University of Technology Sydney
FACULTY OF ENGINEERING

DESIGN AND FABRICATION OF NOVEL NANOFIBER MEMBRANES VIA ELECTROSPINNING TECHNIQUE FOR MEMBRANE DISTILLATION

by

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CERTIFICATE OF ORIGINAL AUTHORSHIP

I certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of requirements for a degree except as part of the collaborative doctoral degree and/or fully acknowledged within the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

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LIST OF ABBREVIATIONS

2D	Two-dimensional
AD	Adsorption desalination
AED	Adsorption energy distribution
AFM	Atomic force microscopy
AGMD	Air gap membrane distillation
APS	Accelerated precipitation softening
ATR-FTIR	Attenuated total reflectance – Fourier transform infrared spectroscopy
$BaSO_4$	Barium sulfate
BET	The Brunauer-Emmett-Teller
BJH	The Barrett-Joyner-Halenda
BNNPs	Boron nitride nanoparticles
BTEAC	Benzyltriethylammonium chloride
CA	Contact angle
$Ca(OH)_2$	Calcium hydroxide
$CaCO_3$	Calcium carbonate
$CaSO_4$	Calcium sulfate
CBD	Coal bed methane
CDI	Capacitive deionization
CFP	Capillary flow porometry
CNTs	Carbon nanotubes
COD	Chemical oxygen demand
C-PVDF	Commercial PVDF membrane
CSG	Coal seam gas

CuO	Copper oxide
DC	Direct current
DCMD	Direct contact membrane distillation
DI	De-ionized
DMF	N, N-dimethylformamide
DS	Draw solution
EDX	Energy dispersive x-ray spectroscopy
ENM	Electrospun nanofiber membrane
ERD	Energy recovery device
$FeCl_3$	Ferric chloride
FO	Forward osmosis
FOHC	The FO-RO hybrid Desalination Research Center
FS	Feed solution
GMVP	The Global MVP project
G/PH	Graphene/Polyvinylidene fluoride-co-hexafluoropropylene
GO	Graphene oxide
GOR	Gain output ratio
HA	Humic acid
HCl	Hydrochloric acid
h-BN	The hexagonal boron nitride
iCVD	Initiated chemical vapor deposition
IP	Interfacial polymerization
IPA	Isopropanol
KORAE	The Korean Optimized RO desalination for Advanced Energy saving
LEP	Liquid entry pressure

LiCl	Lithium chloride
MBR	Membrane bioreactor
MCDI	Membrane capacitive deionization
MCr	Membrane crystallization
MDBR	Membrane distillation-membrane bioreactor
MED	Multi-effect distillation
MEMD	Multi-effect membrane distillation
MD	Membrane distillation
MF	Microfiltration
MGMD	Material gap membrane distillation
MSF	Multi-stage flash
MWNTs	Multi-walled nanotubes
N6	Nylon-6
NaCl	Sodium chloride
NaOH	Sodium hydroxide
NCC	Nanocrystalline cellulose
NIPS	Non-solvent induced phase separation
NOMs	Natural organic matters
NTIPS	Non-solvent with thermally induced phase separation
OCM	Orthogonal collocation method
ODEs	Ordinary differential equations
OMW	Olive mill wastewater
PA	Polyamide
PACl	Polyaluminum chloride
PAM	Polypropylene acid ammonium

PAN	Polyacrylonitrile
PDEs	Partial differential equations
PDMS	Polydimethylsiloxane
PEI	Polyetherimide
PES	Polyethersulfone
PET	Polyethylene terephthalate
PGMD	Permeate gap membrane distillation
PH	Polyvinylidene fluoride-co-hexafluoropropylene (PVDF-co-HFP)
PP	Polypropylene
PRO	Pressure retarded osmosis
PS	Polystyrene
PSD	Pore size distribution
PSf	Polysulfone
PTFE	Polytetrafluoroethylene
PVA	Polyvinyl alcohol
PVAc	Polyvinyl acetate
PVC	Polyvinyl chloride
PVDF	Polyvinylidene fluoride
PVDF-CTFE	Poly(vinylidene fluoride-co-chlorotrifluoroethylene)
RCW	Recirculating cooling water
RED	Reverse electrodialysis
RF	Radio frequency
RO	Reverse osmosis
SA	Sliding angle
SAED	Selected area electron diffraction

SCCM	Standard cubic centimetre per minute
SDS	Sodium dodecyl sulfate
SEC	Specific energy consumption
SEM	Scanning electron microscopy
SFE	Surface free energy
SGMD	Sweeping gas membrane distillation
SiO_2	Silicon dioxide
SMM	Surface modifying macromolecules
$SrSO_4$	Strontium sulfate
SUS	Stainless steel
SWRO	Seawater reverse osmosis
TB	Tri-bore
TCD	Tip-to-collector distance
TCM	Traditional Chinese medicine
TEM	Transmission electron microscopy
TIPS	Thermally induced phase separation
TiO_2	Titanium oxide
TFC	Thin film composite
TGA	Thermogravimetric analysis
TOC	Total organic carbon
TPC	Temperature polarization coefficient
TSS	Turbidity and fine particulates
UF	Ultrafiltration
UTM	Universal testing machine
VIPS	Vapor induced phase separation

VMD	Vacuum membrane distillation
VMEMD	Vacuum multi effect membrane distillation
VODE	Variable coefficient ordinary differential equation
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

LIST OF SYMBOLS

A	Effective area of the membrane
C	Cold fluid
C_{AGMD}	Mass transfer coefficient
$C_{AGMD\text{-}G}$	Mass transfer coefficient related with the graphene effect
C_p	Permeate concentration
C_f	Feed concentration
C_m	Membrane mass transfer coefficient
C_p	Specific heat capacity
D_{AB}	Water vapor diffusion coefficient
d_h	Equivalent hydraulic diameter
$Flux_E$	Flux of each point
$Flux_I$	Flux of the initial point
g	Gravity
h	Heat transfer coefficient
H	Hot fluid
I_D	D band
I_G	G band
J	Water vapour flux
J_{AGMD}	Water vapour flux by AGMD
$J_{AGMD\text{-}G}$	Water vapour flux by AGMD with graphene effect
J/J_o	Normalized flux
k_x	Transversal thermal conductivity
k_z	Axial thermal conductivity

L	Channel length
LMH	L/m^{2}h
M_w	Molecular mass of water
P_{avgm}	Log mean air pressure based from both sides of the membrane
P_{avgma}	Log mean air pressure within the air gap
P_C	Water vapor pressure on the air gap layer
P_H	Water vapor pressure on the membrane surface
Pr	Prandtl number
P_T	Total pressure of water vapor and air
P_w	Vapor pressure of pure water
r	Membrane pore radius
R	Universal gas constant
R_a	Mean roughness
R_{AGMD}	Total mass transfer resistance in the AGMD
γ_m	Surface tension of the membrane in contact with air
γ_{ml}	Surface tension of the membrane in contact with liquid
γ_l	Surface tension of liquid in contact with air
γ_m^T	Total surface free energy
γ_m^{LW}	Lifshitz van der Walls interaction of the membrane
γ_m^{AB}	Lewis acid-base interaction of the membrane
γ_m^+	Electron acceptor parameter
γ_m^-	Electron donor parameter
Re	Reynolds number
R_G	Molecular diffusion resistance related with the graphene effect

R_K	Knudsen diffusion resistance
R_M	Molecular diffusion resistance
$R_{M\text{-}air}$	Molecular diffusion resistance in the air gap
RT	Room temperature
SR	Salt rejection ratio
$T_{avg,a}$	Average temperature based from both sides of the membrane
$T_{avg,m}$	Average temperature at the air gap
u	Flow velocity
W_1	Weight of the saturated membrane
W_2	Weight of the dry membrane
x_{NaCl}	Mole fraction of NaCl
x_w	Mole fraction of water
t	Operating duration
γ_w	Activity coefficient of water
δ	Thickness
δ_m	Membrane thickness
δ_a	Air gap thickness
Δg	Mass of permeate
ε	Membrane porosity
k	Thermal conductivity
λ	Latent heat of water
μ	Viscosity
ρ	Liquid density
ρ_e	Density of ethanol

ρ_d	Density of PVDF material
τ_m	Membrane pore tortuosity
Γ	Total flow rate of condensate at the bottom of the condensing surface
air	Air
cf	Condensate film
cp	Cooling plate
f	Feed
fl	Fluid
gap	Air gap
m	Porous membrane
si	Solid membrane

ABSTRACT

In recent decades, many regions of the world suffer from water scarcity, which is one of the most critical issues in the world. The main challenge is to supply fresh water to water shortage regions. In addition, waterborne illness has been caused through the consumption of the contaminated drinking water in these regions. Seawater desalination is one of the alternative ways to produce freshwater. However, current desalination technologies like reverse osmosis (RO), multi-stage flash (MSF), and multi-effect distillation (MED) have several issues such as high energy consumption, a low recovery rate of total water, and large footprint. Among the several techniques to replace conventional desalination techniques, membrane distillation (MD) is one of the promising technologies. Currently, microfiltration (MF) membranes are implemented for MD application due to their suitable pore size distribution. However, some properties of MD are still needed to be enhanced, especially the high hydrophobicity to avoid membrane pore wetting and high porosity to increase permeate flux. With the development of nanotechnology, electrospinning is becoming a promising technology to fabricate hydrophobic and highly porous membranes. Thus, the objectives of this dissertation are to fabricate a suitable membrane for MD technology by electrospinning technique.

Novel nanofiber membranes fabricated by electrospinning technique are herein proposed for MD application to treat seawater and RO brine from coal seam gas (CSG) produced water. The electrospun membrane could be tailored to have superhydrophobicity, high porosity, adequate pore sizes and narrow pore size distribution, and thin thickness, so it could be used in applications of high-performance MD process. To further improve the MD performance of the electrospun membranes, three different methods were considered: (i) Janus-type hydrophobic/hydrophilic nonwoven membrane to reduce mass transfer resistance, (ii) nano-materials embedded membrane to improve liquid entry pressure (LEP), and (iii) surface modification of electrospun membranes to treat challenging wastewater sources.

Janus-type hydrophobic/hydrophilic dual-layer nanofiber nonwoven membranes were initially fabricated by a facile electrospinning technique and applied for desalination by air gap MD (AGMD). As-spun neat single and dual-layer nanofiber membranes composed of a hydrophobic polyvinylidene fluoride-co-hexafluoropropylene (PH) top layer with different supporting hydrophilic layer made of either polyvinyl alcohol (PVA), nylon-6 (N6), or polyacrylonitrile (PAN) nanofibers were fabricated with and without heat-press post-treatment. Surface characterization showed that the active layer (i.e., PH) of all electrospun nanofiber membranes (ENMs) exhibited a rough, highly porous (>80% porosity), and hydrophobic surface (CA > 140^o), while the other side was hydrophilic (CA<90^o) with varying porosity. Heat-pressing the membrane resulted to thinner thickness (from >129 μm to <100 μm) and smaller pore sizes (<0.27 μm). The AGMD experiments in a cross-flow set up were carried out with constant inlet temperatures at the feed and permeate streams of 60 ± 1.5 and 20 ± 1.5 ˚C, respectively. The AGMD module had a membrane area of 21 cm^2 and the thickness of the air gap was 3 mm. The neat single and dual-layer ENMs showed a water permeate flux of about 10.9 ~ 15.5 L/m^2 h (LMH) using 3.5 wt % NaCl solution as feed, which was much higher than that of a commercial PVDF membrane (~ 6 LMH). The provision of a hydrophilic layer at the bottom layer enhanced the AGMD performance depending on the wettability and characteristics of the support layer. The PH/N6 dual-layer nanofiber

membrane prepared under the optimum condition showed flux and salt rejection of 15.5 LMH and 99.2 %, respectively, which has good potential for AGMD application.

Three different nanomaterials were incorporated in polymeric solutions for the improvement of liquid entry pressure (LEP), which were carbon nanotubes (CNTs), graphene, and hexagonal boron nitride (h-BN). Firstly, superhydrophobic, robust, mixed PH nanofiber membranes were fabricated incorporating CNTs as nanofillers to impart additional mechanical and hydrophobic properties. The electrospun membrane has been designed to have two cohesive layers, a thin CNT/PH top layer and a thick neat PH bottom layer. Through different characterization techniques, CNTs were found to be widely distributed on/in the nanofibers, where more beads-on-string were formed at higher CNT content. However, the beads-on-string did not significantly affect the membrane porosity and pore size, as well as did not degrade the MD performance. Highly-porous structure was observed for all membranes and the nanofiber membrane showed comparable pore sizes with a commercial flat-sheet PVDF membrane but at a much higher porosity (>85%). The contact angle increased to higher superhydrophobicity at 158.5^{o} upon the incorporation of 5 wt% CNTs in the nanofiber due to increased roughness and added effect of hydrophobic CNTs. The liquid entry pressure also increased when 5 wt% CNT was added compared to the neat PH nanofiber membrane. The resulting flux of the 5 wt% CNT-incorporated nanofiber membrane (24-29.5 L/m^2h) was consistently higher than the commercial PVDF membrane (18-18.5 L/m^2h), with an average increase of 33-59% depending on the feed water type (35 or 70 g/L NaCl solution) without compromising the salt rejection (>99.99%). The present nanofiber membranes containing CNTs with one-step electrospinning fabrication show high potential for direct contact MD (DCMD) desalination application.

The following study demonstrated the development of a graphene-loaded electrospun nanofiber membrane and evaluation of their desalination performance in AGMD. Different concentrations of graphene (0-10 wt%) were incorporated in/on electrospun PH membrane to obtain a robust, and superhydrophobic nanocomposite membrane. The results showed that graphene incorporation has significantly enhanced the membrane structure and properties with an optimal concentration of 5 wt% (i.e., G5PH). Characterization of G5PH revealed membrane porosity of >88%, contact angle of >162^o (superhydrophobic), and high LEP of >186 kPa. These favorable properties led to a high and stable AGMD flux of 22.9 L/m^{2}h or LMH (compared with ~4.8 LMH for the commercial PVDF flat-sheet membrane) and excellent salt rejection (99.99%) for 60 h of operation using 3.5 wt% NaCl solution as feed (feed and coolant inlet temperatures of 60 and 20^{o}C, respectively). A two-dimensional dynamic model to investigate the flux profile of the graphene/PH membrane is also introduced. The present study suggests that exploiting the interesting properties of nanofibers and graphene nanofillers through a facile electrospinning technique provides high potential towards the fabrication of a robust and high-performance MD membrane.

Another study focused on h-BN embedded nanofiber membrane to maintain flux stability in a long-term AGMD process. The hexagonal lattices of the BN nanoparticles (BNNPs) were modified by hydroxide-assisted ball milling without damage occurred during the exfoliation processes, and they were encapsulated in PH electrospun nanofiber membrane. Characteristics of the BN-PH membrane indicated almost similar regarding membrane thickness, fiber size, porosity and pore size. However, contact angle (153.2^o) and LEP (214 kPa) of the BN-PH membrane were higher than that of the neat PH membrane, which showed that the BN-PH membrane could have less wetting issues compared with the neat PH membrane. Besides, thermal conductivity of the neat PH and BN-PH was 0.025 W/mK and 0.009 W/mK, respectively, as expected that the BN-PH membranes could lead to a high MD water vapor flux performance due to reduced mass transfer resistance and also reduction in conductive heat loss via the membrane. The initial water vapor flux of the neat PH membrane was 11.42 LMH, however, it suffered wetting problem in less than 4 h operation. On the other hand, the BN-PH membrane showed a stable water vapor flux (18 LMH) and salt rejection (99.99%) performances even after 280 h of MD operation. This membrane has a good potential for long-term application of MD for seawater. Future interest in this study may be to find a mechanism for the improved water vapor flux performance of the BNNPs enabled electrospun nanofiber MD membrane.

MD process is also considered to treat wastewater or other challenging wastewater such as the one from textile, dye, and oil industries. However, MD membranes should be improved for preventing membrane wetting issues commonly caused by low surface tension liquids such as surfactants, benzene, methanol, and hexane. Thus, this study described the development and performance of an omniphobic poly(vinylidene fluoride) (PVDF) membrane fabricated by electrospinning and surface-modified by CF_4 plasma, for AGMD. The effect of different duration of plasma treatment on the nanofiber membrane characteristics was investigated. The AGMD performance of the membranes was evaluated using real RO brine produced from CSG produced water that was added with low surface tension liquid (surfactant) as feed solution. Results indicated the formation of new CF_2-CF_2 and CF_3 bonds after plasma treatment, which lowered the surface energy of the membrane, providing omniphobic property, as indicated by its wetting resistance to different low surface tension liquids such as methanol, mineral oil and ethylene glycol. Though no appreciative changes in morphology of the membrane were observed after plasma treatment, optimal treatment condition of 15 min (i.e., P/CF-15 membrane) exhibited lotus effect membrane surface with increased LEP of 187 kPa compared to 142 kPa for neat membrane. AGMD performance showed stable normalized flux (initial flux of 15.3 L/m^{2}h) and rejection ratio (99.99%) for P/CF-15 even with the addition of up to 0.7 mM sodium dodecyl sulfate surfactant to the RO brine from CSG produced water feed, while commercial PVDF membrane suffered membrane wetting after 0.3 mM of surfactant addition. Based on the results, the present omniphobic membrane has good potential for producing clean water from challenging waters containing high salinity and organic contaminants.

The aim of this study is the development of suitable electrospun nanofiber membranes for MD. This study mainly focuses on the newly-developed one-dimensional and two-dimensional nano-materials embedded nanofiber membranes, which suffer less wetting issue and have improved water vapor flux performance in MD. It also investigates a simple surface modification technique to generate anti-wetting property on the membrane surface. Overall, this author successfully fabricated several electrospun nanofiber membranes with enhanced water vapor flux and stable salt rejection performances for the treatment of seawater, seawater RO brine and CSG RO brine by MD applications. The fabricated electrospun nanofiber membranes exhibited better performances than the commercial PVDF membranes due to their suitable morphologies and characteristics for MD application. Thus, proper membranes were fabricated which led to enhanced membrane properties such as superhydrophobicity and anti-wetting property. And their MD performances have been compared with the ones in the previous reports. This study may therefore contribute to future MD researches regarding using electrospinning for the developments of a commercial electrospun nanofiber MD membrane.

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