanofibre mats, hence reduce their water permeation, thereby resulting in compromised water fluxes.

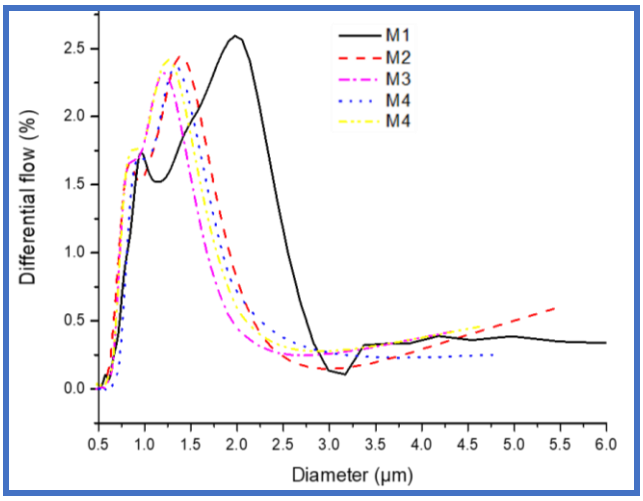

Fig. 3: The pore size measurements of the PVDF nanofibre membranes.

3.4 Salt rejections (NaCl) of the nanofibre membranes

The PVDF nanofiber membranes were tested for the rejection of NaCl on a DCMD configuration. The salt rejection was observed to be 99.9% for the organically modified super-hydrophobic nanofibre membranes. A minimal loss of salt rejection (from 99.9% to 99.4) occurred on the use of pristine PVDF nanofiber membrane. This slight decline in salt rejection was associated with the wetting possibilities inside the pores of the membrane. The main driving force in MD is the vapour gradient across the two interfaces of the membrane, therefore wetting allows the passage of the salt from the feed side to the permeate side. As a result of this phenomenon, the salt rejection decreases as shown in **Fig. 4**.

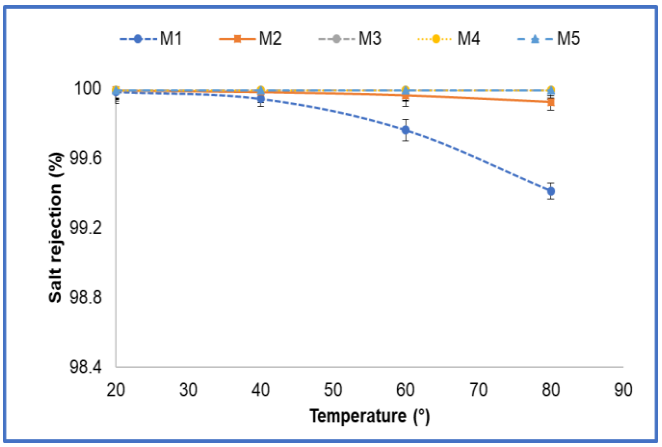

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Fig. 4: The salt (NaCl) rejections efficiencies of the nanofibre membranes.

3.5 Flux measurements

Fig. 5 summarizes the flux of the salty water across the PVDF membranes. There was no water flux observed when the feed temperature was 20° since the vapour gradient was zero at the similar temperatures between the two interfaces. The flux exponentially increased with increase in the feed temperature in all membranes. The flux of all membranes modified with organically functionalized SiO_2 NPs was superior to that of M1 and M2. The observation was associated with the possible occurrence of minimal membrane wetting in the feed side of M1 and M2 as opposed to M3, M4, and M5. M3, M4 and M5 are characterized by CA > 150° (super-hydrophobic membranes) which allows the water passage in the form of vapour, thus preventing membrane wetting. This minimal wetting reduces the passage of water vapour, which subsequently minimises the water vapour flux [11]. The water fluxes of M1, M2, M3, M4, M5 at 60° were 24.8 LMH, 34.1 LMH, 55.2 LMH, 64.4 LMH, and 61.3 LMH. These findings are the evidence of high water production membrane distillation process that could be implemented at higher scale for production of fresh water from the saline/brackish water.

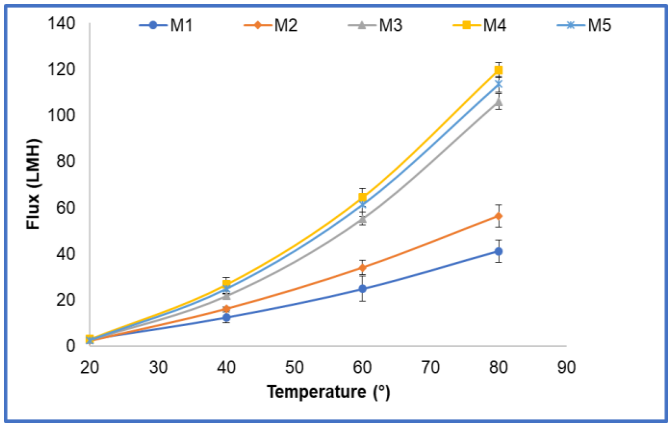

Fig. 5: The water flux of salty water across PVDF nanofiber membranes modified with functionalized SiO_2 NPs.

4 CONCLUSION

In conclusion, this study has demonstrated the possibility of mitigating the wetting and mechanical strength and porosity challenges in MD. The electrospun membranes with intertwined structures were found to be superhydrophobic while maintaining high strength properties with Young's modulus values (E) 377 MPa. The entangled and intertwined structures have also led to the formation of highly porous membranes with pore sizes of 2.25 µm. The resultant ultrahydrophobic nanofibre membranes were found to be highly efficient in removing the salt(s) (NaCl) from water (99% removal efficiencies) while maintaining the high-water fluxes (64.4 LMH). Therefore, these membranes can be used in desalination of brackish at high water recovery rates.

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