Functionalized PVDF Nanofiber Membranes for Desalination by Direct Contact Membrane Distillation

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Abstract: The recent combination of nano particles and polymer in fabricating polymeric membranes has shown immerse potentials in developing composite membrane materials for practical applications including pollutant sequestration, reverse osmosis and membrane distillation. Here, this study reports the functionalization of Polyvinylidene fluoride electrospun nanofibers by the addition of different nano fillers (CuO, TiO_2, SiO_2 and MOF-F300). The composite membrane materials were tested to determine their capability in the production of portable water from seawater by direct contact membrane distillation. Though the MOF composited membranes had the highest porosity, the flux shown by the TiO_2 composited membrane was greatest amongst all the composites (up to 7.2 kg/m^2·h) at a temperature difference of 27^{o}C. The salt rejection for a 35 g/L NaCl solution was >99.9% for all membranes tested with permeate conductivities surpassing the drinking water standard. The attachment of nanofiber and support was significantly improved which is a key functionality in predicting long-term membrane durability, filler compatibility and flux stability of substrate composited membranes. This class of functionalized membranes materials are promising candidates for desalination and other membrane base applications.

Keywords: Membrane distillation, nanofiber, electrospinning, nanoparticles.

1. Introduction

Industrialization, globalization, population growth, pollution, climate change are all key factors contributing greatly to rising scarcity and shortage of portable, clean drinking water [1]. Developing countries have been hit harder with the water crisis due to the added economic constrains. Measures such as water reuse, water treatment, are playing an important role in diminishing the gap between water demand and water supply. With the earth being covered by 72% water, it is tempting for someone to believe that, there will be enough water for the rising population. Since about 97% of the water is ocean and salty water, transformation to clean water is therefore a necessity. Several systems have been employed for desalination like reverse osmosis [2], ultrafiltration, and nanofiltration [3] which are all pressure driven and energy intense process ending up producing drinking water at a higher cost per cubic meter. Membrane distillation (MD) is a less energy intense process which depends on vapour pressure difference brought about by transmembrane temperature difference [4], [5]. With the potentials MD has in producing clean water at a much-reduced cost per cubic meter, it is yet to be commercialized. Issues that have plaque this system include, relatively low and unsteady fluxes of its membranes, membrane fouling, pore wetting, membrane durability for long term operations among others [5]. Since most of the

membranes employed for MD are polymeric membranes made from polymers like PVDF [6], [7], PTFE [8], PAN [9], PVA [10], researchers have gone a long way to improve the performance of these membranes by including nano additives into the preparation process. Also, various fabrication techniques like immersion precipitation [7], electrospinning [11], [12], temperature induced phase inversion have been used to fabricate better membranes for MD. The results achieved thus far with the introduction of nano additives as fillers for MD membranes have brought the high hopes and increased the viability of the process.

In this research, several nano additives including CuO, SiO_2, TiO_2, and metal-organic framework (MOF-F300) have been used to improve the performance of a PVDF electrospun nanofiber membrane tested with a direct contact membrane distillation module. The nanofibers were electrospun on a porous substrate to improve membrane stability. The effect of these different additives was investigated in relation to the stability of their fluxes, the quality of the permeate water produced and the characteristics of the membranes fabricated.

2. Experimental

In this research, the materials used such, Poly (vinylidene fluoride) (PVDF) (M_w=410kDa; melt viscosity 18.5±2.5kPoise; melting temperature, T_m=160.1°C) was donated by Arkema Inc., Philadelphia, PA, dimethyl acetamide (DMAc, >99%) and acetone used as solvent were purchased from Sigma Aldrich Inc. The nonwoven support TA3618 (thickness: 0.19 mm) was obtained from Tianlue Advanced Textile Co. Ltd., (China). Metal organic framework Fe-BTC (F300), Iron 1, 3, 5-Benzenetricarboxylate was purchased from Sigma Aldrich, with a BET surface area of 1300-1600 m^2/g, and bulk density of 0.16-0.35 g/cm^3. CuO (25-55 nm, SA: 13.98 m^2/g purchased from US nano, SiO_2 (10-25 nm, SA: 75-125 m^2/g) and TiO_2 (10-30 nm, SA 50-150 m^2/g) were purchased from Skyspring nano. The concentrations of the total dope mixtures all carried 1 wt. % nano additive. The electrospinning parameters used were; 15KV applied between spinneret and rotating drum (140 rpm) separated by a 15cm space. The flow rate of the syringe pump was 0.15mm/min at room temperature and 40% humidity.

The morphology of the nanofibers was investigated using scanning electron microscopy (SEM), Tescan, Vega-II XMU with Oxford Inca Energy 250X EDS. Membrane/crystal samples were covered with gold to increase conductivity and Transmission electron microscope (TEM), FEI Tecnai G2 F20 TEM, was employed to characterize the size and morphology of the nano additives.

Pieces of each prepared membranes with effective area of 38.5 cm^2 was placed in the DCMD module and subjected to continuous DCMD test over a period of 5 h. In this study, the feed side solution was 35 g/L NaCl aqueous solution and DI water for permeate side with an initial conductivity < 2 μS/cm and the flow rate on both side maintained at 1.5 L/min. The initial temperature of the feed and permeate streams were kept at 43±1.5℃ and 16±1.3℃ respectively. During the test, the conductivity of the permeate stream was measured using a conductivity meter (Oakton con 2700), and the permeate vapor flux was measured using a digital balance (Ohaus adventurer pro av8101) every 20 min. The experiment was conducted for a 5 h test for all membranes.

3. Result and Discussion

The SEM images of the neat and composite membranes confirm the presence of the nano additives as shown in Fig. 1. Compared to the neat membrane, the composited membranes fibres experienced a significant increment in diameter due the incorporation of the nano-additive. The additives also contributed in altering the surface roughness of the membrane which showed a change in the water contact angle of the surface. Though PVDF nanofibers are intrinsically hydrophobic, the hydrophobicity of the composite membranes was enhanced in the presence of all additives (Table 1).

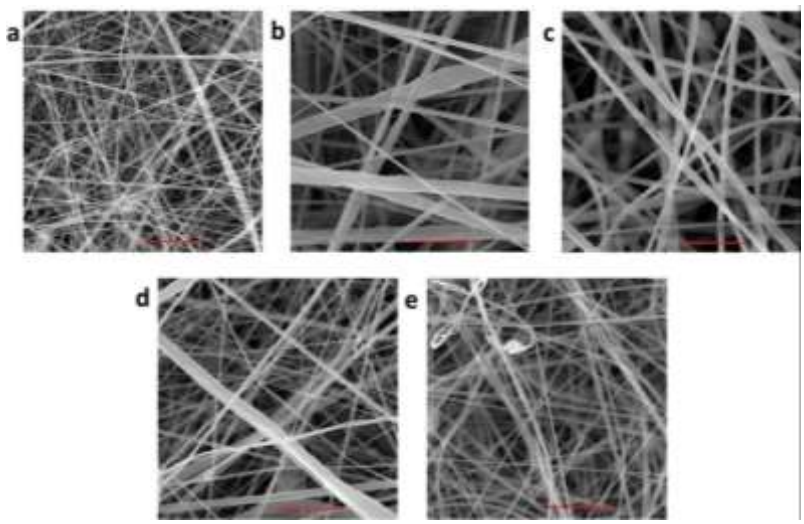

Fig. 1. SEM images of electrospun composited membranes of (a) PVDF, (b) PVDF-SiO_2, (c) PVDF-TiO_2, (d) PVDF-CuO, (e) PVDF-MOF. The scale bar in the bottom is 5 μm.

Table 1. Membranes Characteristic Properties.

	PVDF	SiO_2	TiO_2	CuO	MOF
LEP (KPa)	158±12	58±7	73±4	82±5	68±5
Contact angle (°)	133±3	139±3	138±3	132±5	135±2
Pore size (μm)	0.47±0.14	0.71±0.18	0.82±0.21	0.64±0.20	0.53±0.11
Porosity (%)	60.55	66.12	65.69	63.91	62.52
Salt rejection (%)	99.9	99.99	99.98	99.98	99.99

TEM analysis of the crystals (Fig. 2) revealed that, the particle sizes were appropriate which facilitated the ease of incorporation onto the fibre surface. With exception of F300, all particles had sizes <100 nm which facilitated the incorporation unto the >200 nm diameter fibres.

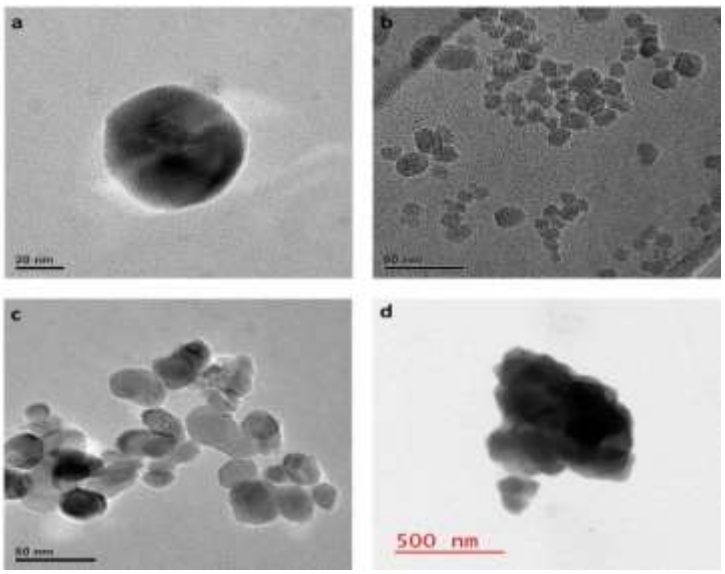

Fig. 2. TEM images of nanoparticles of (a) CuO, (b) SiO_2, (c) TiO_2, (d) MOF

Fig. 3 shows the flux behaviour of all the fabricated membranes. It is evident from the porosity and pore size data on table 1 that, the greater the porosity, the more likely the transmembrane flux will be higher. Since porosity indicates more channels for water vapour passage, the MOF with the highest surface area was expected to produce the most porous membranes and hence highest flux. Due to its particle size

compared to the other particles for this study, agglomeration was evident which contributed greatly to reduce the effective surface area for vapour passage for PVDF-MOF membranes. PVDF-TiO_2 membranes had the largest pore size and porosity, hence the greatest flux recorded.

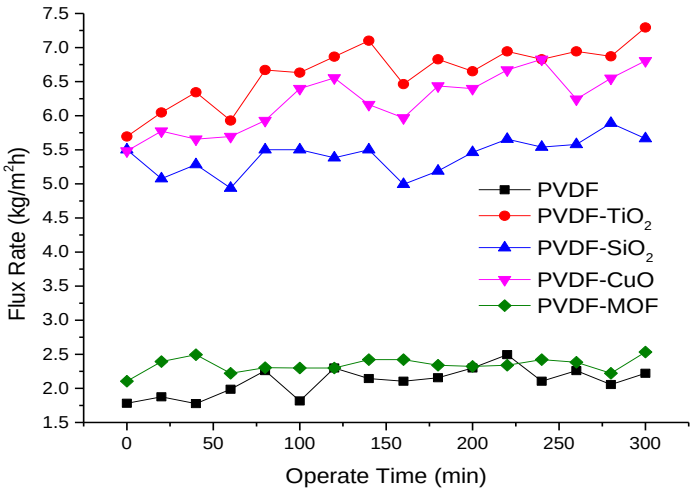

Fig. 3. Flux analysis of all the prepared membranes.

It must be noted that, though the PVDF-TiO_2 membrane had the larges flux, PVDF-SiO_2 and PVDF-MOF showed the most stable flux. Flux stability is one of a key characteristics of MD membrane research. Since the test was conducted for 5 h, the rejection obtained for 35 g/L NaCl feed surpassed 99.98% which indicated the membranes are good candidates for desalination. With the low temperature difference of 27^{o}C used, it implies doubling the difference (driving force) will result in exponential flux increase.

4. Conclusions

PVDF nanofibers functionalized with nano-additives have been successfully prepared on a micro-porous substrate with good attachment between nanofiber and substrate. The nanofiber membrane contained different nano additives at 1 wt. % and tested for desalination by DCMD. The following conclusions were drawn;

1) The presence of additives improved the porosity and pore size of the membrane by up to 30% by adding just 1 wt. % particles. The MOF nanofiber did not produce the most porous membrane because the particles size allowed for easy agglomeration which caused the particles to lose some functionalities.
2) The water contact angle of all composite membranes was improved in the presence of additives resulting from increased surface roughness, thus enhancing the surface hydrophobicity which is essential for MD and DCMD applications.
3) With the enhancement of porosity in the composite membranes, the flux was improved compared to the neat membrane. Though the MOF particles had highest porosity, due to their particle sizes, agglomeration restricted the composite membrane to benefit from the MOF presence as expected. SiO_2 which produced the most hydrophobic membrane and second best porous composite produced the highest transmembrane flux. It is therefor worth noting that, reducing agglomeration is essential to particle functionality.
4) Addition of suitable nano additives help produce membrane with stable flux which is a key research aspect of MD.

5) Future works for this process shall focus on long term process analysis with desalination time of at least 50 h of operation. By so doing, flux, fouling and permeate quality can be better modelled.

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