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**NANYANG
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UNIVERSITY**

SINGAPORE

**MATERIAL AND FLOW ENGINEERING APPROACH IN
IMPROVING THE MEMBRANE DISTILLATION
PROCESS**

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SCHOOL OF CHEMICAL AND BIOMEDICAL ENGINEERING

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MEMBRANE DISTILLATION PROCESS**

TAN YONG ZEN

School of Chemical and Biomedical Engineering

A thesis submitted to the Nanyang Technological University
in partial fulfillment of the requirement for the degree of
Doctor of Philosophy

2018

STATEMENT OF ORIGINALITY

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

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SUPERVISOR DECLARATION STATEMENT

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

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Assoc. Prof. Chew Jia Wei

AUTHORSHIP ATTRIBUTION STATEMENT

This thesis contains material from 5 paper(s) published in the following peer-reviewed journal(s) where I was the first author.

Chapter 2 is published as **Y.Z. Tan**, J.W. Chew, W.B. Krantz, Effect of humic-acid fouling on membrane distillation, *Journal of Membrane Science*, 504 (2016) 263-273.

The contributions of the co-authors are as follows:

- Prof Chew Jia Wei provided the initial project direction and edited the drafts of the manuscript.
- Prof Krantz provided the initial project direction, analyzed the data and wrote the manuscript.
- I performed all the laboratory work at the School of Chemical and Biomedical Engineering, NTU. Furthermore, I analyzed the data and wrote the manuscript.

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The contributions of the co-authors are as follows:

- Prof Chew Jia Wei provided suggestions for the study and edited the drafts of the manuscript.
- Prof Anthony Gordon Fane provided suggestions for the study and edited the drafts of the manuscript.
- Dr Han Le provided valuable suggestions with his expertise to improve the study. He carried out some experiments and helped with the writing of the manuscript.
- Mr Chow Wai Hoong designed and machined the module which was essential for the success of this experiment.

- I came up with the idea of the study and performed all the laboratory work at the School of Chemical and Biomedical Engineering, NTU. Furthermore, I analyzed the data and wrote the manuscript.

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- I came up with the idea of the study and performed all the laboratory work at the School of Chemical and Biomedical Engineering, NTU. Furthermore, I analyzed the data and wrote the manuscript.

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MATERIAL AND FLOW ENGINEERING APPROACH IN IMPROVING THE MEMBRANE DISTILLATION PROCESS

ABSTRACT

Membrane distillation (MD) is a thermally-driven process involves distillation through a microporous hydrophobic membrane, which acts as a physical interface between the hot feed and cool permeate. Despite being a promising easy to integrate, low-cost, energy-saving alternative to conventional separation processes like distillation and reverse osmosis (RO), MD have not gained much commercial attention due to low fluxes or output per unit energy and pore-wetting problems, limiting its uses to desalination and tertiary wastewater treatment. In view of the problems which plagues the MD process, a series of research were carried out to understand the underlying mechanisms contributing to the problems and investigate the various proposed solutions through a two-pronged approach to the problem.

Firstly, in chapter 2, fouling and its effect was studied in depth by correlating a previously developed theoretical model with experimental results using a laboratory direct-contact membrane distillation (DCMD) setup. This in turn helped proved that significant decrease in MD flux in fouling occurred due to the vapor-pressure pressure reduction largely attributed to the small pore size of the fouling layer rather than the heat- and mass-transfer resistance of fouling layer. Hence, the effect of fouling in MD can be significantly reduced by increasing the pore size of the fouling layer. Furthermore, membrane modification of membranes used in MD via coating which is essentially a fouling layer could be designed with bigger pores to minimize the negative impact on MD flux.

After which, a proposed approach of altering the module orientation and design to solve the problem of fouling and wetting was investigated in chapter 3. The results show that fouling and wetting could be mitigated by changing the module orientation and manipulating the flow trajectory within an MD module. In line with module orientation and design, in chapter 4 a sweep-gas MD (SGMD) hybridized with a heat pump was studied to evaluate the feasibility of such system in being able to simultaneously cool and carry out water treatment without the need of an additional condenser and at no additional power. Results obtained confirms the feasibility of this hybridized system through the improvement in heat pump electrical efficiency from the evaporative cooling occurring at the MD modules.

The material engineering solution of the two-pronged approach starts in chapter 5, in which a facile synthesis method was proposed to synthesize ligand-carrying nanoparticles (LC-NPs) with polystyrene cores and branched polyethyleneimine (b-PEI) which are cross-linked to form stable LC-NPs that can be reused after desorption of absorbed heavy metal ions. These LC-NPs can be used to remove heavy metal ions from wastewater. However, due to incompatibility of LC-NPs with solvents used in the membrane coating matrix, the coating of MXene with photothermal properties to provide localized heating in MD was studied in chapter 6. Results demonstrated the practical use of MXene for coating membranes to improve the performance of a lab-scale DCMD setup by providing localized photothermal heating and anti-fouling effects. Lastly, to compare the effect of membrane coating and spacer coating of photothermal material, in chapter 7, the growth of photothermal material on metallic spacer was carried out to provide localized heating. Since there was lack of studies done on the use of metallic spacers along the feed-membrane interface, simulations and experimental study was carried out to compare the performance of metallic spacers in MD before comparing them to the surface-modified metallic spacer with photothermal material. The results show that metallic spacers improve the energy efficiency of the MD process by improving temperature uniformity on the surface of the feed-membrane interface, and by modifying the metallic spacer with photothermal material, solar-assisted MD could be carried out to reduce the heating load of external heaters.

Keywords: Membrane distillation; direct-contact membrane distillation (DCMD); Kelvin effect; fouling, wetting; vapor-pressure reduction; module orientation and design; mixed convection flow; ligand-carrying nanoparticles; membrane modification; photothermal; energy efficiency; thermal conductivity

CHAPTER 1 : INTRODUCTION

2.1. Background

Living on Earth where about 71 % of the surface is covered by water, and yet water scarcity affects every continent and around two-thirds of the global population at least one month out of a year. This is due to the lack of potable water, as seawater makes up 96.5 % of the water on Earth [1]. Hence, most countries have been turned to desalination of sea- and brackish water. Desalination processes are predominantly classified into two categories; thermal or membrane-based technologies. With the rapid development of membrane-based processes such as reverse osmosis (RO), thermal processes are being surpassed. However, the primary drawback with desalination is the high cost attributed to the high energy consumption which makes up 30 % of the total cost of desalinated water using RO [2].

Membrane distillation (MD), the overlap of the two broad categories of desalination processes, is a promising easy to integrate, low-cost and energy-saving (based on use of waste-heat) alternative to conventional separation processes like distillation and reverse osmosis that is gaining attention in the scientific community [3-17]. The lack of membranes which need to be hydrophobic yet highly permeable to vapors, and be able to withstand the thermal operating conditions meant that MD was not a cost-effective water treatment solution when it was patented by Bodell [18] in 1968 [19]. However, economically feasible commercial hydrophobic membranes such as polypropylene, PVDF and PTFE used for microfiltration came along as membrane fabrication technology advanced. These membranes which are viable for MD [19-22] allowed MD to fulfil its potential in treating a multitude of feeds. This led to the discovery of many key advantages of MD including the high rejection of solutes, the ability to operate at lower pressures because the osmotic pressure difference does not need to be overcome and the ability to make use of waste heat [5].

Despite MD being an attractive green technology, two of the primary issues that plague MD are the low fluxes or output per unit energy and pore-wetting which compromises permeate quality [23]. Hence, most active research area in MD involves improving the flux and/or output per unit energy, adding functionalities such as fouling resistance and antimicrobial properties, or improving thermal efficiency through membrane modifications to compensate for the lower flux [24-27], and improving wetting resistance through membrane modifications [28-30].

2.2.Objectives

Despite membrane modification offers great potential able to provide solutions to the two primary issues, the design and orientation of MD modules being an economical alternative to changing the hydrodynamic conditions could be considered to improve the robustness of the MD system [31]. Hence, the performance enhancement of MD from membrane modification and design and orientation of MD modules are independent of each other, a two-pronged approach was taken to improve the MD process (Fig. 1.1). This approach first involved the understanding fouling and its effect on MD to check if membrane coating using nanomaterials of specific sizes could be used without a significant negative impact on flux. Following which the design and orientation of MD modules were studied in parallel with the design and synthesis of nanomaterials for coating on hydrophobic PVDF membranes. The synthesized nanomaterials were then coated on membranes and tested in laboratory scale DCMD set up to evaluate their effectiveness in providing added functionalities without negatively affecting flux. Similar functionalities were then evaluated on spacer materials to compare the effectiveness of both membrane and spacer modification.

Figure 1.1. Flow chart for the two-pronged approach used in this thesis work.

1.2.1. Understanding fouling and its effect on MD

Before diving straight into improving the membrane distillation process via membrane modification, a study was carried out to understand fouling and its effect on MD. This allows us to better understand the impact of membrane coating, which is essentially a uniform layer of foulant, on the MD process. Due to the unique combination of heat and mass transfer affecting the flux in an MD process, models developed to predict flux in a DCMD system accounted for the vapor pressure difference across the membrane and the mass transfer coefficient across the membrane, such as the model developed by Schofield et al. [32]. However, when fouling occurs, such flux prediction model becomes inaccurate, leading to the adaptation of the model by Schofield et al. [32] to include both an added heat- and mass-transfer resistance and a vapor-pressure depression owing to the presence of a fouling layer with very small pores, developed by Chew et al. [33]. Without carrying out any experiments, Chew et al. [33] recasted the data of Hanbury and Hotchkiess [34] for MD ran with a deionized water feed, to prove that the same data that fits Schofield et al. model [32] would be widely scattered when subjected to a vapor-pressure depression caused by a fouling layer of 10 nm pore size.

Despite being able to prove that vapor-pressure depression plays a non-negligible role in flux reduction, the parameters obtained from the correlation combines heat-transfer and mass-transfer resistances in the MD system as a lumped parameter; making it difficult to isolate the different effects of a fouling layer in MD process. Hence, we propose to design an experiment, using a lab-scale DCMD (Fig. 1.2), that would allow us to separate the effects of a fouling layer on MD; to determine if the heat- or mass-transfer resistance, or the vapor-pressure depression plays a bigger role in the affecting the flux across a fouled membrane. This would allow us to be able to develop advanced strategies to mitigate the effects of fouling and design a coating layer to have lesser negative impact on flux while providing additional useful functionalities to the MD process.

Figure 1.2. A schematic diagram of the lab-scale DCMD setup, consisting (1) a feed tank heated by a hot plate and agitated with a magnetic stirrer, (2) three peristaltic pumps, (3) a cross-flow flat-sheet acrylic membrane module, (4) a permeate tank (i.e., 1-L acrylic tank with a spout) cooled by a recirculating chiller and with a conductivity meter inserted, and (5) an overflow permeate tank (300 ml beaker) atop a mass balance.

1.2.2. Altering module orientation and channel geometry to improve the MD process

Given that designing and synthesizing nanomaterials for membrane modification takes time, the laboratory DCMD setup was run in parallel to investigate the effect of module orientation and channel geometry on the MD process. The lack of research in the area of flow manipulation to mitigate fouling in MD processes and a study done by Zamani et al. [35] on fouling mitigation via manipulation of the convective flow in cross-flow membrane applications, inspired us to carry out similar flow-field manipulation in the MD module.

Potentially, by simply manipulating the flow through tapered channel flow and/or changing the module orientation in cross-flow membrane applications, the trajectory of particulate foulants could be altered to reduce or even avoid interaction with the membrane [35]. This in turn extends the operating time before maintenance, which improves the service lifetime of the membrane, reducing the cost required for membrane replacement. Intuitively, similar results should be observed in cross flow MD modules. However, in MD a larger temperature difference across the membrane could induce a natural convection pattern which is different from that observed by Youm et al. [36] in dead-end ultrafiltration experiments which is a pressure driven filtration process similar

to the microfiltration process in which the flow manipulation idea was tested on by Zamani et al. [35]. Hence, depending on previous understandings of pressure driven filtration processes to come up with MD module design and decide on the module orientation, might not be optimal. Furthermore, Zamani et al. only tested his system on polystyrene beads which is slightly denser than water, which could have favoured his feed on the bottom configuration since gravity along with the flow field alteration could have both played a role in reducing the foulant and membrane interaction.

Hence, a proposal was made to study the impact of module orientation, module geometry and particulate foulant density on the MD performance parameters of flux and membrane pore wetting. Experiments and simulations would be carried out to evaluate the aforementioned parameters on foulant interaction with the membrane.

1.2.3. MD hybridized with heat pump for water treatment and space cooling

MD systems can be hybridized with other processes such as crystallizers or bioreactors to make use of the low-quality waste heat generated by such processes. In the case of a crystallizer, MD can be used to concentrate, cool down and crystallize the feed while recovering clean solvent [37, 38]. When coupled with a bioreactor, MD can make use of the low-temperature waste heat generated by the activated sludge that contain microorganisms that metabolize organic compounds, to produce clean water simultaneously [39].

One other system common which produces a huge amount of low-quality waste heat is the building space cooling solution tropical regions such as Singapore heavily relies on for indoor climate control. A system for simultaneous space cooling and water treatment can be achieved by coupling such heat pumps with membrane distillation (MD). The feasibility of this hybrid system has not been proven to date, thus a study with a goal of doing so was proposed as a solution in the two-pronged approach to improve the MD process. Conceivably, the heat from the heat pump can be used to heat up the MD feed and the water vapor from MD system can be cooled by the surrounding air and condensed on the cold surface of the heat pump (Fig. 1.3).

Figure 1.3. Overview of the TCMD concept.

This MD hybridized with a heat pump can potentially be used for, but is not limited to, space-cooling, refrigeration, dehumidification and decentralized water treatment. Furthermore, there lies potential in extending this invention to complement commercial space-cooling, chilled drinks vending machines, ice-makers and water-coolers. We foresee substantial impact of this technology in tropical countries where space-cooling and refrigeration are heavily utilized, and greater impact for such countries facing water scarcity.

1.2.4. Designing and synthesizing nanomaterials with multifunctional properties for coating on hydrophobic PVDF membranes

With the intent of merging nanotechnology and membrane technology to be used in an actual lab-scale process, this research started with the selection of functionalities useful in MD with the possibility to be easily coated on hydrophobic PVDF membrane and possibly be modified for added functionalities in the future. Two such interesting materials are ligand-carrying nanoparticles (LC-NPs) and MXene. LC-NPs can be made to bind with organic [40, 41] or heavy metal [42–44] contaminants which could potentially be used to remove such contaminants in MD feed. While MXene is known

for its ability to efficiently convert light to heat and be easily modified due to its highly functionalized surface [45-47].

1.2.4.1. LC-NPs

Firstly, ligand-carrying NPs (LC-NPs) with high ligand binding site homogeneity will be synthesized to be able to bind to most metal ions, endowing it the potential to be used for metal ion absorption for the recovery of toxic and precious metal in wastewater treatment and/or post-modified to be used in many different ways. One such useful modification involves cross-linking polymers containing primary amine groups such as chitosan[48, 49] and branched polyethyleneimine (b-PEI)[50-52] using dialdehydes. The amine group being one of the most versatile functional groups in organic chemistry[53, 54], the presence of such groups on the NPs allows for them to be used as base catalysts [54] (in place of liquid molecular base catalyst which are difficult to recover and corrosive [55]), be quaternized to yield polymers with different solubility [54], and function as binding ligands to different metals [50, 51, 54, 56-59]. Of which, the function of binding specific metals might prove to be interesting in targeting toxic or valuable metal ions for valuable metal recovery [42], hydrological mining wastewater treatment [50] or the recovery of soluble radioactive materials in the seawater coming from the recent Fukushima nuclear reactor meltdown. Such metal ions absorption capacity could reach up to a 120 mg of metal ions/g of nanoparticles with negligible degradation after 10 use cycles [50].

Secondly, a method to embed metallic nanoparticles is developed to synthesize homogenous or Janus[60] bifunctional nanoparticles with empty sites which contains the already present amine groups on the ligands and the catalytic sites of the metallic catalyst embedded on the LC-NPs. Of which, the amine groups serve to be quaternized or left as-is to improve binding ability of different organic compounds to it, while the metallic catalytic sites serve as a site for reaction to occur. Reaction which could be catalysed includes but does not limit to organic compound degradation and carbon fixation.

Lastly, the nanoparticles will be incorporated into membrane via surface coating and polymerization, creating functional membranes which could be used in pollution treatment processes such as dye degradation in dye polluted water, organic compound

degradation in oil wastewater treatment, absorption of toxic metal ions, or carbon capture and fixation in flue gas treatment. Of which, studies of effectiveness and efficiency this modification brings, as well as the interface and interphase stability can be carried out to provide insights on the potential of such modifications in the different membrane processes.

1.2.4.2. MXene

MXene are the latest group of layer-structure or 2D materials made of transition metal carbides/carbonitrides/nitrides with the metal-carbon and/or nitrogen host layer decorated with or without functional groups in surface termination [17–19]. MXene has a plethora of unique properties including good optical absorption, thermal property and tunable band gap [61], which are useful to the MD process in terms of providing photothermal-induced localized heating and possibly photocatalytic degradation [62]. Furthermore, stable MXene materials can be synthesized using a wide variety of metal elements (Sc, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, Mn, etc) with various composition as well as proportion and arrangement, along with the tuning of metallic conduction and active sites to improve photocatalytic performance under different wavelengths of light, providing a whole new array of coating materials that could possibly be used to significantly improve the MD process.

Studies by Mashtalir et al. [35] and Ran et al. [24] pointed towards the design of MXene-based nanoarchitectures to increase the light harvesting ability, attain greater quantum efficiency and enhance the exciton separation with superior photo-redox applications. This inspired a facile in situ hydrothermal synthesis method of novel quasi-core-shell $\text{In}_2\text{S}_3/\text{anatase TiO}_2$ @metallic $\text{Ti}_3\text{C}_2\text{T}_x$ MXene hetero-structured hybrids (Fig. 1.4) which exhibit superior photocatalytic performance towards pollutant degradation under visible light irradiation which can be potentially applied for photocatalysis in various applications [62], including MD.

Figure 1.4. Illustration of the synthesis process for the $\text{In}_2\text{S}_3/\text{Ti}_3\text{C}_2\text{T}_x$ hybrids [62].

A –O-, –F- and –OH-containing surface-terminated MXene, $\text{Ti}_3\text{C}_2\text{T}_x$, is a photothermal material, which was reported to have a photothermal conversion of 100 % using a 473 or 785 nm single-wavelength laser [45]. Hence, prior to any modification, $\text{Ti}_3\text{C}_2\text{T}_x$ can be coated on hydrophobic PVDF membrane to provide localized photothermal heating to make use of sustainable solar energy for solar-assisted MD. $\text{Ti}_3\text{C}_2\text{T}_x$ can be easily synthesized using the method reported in literature [63–65], similar to the top half of Fig x. The low cost of Ti_3AlC_2 and the simple synthesis method of $\text{Ti}_3\text{C}_2\text{T}_x$, makes $\text{Ti}_3\text{C}_2\text{T}_x$ a suitable MXene material for membrane modification to be used in MD processes.

1.2.4.3. Coating of synthesized materials on membrane

Coating of functional materials onto polymeric membranes can be done using methods including, in-situ polymerization, film casting, ion assisted deposition, aerosol deposition, ion exchange, dip coating, hydrothermal synthesis, sputtering and etching, surface adsorption, layer-by-layer deposition and spray coating [66]. Membrane coating could potentially result in adverse effects in terms of flux or even wetting if the ratio of ingredients or process are not well optimized [7]. Hence, after deciding on the materials to incorporate with the MD membrane to be used in the MD process, the coating matrix and/or coating method should be determined and tested out. Two more commonly used

coating matrix for membranes used for MD are polyvinyl alcohol (PVA) [67-69] and polydimethylsiloxane (PDMS)[45, 68, 70, 71].

Starting with the LC NPs we have designed and synthesized, they consist of a polystyrene (PS) core covered with b-PEI many amine groups which could be bind to toxic heavy metal ions in wastewater [42-44] or further react to form other more specific ligands or reduce bounded metal ions to form metals which are useful photocatalyst, such as silver, to degrade organic contaminants in wastewater [72]. However, in order to do so, the ligands should be exposed to the feed. A proposed idea to do so is to form a Janus nanoparticle with a silica lobe which could be easily done via seed polymerization of PS (Fig. 1.5), a method proposed by Wu et al. [73]. Similarly, this can be achieved using the LC NPs with PS core.

Figure 1.5. Synthesis route of Janus PS NPs.

With the silica lobe, we can then use PDMS as a coating matrix to anchor the LC NPs onto the hydrophobic PDVF membrane, leaving the ligand part exposed to the feed as depicted in Fig. 1.6. The size of the silica lobe can be adjusted by varying the amount of 3-(Trimethoxysilyl)propyl methacrylate [73] to possibly control how the Janus particle self-assemble on the surface of the PDMS coating matrix mixture. Hence, by applying vacuum filtration of the coating solution with a layer of stable Janus LC NPs onto the hydrophobic PVDF membrane, a layer of LC NPs exposed to the feed could be obtained. This leaves the silica lobe to be bonded to the PDMS layer to anchor the LC NPs to the membrane, which can be achieved by curing the PDMS at elevated temperature of 70 °C [74, 75]. In order to not negatively affect flux across the membrane, the Dow Corning Sylgard 184 PDMS must be diluted before mixing the Janus LC-NPs, so as not to create a viscous mixture which will form a dense layer atop the membrane pores, significantly reducing flux across the membrane. It was through

the use of many different solvents commonly used to dilute PDMS, such as hexane, heptane and cyclohexane, that we found out that most of them were incompatible with the LC-NPs, resulting in PS core and ligand mix being damaged in the process. Furthermore, after vacuum filtration the coating solution formed an uneven layer on the surface of the hydrophobic PVDF which reduced the flux significantly.

Figure 1.6. Proposed method for coating of Janus LC-NPs on hydrophobic PVDF membrane

MXene on the other hand can be easily coated on the membrane surface with PDMS as reported by Li et al. [45]. Reproducing the MXene coating on hydrophobic PVDF was easily achieved, giving us the opportunity to channel our efforts in optimizing the amount of MXene and the concentration of the PDMS solution used for coating to improve coating stability while not compromising much of the flux, because the dilute PDMS coating matrix clings only to the PVDF membrane porous structure without sealing of majority of the pores. Both LC-NPs and MXene have the potential to improve the MD process. However, the coating of LC-NPs require much more research on aligning the NPs and coating to achieve to make the ligands available to capture specific contaminants from the feed. Hence, we decided on the investigation of localized heating in MD for the experiments which follows in the two-pronged approach in improving the MD process.

1.2.5. Localized heating in MD

The flux across the membrane in MD is driven by the vapor pressure differential between the two faces of the membrane:

$$N = K_p(p_h^\circ - p_c^\circ) \quad (1)$$

where N is the mass-transfer flux and K_p is the overall mass-transfer coefficient of water vapor through the membrane. Specifically, the vapor pressure is calculated by:

$$p^\circ = \exp\left(23.328 - \frac{3841}{T-45}\right) \quad (2)$$

where T is the surface-averaged temperature of the membrane. Therefore, MD is a thermal-driven process, and increasing the temperature difference between the two faces of the membrane will enhance the flux across the membrane. The concept of localized heating as Boo et al. [76] recently highlighted, is essentially providing heat at the feed-membrane interface where it provides the highest impact on MD flux. The heating of a material along the feed-membrane interface within the feed channel of an MD cell would create the same localized heating as well as feed heating effect (Fig. 2b) which has been proven to be advantageous to the MD process [67, 69, 76-78].

An interesting research by Dudchenko et al. shows that Joule heating of porous carbon nanotubes (CNT), by directly passing an electrical current them, is sufficient to heat up the feed in a single pass DCMD setup with an active membrane area of 450 cm² up to 325 K or 52 °C [69].

Similar localized heating effect could be possible by both Joule heating and photothermal heating of a layer of MXene coated on hydrophobic PVDF membrane, given that MXene is both electrically conductive and possesses photothermal properties (Fig. 1.7). Comparing between Joule heating and photothermal heating, we can immediately observe that Joule heating of MXene layer is limited by the degradation of MXene under high current, whereas photothermal heating using sustainable solar energy is constrained by the limited surface area and the limited flux density of solar irradiance (~1.362 kW/m²). This makes Joule heating a more attractive option for localized heating as the limitation of photothermal heating using solar energy results in modifications being only able to supplement external heating to reduce heating load. However, the design of a membrane module for Joule heating experiments and

increasing MXene layer thickness without compromising coating stability to rival the results of Dudchenko et al. Joule heating of porous carbon nanotubes (CNT), requires further research trials.

Figure 1.7. Graphic representation of the separation process in a (a) conventional DCMD with feed being externally heated and (b) DCMD using MXene on the feed side with localized heating.

On the contrary, the previously used MD module could easily be modified to have a 6 mm thick clear acrylic window for a 50 W LED light source to be placed above to provide light energy for photothermal conversion using MXene coated membrane. Hence, given the difficulties of a joule heating at the current stage and the possibility of using Joule heating together with photothermal heating, we decided on investigating the localized photothermal effect in solar-assisted MD processes before attempting Joule heating. Such photothermal conversion is currently used in a form of solar thermal panels on the roof for heating water for home use. By having such solar-assisted MD modules, clean and heated water it is possible to be obtained simultaneously.

1.2.6. Photothermal materials on membrane and metallic spacers

In order to achieve localized heating on membrane using solar energy as proposed in the previous section, the photothermal materials can either be present on the membrane or on the spacers. For the membrane modification the coating method discussed in section 1.2.4.3. Whereas to improve the ease of modification of spacers, metallic spacers were chosen with the intent of plating photothermal metals over them.

With the synthesized MXene easily coated on hydrophobic PVDF membranes using vacuum filtration and dip coating in PDMS, such modified membrane could be studied in the laboratory to investigate its possible use in solar-assisted MD to replace part of the energy required for heating the feed with a sustainable energy source. Furthermore, the usefulness of other functional characteristics, such as fouling mitigation and photocatalytic degradation, of MXene could also be tested in the same MD setup.

On the other hand, the use of metallic spacers itself is controversial as heat loss across the membrane could reduce the energy efficiency of the MD system. That is one of the reasons almost all the spacers used are typically made of low-cost polymeric material (e.g., polypropylene). However, it is possible to achieve a more uniform temperature distribution near the surface of the membrane with a thermally conductive spacer. This concept was proposed by Ma et al. [79] and Jaichanda et al. [80] through the use of conductive gap membrane distillation (CGMD), where metallic spacers were used along the distillate-membrane interface to improve performance based on the inherently higher conductivity. This suggests that proper selection of the spacer material is beneficial for enhancing MD performance and that research could be carried out by placing metallic spacers along the feed-membrane interface which have not been done before. Hence, inspiring a work that would include an experimental and simulation study on metallic spacers in membrane distillation, along with the possibility of surface modification with platinum to provide photothermal localized heating to further improve the MD process. The use of metallic spacers potentially paves way for other methods or localized heating such as Joule heating and induction heating. Where Joule heating is the generation of heat by directly passing an electrical current through a conductor, and induction heating is the generating heat from electrical current induced by means of electromagnetic induction passing through a conductor. The latter involves the use of fast switching poles of electromagnetic field which makes it a non-contact

heating process which only heats up electric conductors which are affected by the electromagnetic field. This interesting property of induction heating makes it possible provide heat across electrical insulators allowing for non-invasive heating of metallic membrane spacers with most of the heat generated being absorbed by the feed. In fact, this non-invasive heating process has been favoured in food industries for its faster, better controlled and uniform, and more energy-efficient heating [36].

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CHAPTER 2 : UNDERSTANDING FOULING AND ITS EFFECT ON MD

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2.1. Introduction

MD offers several advantages relative to other separation technologies. These include operation at atmospheric pressure and moderate temperatures that translates to reduced operating and capital construction costs, use of non-selective highly permeable membranes, complete rejection of particulates and nonvolatile solutes, reduced membrane fouling, and the ability to be integrated into a hybrid process such as the membrane distillation bioreactor (MDBR) [1]. As such, MD is particularly well-suited for wastewater treatment via MDBR technology and concentrating heat-sensitive solutions such as those containing biomaterials and fruit juices. However, MD flux is affected by membrane scaling and fouling that could add resistances to the heat transfer and mass transfer, and can reduce the vapor pressure as has been shown recently by Chew et al. [2].

A comprehensive review of fouling and its control in MD has recently been published by Tijing et al. [3]. Fouling in MD occurs in the form of inorganic scaling, particulate or colloidal fouling, natural organic matter (NOM) fouling, and biofouling [4,5]. Scaling owing to the precipitation of inorganic solutes occurs only for nearly saturated feed solutions [6,7] such as in the continuous MD crystallization (CMDC) process [8]. NOM in the form of humic acids, proteins, aminosugars, polysaccharides and polyhydroxyaromatics, and biofouling caused by the growth of bacteria on a membrane can create a fouling layer with very small pores or free volume that can offer a resistance to both heat and mass transfer in MD and possibly can have other effects as well [5,2,9,10,11].

In his study of using MD to concentrate saline wastewater containing proteins and polysaccharides Gryta [5] observed a 70% flux decline over 55 hours that could not be explained by the added heat-transfer resistance owing to estimated fouling layer thickness of 90 μm . Gryta speculated that the disparity between his predictions and observations might be caused by an added hydraulic resistance owing to the fouling layer. In their studies using an MDBR to treat a synthetic wastewater, Phattaranawik et al. [12] observed flux declines of over 80% in 5 to 7 days that could not be explained by any added resistance to heat transfer. They also speculated that the fouling layer might cause a hydraulic resistance to liquid water transport to the membrane. In a similar study Goh et al. [13] observed a flux decline of 51% over 23 days owing to a biofouling layer whose thickness of 20 μm determined by confocal microscopy could not offer any significant heat-transfer resistance, but which they speculated could result in an added resistance to mass transfer. In an MD study using two sludges with different hydrophilicities Goh et al. [14] observed a 60% flux decline over 180 hours owing to a biofouling layer having a thickness of 7.4 to 15.1 μm determined by confocal microscopy that again could not contribute a significant heat-transfer resistance. Gravimetric experiments during evaporation of water from the two sludges indicated a significant vapor-pressure depression. In addition, determination of the pore-size distribution for the two sludges using evaporimetry [15,16], which is based on the relationship between pore diameter and vapor pressure dictated by the Kelvin equation [17,18], indicated average pore diameters for the two sludges ranging between 5 and 10 nm. Hence, they concluded that the large flux decline was due primarily to a vapor-pressure depression owing to the very small pores in the biofouling layer.

Chew et al. [2] subsequently adapted the MD model of Schofield et al. [19] to include both an added heat-transfer resistance and a vapor-pressure depression owing to the presence of a fouling layer with very small pores. Their model was able to explain the flux declines observed by Gryta [5], Phattaranawik et al. [12], and Goh et al. [13,14] based on a vapor-pressure depression owing to small pores whose average diameter ranged between 4 and 9 nm. In the absence of any comprehensive data set for MD fouling, Chew et al. [2] used their model to recast the data of Hanbury and Hotchkiss [20] for MD using DI water, which correlated well with the original model of Schofield et al. [19], to show how these same data would be widely scattered if there were a vapor-pressure

depression owing to an average pore size of 10 nm. However, a problem with using the modified model of Schofield et al. [19] to correlate data for fouling in MD is that the parameters extracted from the correlation involve combinations of the resistances of the fouling layer, feed side, distillate side, and the membrane in addition to the mass-transfer resistance of the membrane. The vapor-pressure-depression effect enters as an adjustable parameter in the ordinate involved in correlating the data. As such, it is difficult to conclude with any certainty what effects a fouling layer has on MD based on correlating the data via the modified correlation of Schofield et al. [19] developed by Chew et al. [2].

This brief review indicates that biofouling and fouling owing to organic matter in MD is not well-understood. The marked flux decline observed by several investigators cannot be explained by any additional resistance to heat transfer offered by the thin fouling layers. It has been speculated that the unexplained flux decline might well be due to an additional mass-transfer or hydraulic resistance in the fouling layer, although no definitive experimental studies have confirmed this. The speculation of Goh et al. [14] that the small pores in a biofouling layer might cause a vapor-pressure depression was shown to be possible in the modeling study of Chew et al. [2]. However, no data are available to confirm definitively that vapor-pressure depression in fact can occur during MD fouling. Whereas Srisurichan et al. [21] were able to explain the flux decline observed in their humic acid fouling studies by incorporating a heat-transfer resistance owing to the fouling layer, this could have resulted equally well from a vapor-pressure depression that they did not consider. Hence, the objectives of this study were the following: to design an experiment that would permit isolating the effects of a fouling layer in MD; to determine if a fouling layer can offer any significant heat- or mass-transfer resistance in MD; to determine if a fouling layer can cause any vapor-pressure depression in MD; and to advance a strategy to mitigate the effects of fouling on MD. This study would also provide insights to how feasible functional membrane coatings can be, since a membrane coating is essentially a fouling layer which provides the membrane with additional functions.

2.2. Theoretical considerations

The water-vapor flux in MD is driven by the difference in vapor pressure of the liquid on the feed and distillate sides of the membrane for which the principal mass-transfer resistance is that of the membrane. However, the vapor pressures on both sides

of the membrane are determined by the temperatures on each side of the membrane. As shown in Fig. 2.1 these temperatures are controlled by the heat-transfer resistances on the feed side, distillate side, within the membrane itself, and by the presence of a fouling layer. The latter also can possibly introduce a hydraulic resistance to the transfer of liquid through it and can contribute directly to a reduction in the vapor-pressure driving force owing to the presence of small pores. Hence, in general MD involves coupled mass and heat transfer.

Figure 2.1 . Schematic of the membrane distillation process showing the temperature profile from the hot feed side across a hydrophilic fouling layer and the hydrophobic microporous membrane to the cold distillate side.

Clearly it is necessary to have a model for the coupled mass- and heat-transfer process in order to design an experiment that will permit extracting the effects of a fouling layer on the MD process. Hitsov et al. [22] recently published a review of modeling approaches in MD. Modeling studies can be broadly classified into those based on a differential approach that require solution via a finite difference or finite element method and those based on a lumped parameter approach that can be solved algebraically. The latter is adequate for the present study since the experiments will be designed to isolate the effects of the fouling layer, thereby greatly simplifying the describing equations.

Fig. 2.2 shows an electrical analogue of the MD process where T_f , T_d , T_h and T_c are the temperatures of the feed, distillate, hot side of the membrane, and cold side of the membrane, respectively. Whereas T_f and T_d are imposed input process parameters, T_h

and T_c are determined by the heat-transfer resistances R_1, R_2, R_m, R_4 and R_v that are associated with the hydrodynamic boundary layer on the feed side, fouling layer, membrane, hydrodynamic boundary layer on the distillate side, and the pseudo-resistance associated with the vaporization of water, respectively. Chew et al. [2] modified the lumped-parameter coupled mass- and heat-transfer model developed by Schofield et al. [19] based on the electrical analogue shown in Fig. 2.2 to obtain the following relationship between the MD flux N and the vapor-pressure driving force:

$$\frac{T_f - T_d}{\lambda N} \left(1 - \frac{\beta}{1 - \frac{p_c^0}{p_h^0}} \right) = \frac{1}{\Delta H_v K_p \frac{dp^0}{dT}} \left(1 + \frac{R_{124} k_m}{\delta_m} \right) + R_{124} \quad (1)$$

where ΔH_v is the latent heat-of-vaporization, p_h^0 is the vapor pressure at T_h , p_c^0 is the vapor pressure at T_c , β is a dimensionless parameter characterizing the vapor-pressure depression, K_p is the mass-transfer coefficient for vapor transport through the pores of the membrane, R_{124} is the sum of the series resistances R_1, R_2 and R_4 , k_m is the effective thermal conductivity of the membrane, δ_m is the thickness of the membrane, and dp^0/dT is the temperature derivative of the vapor pressure evaluated at the average temperature across the membrane. In general, for MD in the presence of a fouling layer a plot the left-hand side of Eq. (1) versus dp^0/dT should give a straight line. Unfortunately, the slope and intercept of this line involve combinations of the mass- and heat-transfer resistances and therefore do not permit isolating either the heat-transfer resistance or any vapor-pressure reduction effect owing to the presence of a fouling layer. However, if

$$\frac{R_{124} k_m}{\delta_m} \ll 1 \quad (2)$$

the MD process will be mass-transfer controlled and can be represented by a much simpler model.

Figure 2.2. Electrical analogue for the membrane distillation process showing the feed-side resistance R_1 , fouling layer resistance R_2 , membrane resistance R_m , vaporization pseudo-resistance R_v and distillate-side resistance R_4 .

In order for the condition dictated by Eq. (2) to be satisfied, the sum of the resistances to heat transfer offered by the fluid on the feed side, the fluid on the distillate side, and the fouling layer must be negligible in comparison to the effective resistance to heat transfer offered by the membrane. The resistances R_1 and R_4 can be made small by employing a spacer mesh on both the feed and distillate sides of the membrane to generate secondary flows to increase the heat-transfer. However, spacers will have no effect on any heat-transfer resistance offered by the fouling layer. In order for the fouling layer resistance R_2 to be insignificant in comparison to the effective resistance offered by the membrane that consists of the two parallel resistances R_m due to conduction through the porous membrane and R_v due to convective transfer owing to the vaporization, the following condition must be satisfied:

$$\frac{R_2}{R_3} = \frac{R_2}{\left(\frac{R_v R_m}{R_v + R_m} \right)} \ll 1 \quad (3)$$

in which

$$R_2 = \left(\frac{k_f}{\delta_f} + \frac{NC_p T_h}{\Delta T} \right)^{-1} \quad (4)$$

$$R_m = \left(\frac{\varepsilon k_{air} + (1 - \varepsilon) k_{polymer}}{\delta_m} \right)^{-1} \quad (5)$$

and

$$R_v = \left(\frac{N \Delta H_v}{T_h - T_c} \right)^{-1} \quad (6)$$

where ε is the porosity of the membrane, k_{air} and $k_{polymer}$ are the thermal conductivities of air and the polymer in the membrane, k_f , δ_f and C_p are the thermal conductivity, thickness, and effective heat capacity of the fouling layer, respectively, and ΔT is the temperature difference across the fouling layer. The following parameters are representative of the maximum possible value of the ratio in Eq. (3) based on the MD fouling study in this paper: $\varepsilon = 0.75$; $k_{air} = 0.028 \text{ W/m} \cdot \text{K}$; $k_{polymer} = 0.19 \text{ W/m} \cdot \text{K}$; $k_f = 0.60 \text{ W/m} \cdot \text{K}$, $\delta_f = 100 \times 10^{-6} \text{ m}$ $\delta_m = 125 \times 10^{-6} \text{ m}$; $C_p = 4066 \text{ J/kg} \cdot \text{K}$; $N = 5.42 \times 10^{-4} \text{ kg/m}^2 \text{ s}$; $T_h = 33.9 \text{ }^\circ\text{C}$; $T_h - T_c = 24.3 \text{ }^\circ\text{C}$; $\Delta H_v = 2257 \times 10^3 \text{ W} \cdot \text{s/kg}$; and $\Delta T \cong 5 \text{ }^\circ\text{C}$. The fouling layer has been assumed to have the thermal conductivity of liquid water since it is saturated with water, and it has been assumed to be $100 \text{ } \mu\text{m}$ thick based on the study of Gryta [5]. The temperature difference across the fouling layer has been assumed to be $5 \text{ }^\circ\text{C}$, which will overestimate the heat-transfer resistance of the fouling layer if indeed the latter is found to be negligible in comparison to that of the membrane. When these values are substituted into Eqs. (3–6), we obtain the following for the ratio of the heat-transfer resistance of the fouling layer relative to the effective heat-transfer resistance of the membrane:

$$\frac{R_2}{R_3} = \frac{R_2}{\left(\frac{R_v R_m}{R_v + R_m} \right)} \cong \frac{R_2}{R_m} = 0.089 \quad (7)$$

The conductive resistances in both the membrane and the fouling layer are controlling. However, the heat-transfer resistance of the membrane is more than an order-of-magnitude larger than the heat-transfer resistance of the fouling layer. Hence, a humic acid fouling layer does not offer any significant resistance to heat transfer in MD. Moreover, it is doubtful that any fouling layer in MD could offer any significant resistance to heat transfer.

If the heat-transfer resistances on the feed and distillate sides of the membrane can be made very small by employing a spacer mesh in the flow channels and the fouling layer offers no significant heat-transfer resistance, the MD process will be mass-transfer controlled. However, it is possible that the fouling layer could offer a hydraulic resistance to mass transfer. Note that in the MD process, water is not drawn through a fouling layer by diffusive mass transfer since there is no water concentration gradient across it. Rather, water is drawn through the porous hydrophilic fouling layer by capillary suction induced by the curvature of the water-air interface. The mass flux owing to an imposed pressure differential ΔP for laminar flow in a cylindrical tube having diameter d is given by the following:

$$N_c = \frac{d^2 \rho \Delta P}{32 \mu \delta_f} \quad (8)$$

where ρ and μ are the mass density and shear viscosity of the liquid, respectively, and δ_f is the length of the tube, which here is assumed to be the thickness of the fouling layer. The capillary suction ΔP developed in a wetting liquid in a pore having a diameter d is given by the following:

$$\Delta P = \frac{4\gamma \cos \theta}{d} \quad (9)$$

where γ is the surface tension and θ is the contact angle of the liquid on the pore wall. Substituting Eq. (9) into Eq. (8) then gives the following equation for the hydraulic flux N_h through a fouling layer owing to capillary action:

$$N_h = \frac{d \rho \gamma \cos \theta}{8 \mu \delta_f} \quad (10)$$

The condition that must be satisfied in order to assume that the fouling layer does not offer any significant hydraulic resistance to liquid water transfer to the membrane surface is the following:

$$\frac{N}{N_h} = \frac{8 \mu \delta_f N}{d \rho \gamma \cos \theta} \ll 1 \quad (11)$$

The following parameters are representative of the MD fouling study presented in this paper: $\gamma = 0.07 \text{ N/m}$; $\mu = 5.0 \times 10^{-4} \text{ kg/m} \cdot \text{s}$; $\delta_f = 100 \times 10^{-6} \text{ m}$; $N < 1 \times 10^{-2} \text{ kg/m}^2 \text{ s}$; $\rho = 10^3 \text{ kg/m}^3$; $\theta = 0^\circ$; and $10^{-8} \text{ m} \leq d \leq 10^{-6} \text{ m}$. These values imply the following:

$$5.71 \times 10^{-5} < \frac{N}{N_h} < 5.71 \times 10^{-3} \quad (12)$$

Clearly capillary action can supply water through the fouling layer as fast as it evaporates. Hence, the fouling layer offers no significant hydraulic resistance in the current study, nor is it likely to have had much effect on the mass transfer in any prior studies of fouling in MD.

If the MD process is mass-transfer controlled and if the conditions given by Eqs. (3) and (11) for neglecting any heat-transfer or hydraulic resistance offered by the fouling layer are satisfied, the MD flux can be expressed directly in terms of the driving force for diffusive transfer of water vapor through the porous membrane given by the following:

$$N = K_p \left(p_h^0 e^{-\beta} - p_c^0 \right) \quad (13)$$

where the term $e^{-\beta}$ accounts for the vapor-pressure depression relative to the normal vapor pressure p_h^0 . It is better to use Eq. (13) to describe the MD flux rather than the appropriately simplified form of Eq. (1) because the latter has some approximations that are unnecessary when the MD is mass-transfer controlled. If the MD process is mass-transfer controlled, the vapor pressures p_h^0 and p_c^0 are evaluated at the feed and

distillate temperatures, T_h and T_c , respectively, since the heat transfer resistances on the feed and distillate sides of the membrane are negligible. Moreover, the mass-transfer coefficient K_p should be the same as that for MD using DI water for which no membrane fouling occurs. Eq. (13) implies that a plot of the MD flux N versus the adjusted vapor-pressure driving force $p_h^0 e^{-\beta} - p_c^0$ should be a straight line having a slope K_p and a zero intercept. The dimensionless parameter β that characterizes the vapor-pressure depression depends on the average pore diameter in the fouling layer; as such, it must be determined by some ‘best-fit’ criterion. The characteristic average pore diameter d of the fouling layer can be determined from β via the following:

$$d = \frac{4\gamma V_w}{RT_h \beta} \quad (14)$$

where V_w is the molar volume of the liquid, and R is the universal gas constant.

2.3. Experiment design and materials

2.3.1. Design considerations

The experimental design for this study of organic fouling in MD had to satisfy the following conditions:

- Employ well-characterized highly permeable hydrophobic membranes
- Use a fouling agent that will give reproducible results
- Establish flow conditions on the feed and distillate sides to minimize the heat transfer resistance
- Control and measure the temperature driving force for MD
- Maintain equal pressures on both sides of the membrane
- Accurately measure the MD flux
- Employ system components that are not attacked by a saline water feed

2.3.2. Overview of design

Fig. 2.3 shows a schematic of the experiment apparatus that consisted of recirculating flow loops on both the feed and distillate sides of the membrane. The feed and distillate flow rates were controlled by peristaltic pumps. The flow cell chambers on

the feed and distillate sides were identical to facilitate maintaining the same pressure on both sides of the membrane. The feed and distillate side temperatures were controlled by a recirculating heated bath and chiller, respectively. The temperature driving force was determined via temperature probes at the inlet and outlet of the feed and distillate flows. The flow channels were filled with spacer mesh to minimize the resistance to heat transfer. Commercial polytetrafluoroethane (PTFE) and polyvinylidene fluoride (PVDF) hydrophobic flat sheet microfiltration membranes were used; their pore-size distribution was determined via liquid-displacement porometry (LDP). An aqueous feed solution of humic acid buffered with calcium chloride was used for the fouling studies. The mass flux was determined gravimetrically. For each membrane two to four replicate

Figure 2.3. Schematic of the apparatus for controlled studies of membrane distillation, consisting of (a) Jacketed feed tank heated and agitated by a hotplate stirrer, (b) Peristaltic Pumps, (c) Cross-flow flat-sheet acrylic membrane module, (d) Distillate tank cooled by a cooling recirculator, and (e) Overflow distillate tank rested on a mass balance. Feed solutions consist of distilled deionized water and an aqueous solution of 160 mg/L of humic acid and 3.775 mM of calcium chloride.

experiments were made for both the control run using DI water and for the humic acid fouling run. The same membrane sample was used for both the control run using DI water and the humic acid fouling run for each replicate experiment.

2.3.3. Materials and apparatus

The PTFE flat sheet membrane (Sartorius 11807-640-320PR) had a nominal pore diameter of $0.2\ \mu\text{m}$ and a porosity of 62%, and the PVDF flat sheet membrane (Durapore GVHP) had a nominal pore diameter of $0.22\ \mu\text{m}$ and a porosity of 75%. Liquid displacement porometry (LDP) characterization of the pore-size distributions indicated a mean-flow pore diameter of $0.187\ \mu\text{m}$ for the PTFE and $0.209\ \mu\text{m}$ for the PVDF membrane.

The membrane cell was fabricated from two parallel acrylic plates. Sterlite[®] polypropylene spacers were used to create a cavity for inserting the membrane. The flow-channel dimensions were identical on the feed and distillate sides; the length, width, and height of the flow channels were 0.08 m, 0.07 m, and 0.02 m, respectively; the active membrane area was $6.3 \times 10^{-3}\ \text{m}^2$. In order to significantly increase the heat-transfer coefficients on the feed and distillate sides of the membrane, the flow channels were filled with two layers of polypropylene spacers. The modeling and experimental studies of Phattaranawik et al. [23] indicate that filling the channel cross-section with spacers can

result in negligible resistance to heat transfer relative to the heat-transfer resistance offered by the membrane in MD.

The feed solution was DI water for the MD runs in the absence of fouling. For the fouling runs the feed was an aqueous solution of 160 mg/L of humic acid (Sigma-Aldrich CAS No. 68131-04-4) and 3.775 mM of calcium chloride (Merck-Millipore CAS No. 10043-52-4), which was added to control the formation of humic acid coagulates as recommended by Srisurichan et al. [24].

A closed loop recirculating system was used whereby the feed and distillate streams were maintained in countercurrent flow at the same constant flowrate of 400 ml/min via peristaltic pumps (Masterflex L/S Digital Drive). The peristaltic pumps were recalibrated regularly via direct volumetric flow rate measurements. Masterflex Norprene food tubing was used on the feed side and Masterflex Tygon E-LFL tubing was used on the distillate side. The hot side feed was continuously recirculated from a jacketed pyrex beaker. The cold side water was continuously recirculated from a stainless-steel tank. The temperature on the feed side was controlled by a recirculating bath (Julabo ME) and the temperature on the cold side was controlled by a recirculating chiller (Polyscience). In order to maintain constant flow rates and feed-side concentration, the overflow from the cold side stainless-steel tank owing to the MD flux was recycled back to the pyrex beaker on the feed side by another peristaltic pump. Maintaining the same flow rate on both sides of the membrane ensured that there was no pressure differential across the membrane. Periodic conductivity checks were made to make certain that there was no liquid cross-over from the feed to the distillate side of the membrane.

The distillate flux was determined gravimetrically by weighing the overflow from the stainless steel tank via an electronic balance (Mettler-Toledo ME4002). The feed side inlet and outlet temperatures were measured using a thermal probe (Lutron PT100) connected to a temperature logger (Lutron TM-946). The distillate side inlet and outlet temperatures were measuring using thermocouples (Centertek k-type) connected to a temperature logger (Centertek 309). The flow rates and temperatures were recorded every five minutes.

2.3.4. Procedure

In order to carry out both the DI water and humic acid fouling experiments on the same membrane sample while changing the temperature driving force for both sets of experiments, the following stepwise procedure was used:

1. The membrane sample was cut to size and mounted in the flow cell.
2. DI water was circulated through the flow loop for fixed inlet feed and distillate side temperatures to purge the system of air bubbles and achieve steady-state operation.
3. When steady-state was achieved data logging of the distillate flux and temperatures was done every 5 minutes for a period of 3 hours.
4. The temperature of the feed then was increased to increase the overall temperature driving force.
5. When steady-state was achieved data logging again was done for a period of 3 hours.
6. Steps 4 and 5 then were repeated in order to cover a range of the temperature driving force.
7. The feed temperature then was reduced to the lowest desired value for the humic acid fouling experiments.
8. 50 ml of DI water then was removed from the feed tank and 50 ml solution of a concentrated mixture of humic acid and calcium chloride then was introduced into the feed tank to establish a feed concentration of 160 mg/L of humic acid and 3.775 mM of calcium chloride.
9. The fouling run was continued at the fixed initial temperature in order to establish an equilibrium fouling layer thickness as indicated by a constant MD flux.
10. When a steady-state flux was achieved data logging was initiated as described in step 3.
11. The temperature of the feed then was increased to increase the overall temperature driving force.
12. When steady-state was achieved data logging again was done for a period of 3 hours.

13. Steps 11 and 12 then were repeated in order to cover a range of the temperature driving force.
14. Replicate runs then were carried out using different samples of the same membrane to assess the experiment error.

2.3.5. Data analysis

A schematic diagram of the data analysis steps can be found in Fig. 2.4. The pooled data (i.e., from all replicate runs) for the MD flux were plotted as a function of the vapor-pressure driving force for the DI water experiments on a given type of membrane. A trendline was inserted through the plot of these data for which the coefficient-of-determination (R^2) for the fit of the trendline through the pooled data was determined. The mass-transfer coefficient K_p is the slope of this line based on Eq. (13) with $\beta = 0$ (i.e., in the absence of any vapor-pressure depression). The intercept of this plot should be essentially zero if the MD process is mass-transfer controlled. This same value of K_p should describe the mass-transfer for the humic acid experiments. However, the latter can be influenced by a vapor-pressure depression owing to the small pores in the hydrophilic humic acid fouling layer. The value of β corresponded to that which minimized the difference between the predicted and measured values of the MD flux. The R^2 for the fit of the predicted to the measured MD flux then was determined. This value should be well above 0.9 to confirm a good correlation. The average pore diameter in the humic acid fouling layer then was determined from the value of β and Eq. (14).

Figure 2.4. Schematic diagram of the data analysis steps.

2.4. Presentation and discussion of results

2.4.1. DI water experiments

Fig. 2.5 shows a plot of the MD flux in $\text{kg}/\text{m}^2\text{s}$ as a function of the vapor-pressure driving force in kPa for 43 data points associated with four replicate runs (i.e., on four different membrane samples shown by different markers) for the PTFE membrane. The following trendline fits these data for the MD flux in $\text{kg}/\text{m}^2\text{h}$ as a function of the vapor-pressure driving force in kPa with an $R^2 = 0.977$:

$$N = 2.74 \times 10^{-4} (p_h^0 - p_c^0) - 2.38 \times 10^{-4} \quad (15)$$

Figure 2.5. Membrane distillation flux as a function of the vapor-pressure driving force for a DI water feed; four replicate runs using a PTFE membrane: ● Run 1; ○ Run 2; ▲ Run 3; △ Run 4.

The slope of this trendline is the mass-transfer coefficient K_p . The very small intercept confirms that there is no significant resistance to heat transfer offered by the flow on the feed and distillate sides of the membrane owing to the presence of spacer mesh in the flow channels.

Fig. 2.6 shows a plot of the MD flux in $\text{kg}/\text{m}^2\text{s}$ as a function of the vapor-pressure driving force in kPa for 34 data points associated with three replicate runs (shown by different markers) for the PVDF membrane. The following trendline fits these data for the MD flux in $\text{kg}/\text{m}^2\text{h}$ as a function of the vapor-pressure driving force in kPa with an $R^2 = 0.984$:

$$N = 2.85 \times 10^{-4} (p_h^o - p_c^o) - 1.75 \times 10^{-4} \quad (16)$$

Again, the slope of this trendline is the mass-transfer coefficient K_p . The very small intercept again indicates that there is no significant resistance to heat transfer offered by

the flow on the feed and distillate sides of the membrane owing to the presence of the spacer mesh.

Figure 2.6. Membrane distillation flux as a function of the vapor-pressure driving force for a DI water feed; three replicate runs using a PVDF membrane: ● Run 1; ○ Run 2; ▲ Run 3.

The mass-transfer coefficient for the PTFE membrane is slightly smaller than that for the PVDF membrane. This is surprising since the PTFE membrane is considerably thinner than the PVDF membrane (65 μm versus 125 μm). The PTFE membrane does have a smaller porosity (62% versus 75%) and a slightly smaller mean flow pore diameter (0.187 μm versus 0.209 μm) than the PVDF membrane. The mass transfer through the membrane can occur either by Knudsen diffusion for which the flux is proportional to $d\varepsilon/\delta_m$ or by Fickian diffusion for which the flux is proportional to ε/δ_m . Neither model can explain the observed lower value of K_p for the PTFE relative to the PVDF membrane based on just the membrane thicknesses, porosities, and mean flow pore diameters. In fact, both models suggest that K_p for the PTFE membrane should be considerably larger than that for the PVDF membrane.

These seemingly anomalous results for the mass-transfer coefficient can be explained by considering whether the diffusion of the water vapor occurs in the Fickian (ordinary diffusion) or Knudsen regime, or possibly via some combination of these two mechanisms owing to the pore-size distribution in the membrane. Whether any diffusion occurs in the Knudsen regime is determined by whether the mean free path of the water vapor molecule in air, λ , is larger than the pore diameter, d ; that is, whether $\lambda/d > 1$. For a water molecule at saturation conditions at 50.4°C, the average temperature of the hot feed, $\lambda = 0.074 \mu\text{m}$; this value accounts for the presence of the air that has a somewhat larger effective collision diameter than the water molecule. Whereas the PVDF membrane had some pores smaller than $0.074 \mu\text{m}$, none of the pores in the PTFE membrane are this small. This implies that the mass transfer in the PTFE membrane is entirely by Fickian diffusion, whereas the mass transfer in the PVDF membrane occurs by a combination of Knudsen diffusion in the smaller pores and Fickian diffusion in the larger pores. In order to assess the relative importance of these two mechanisms, it is necessary to convert the flow-based pore-size distribution determined by liquid-displacement porometry (LDP) to an equivalent number-based pore-size distribution. When this was done, it was found that Knudsen diffusion occurred in 34% of the pores in the PVDF membrane. The fact that the Knudsen diffusion coefficient is larger than the Fickian diffusion coefficient for the conditions of this study [19] explains why the mass-transfer coefficient for the PVDF membrane is larger than that for the PTFE membrane even though the latter is significantly thinner.

2.4.2. Humic acid fouling experiments

Fig. 2.7 shows a plot of the MD flux in $\text{kg}/\text{m}^2\text{s}$ as a function of the vapor-pressure driving force in kPa based on Eq. (13) for 22 data points associated with two replicate runs (shown by different markers) for humic acid fouling on the PTFE membrane. The line in Fig. 2.7 is not a trendline through the data, but rather is the predicted flux based on K_p from the DI water runs for the same membrane and the optimum value of $\beta = 0.220$; the latter is the value of β that minimized the average difference between the predicted and measured MD fluxes. The predicted flux in $\text{kg}/\text{m}^2\text{h}$ as a function of the vapor pressure in kPa given by the following equation agrees with the measured flux with an $R^2 = 0.912$:

$$N = 2.74 \times 10^{-4} (p_h^0 e^{-0.220} - p_c^0) \quad (17)$$

Figure 2.7. Membrane distillation flux as a function of the vapor-pressure driving force for an aqueous feed solution containing 160 mg/L of humic acid and 3.775 mM of calcium chloride; two replicate runs using a PTFE membrane: ● Run 1; ▲ Run 2.

The average error in predicting the flux is 14.7%. The value $\beta = 0.220$ corresponds to an average pore diameter in the humic acid fouling layer of 8.3 nm. The vapor-pressure depression owing to the humic acid fouling layer caused an average reduction in the MD flux of 29.9%.

Fig. 2.8 shows a plot of the MD flux in $\text{kg}/\text{m}^2\text{s}$ as a function of the vapor-pressure driving force in kPa based on Eq. (13) for 38 data points associated with three replicate runs (shown by different markers) for humic acid fouling on the PVDF membrane. The line in Fig. 2.8 is not a trendline through the data, but rather is the predicted flux based on K_p from the DI water runs for the same membrane and the

optimum value of $\beta = 0.147$; the latter is the value of β that minimized the average difference between the predicted and measured MD fluxes. The predicted flux in $\text{kg}/\text{m}^2 \text{ h}$ as a function of the vapor pressure in kPa given by the following equation agrees with the measured flux with an $R^2 = 0.936$:

$$N = 2.85 \times 10^{-4} (p_h^0 e^{-0.147} - p_c^0) \quad (17)$$

Figure 2.8. Membrane distillation flux as a function of the vapor-pressure driving force for an aqueous feed solution containing 160 mg/L of humic acid and 3.775 mM of calcium chloride; three replicate runs using a PVDF membrane: ● Run 1; ○ Run 2; ▲ Run 3.

The average error in predicting the flux is 10.9%. The value $\beta = 0.147$ corresponds to an average pore diameter in the humic acid fouling layer of 12.4 nm. The vapor-pressure depression owing to the humic acid fouling layer caused an average reduction in the MD flux of 21.0%.

The comparison between the predictions for the mass-transfer controlled model and the measured MD fluxes shown in Figs. 2.7 and 2.8 clearly indicate that filling the

cross-section of the feed and distillate channels with spacer mesh eliminated any significant resistance to heat transfer external to the membrane. The fact that the mass-transfer coefficient determined from the DI water runs also fit the humic acid fouling runs very well indicates that the fouling layer did not offer any significant heat- or mass-transfer resistance. However, a marked vapor-pressure depression was observed associated with the small pores in the humic acid fouling layer. Interestingly, the more hydrophobic (water contact angle of 108°) PTFE membrane had a smaller average pore diameter in the fouling layer (8.3 nm) than did the less hydrophobic (water contact angle of 37.2°) PVDF membrane (12.4 nm). This is a consequence of the lower porosity of the PTFE membrane relative to the PVDF membrane (62% versus 75%). A lower porosity implies a higher flux through the pores; a measure of this is the ratio K_p/ε , which is equal to $4.42 \times 10^{-4} \text{ kg/m}^2\text{s} \cdot \text{kPa}$ for the PTFE membrane but only $3.80 \times 10^{-4} \text{ kg/m}^2\text{s} \cdot \text{kPa}$ for the PVDF membrane. A higher flux through the pores causes more compaction and therefore a smaller average pore size in the humic acid fouling layer for the PTFE membrane relative to the PVDF membrane.

2.5. Conclusions

This study has shown that by filling the flow channels with spacer mesh, the heat-transfer resistances on the feed and distillate sides in MD can be minimized relative to the heat-transfer resistance offered by the membrane itself. Moreover, calculations based on the parameters for this study indicated that the humic acid fouling layer was too thin to offer any significant resistance to heat transfer in MD. Theoretical considerations also established that capillary action was sufficient to supply water to the membrane as fast as it evaporated even for the smallest pores encountered in a humic acid fouling layer; as such, the humic acid fouling layer did not offer any hydraulic resistance to the transport of water to the membrane.

In the absence of any external heat-transfer resistances owing either to the feed and distillate flows or to a fouling layer, the temperatures immediately adjacent to the membrane will be the same as those of the feed and distillate flows. These temperatures control the vapor-pressure driving force for diffusive mass transfer through the membrane in MD. As such, the MD process will be mass-transfer controlled and described by a simple model in which the flux is directly proportional to the vapor-pressure driving force

across the membrane. However, this driving force can be affected by a vapor-pressure depression owing to the curvature of the interface of the liquid water in the small pores of a hydrophilic fouling layer such as humic acid.

For a mass-transfer controlled MD process, the mass-transfer coefficient can be determined from MD runs using DI water as the feed. The mass-transfer coefficient determined for the PTFE membrane was smaller than that for the PVDF membrane even though the latter was nearly twice as thick as the former. This was a consequence of the markedly different pore-size distributions in the two membranes. Most of the pores in the PVDF membrane were in the range where Knudsen diffusion controlled the mass-transfer rate. In contrast, most of the pores in the PTFE membrane were in the range where the slower Fickian diffusion controlled the mass-transfer rate. This underscores the importance of characterizing the pore structure in a membrane using the number-based pore-size distribution rather than just the flow-based pore-size distribution that is obtained directly from characterization via liquid-displacement porometry (LDP). It also indicates that the importance of determining the mode of mass transfer through the membrane since Knudsen diffusion can be occurring in the smaller pores and Fickian diffusion in larger pores.

In the absence of any heat- or mass-transfer resistances offered by the fouling layer, the mass-transfer coefficient determined from the DI water runs should also describe the relationship between the MD flux and vapor-pressure driving force in the presence of membrane fouling. This was confirmed in this study for both humic acid fouling on a PTFE membrane and on a PVDF membrane.

A plot of the MD flux versus the vapor-pressure driving force for the humic acid fouling experiments permits determining the dimensionless parameter β that is inversely proportional to the characteristic membrane pore diameter. The resulting values of the characteristic pore diameters were in the range of the values estimated for prior studies of humic acid fouling and biofouling. However, the characteristic pore diameter for the more hydrophobic PTFE membrane was somewhat less than that of the considerably less hydrophobic PVDF membrane. This was attributed to the formation of a more densely packed fouling layer in the PTFE membrane owing to its lower porosity and hence higher flux through the pores relative to the PVDF membrane.

This study establishes beyond reasonable doubt that a fouling layer such as humic acid can cause a flux decline owing to a direct reduction in the vapor-pressure driving force, which is caused by the Kelvin effect associated with the curvature of the interface between the liquid water and ambient gas phase at the mouth of the pores in the fouling layer. This effect was found to cause flux declines of 29.9 % and 21.0% for the PTFE and PVDF membranes, respectively. The vapor-pressure depression increases markedly with a decrease in the characteristic pore diameter in the fouling layer. Hence, one would anticipate a larger flux decline for biofouling for which the fouling layer has a gel-like structure.

Several suggestions for improving the performance of the MD process emerge from this study. The flow-based pore-size distribution of the membranes determined from liquid-displacement porometry (LDP) should be recast in terms of the number-based pore-size distribution in order to assess how much of the mass-transfer flux is occurring in the Knudsen flow regime for which the mass-transfer coefficients are larger than for the Fickian diffusion regime. A good MD membrane should have a high porosity with most of the pores in the Knudsen flow regime.

Temperature polarization can be minimized in MD by employing spacers on both the feed and distillate sides of the membrane to reduce the heat-transfer resistances external to the membrane. It also can be reduced by increasing the heat-transfer resistance of the membrane by using a higher porosity membrane with a lower thermal conductivity. Increasing the thickness of the membrane will also decrease the conductive heat transfer; however, it also will decrease the diffusive mass transfer.

A very effective way to improve the performance of the MD process is to employ an asymmetric hydrophobic ultrafiltration membrane for which the side facing the hot feed solution has a very thin layer of very small pores. These small pores will cause a vapor-pressure increase and will eliminate any vapor-pressure decrease associated with the water in any hydrophilic fouling layer; that is, liquid water will be drawn by capillary action through the hydrophilic fouling layer up to its interface with the hydrophobic layer containing very small pores. The only vapor-pressure effect then will be a marked increase in the vapor-pressure driving force owing to the small pores on the feed side of the hydrophobic membrane. Note however that this layer of small pores needs to be very

thin to avoid presenting any significant resistance to the diffusive mass transfer of water vapor through the hydrophobic membrane. This type of highly asymmetric hydrophobic membrane structure could be created by deposition or grafting as well as other means.

Appendix

Analysis to Estimate the Hot and Cold Side Membrane Temperatures

Since the current flow through R_1 is the same as the current flow through R_4 we have

$$(T_f - T_h)h_1 = (T_c - T_p)h_2 \Rightarrow T_c = T_p + (T_f - T_h)\frac{h_1}{h_2} \quad (1)$$

The above assumes that the resistance of the fouling layer is negligible since it is very thin. Since the combined current flow through the membrane and owing to the vaporization of the water is equal to the current flow through R_1 we have

$$N\lambda + \frac{k_3}{\delta}(T_h - T_c) = (T_f - T_h)h_1 \quad (2)$$

Substitute Eq. (1) into Eq. (2)

$$\begin{aligned} N\lambda + \frac{k_3}{\delta} \left\{ T_h - \left[T_p + (T_f - T_h)\frac{h_1}{h_2} \right] \right\} &= (T_f - T_h)h_1 \\ N\lambda + \frac{k_3}{\delta}T_h - \frac{k_3}{\delta}T_p - \frac{k_3}{\delta}\frac{h_1}{h_2}T_f + \frac{k_3}{\delta}\frac{h_1}{h_2}T_h &= T_fh_1 - T_hh_1 \\ T_h = \frac{T_fh_1 - N\lambda + \frac{k_3}{\delta}T_p + \frac{k_3}{\delta}\frac{h_1}{h_2}T_f}{\frac{k_3}{\delta} + \frac{k_3}{\delta}\frac{h_1}{h_2} + h_1} &\Rightarrow T_h = \frac{T_fh_1 - N\lambda + \frac{k_3}{\delta} \left(T_p + \frac{h_1}{h_2}T_f \right)}{\frac{k_3}{\delta} \left(1 + \frac{h_1}{h_2} \right) + h_1} \end{aligned} \quad (3)$$

Note that

$$k_m = \varepsilon k_g + (1 - \varepsilon)k_p \quad (4)$$

The thermal conductivities of air, PVDF, and PTFE are given by the following:

$$k_g \cong 0.027 \frac{\text{W}}{\text{m} \cdot \text{K}}; \quad k_{\text{PVDF}} \cong 0.19 \frac{\text{W}}{\text{m} \cdot \text{K}}; \quad k_{\text{PTFE}} \cong 0.25 \frac{\text{W}}{\text{m} \cdot \text{K}}$$

Using the values of the flux and temperatures from the experimental runs along with the estimated values of the heat-transfer coefficients in Eq. (3) permits obtaining an improved estimate of T_h . The resulting value of T_h then can be used in Eq. (1) to obtain

an improved estimate of T_c . A reasonable value for the porosity of RO membranes is 75%.

Sample Calculation for the Millipore PVDF data:

$$T_h = \frac{T_f h_1 - N\lambda + \frac{k_3}{\delta} \left(T_p + \frac{h_1}{h_2} T_f \right)}{\frac{k_3}{\delta} \left(1 + \frac{h_1}{h_2} \right) + h_1}$$

$$T_h = \frac{\left(68.7 \text{ }^\circ\text{C} \right) \left(3.15 \frac{\text{kW}}{\text{m}^2\text{K}} \right) - \left(0.001919 \frac{\text{kg}}{\text{m}^2\text{s}} \right) \left(2257 \frac{\text{kJ}}{\text{kg}} \right) \left(\frac{\text{kWs}}{\text{kJ}} \right) + \frac{6.78 \times 10^{-5} \frac{\text{kW}}{\text{m}\cdot\text{K}}}{125 \times 10^{-6} \text{m}} \left[20.8 \text{ }^\circ\text{C} + \frac{3.15 \frac{\text{kW}}{\text{m}^2\text{K}}}{3.26 \frac{\text{kW}}{\text{m}^2\text{K}}} (68.7 \text{ }^\circ\text{C}) \right]}{\frac{6.78 \times 10^{-5} \frac{\text{kW}}{\text{m}\cdot\text{K}}}{125 \times 10^{-6} \text{m}} \left(1 + \frac{3.15 \frac{\text{kW}}{\text{m}^2\text{K}}}{3.26 \frac{\text{kW}}{\text{m}^2\text{K}}} \right) + 3.15 \frac{\text{kW}}{\text{m}^2\text{K}}} \quad (5)$$

$$T_h = \frac{216 - 4.33 + 0.542(20.8 + 66.4)}{0.542(1.97) + 3.15} = 61.4 \text{ }^\circ\text{C}$$

$$T_c = T_p + (T_f - T_h) \frac{h_1}{h_2} = 20.8 \text{ }^\circ\text{C} + (68.7 \text{ }^\circ\text{C} - 61.4 \text{ }^\circ\text{C}) \frac{3.15 \frac{\text{kW}}{\text{m}^2\text{K}}}{3.26 \frac{\text{kW}}{\text{m}^2\text{K}}} = 27.9 \text{ }^\circ\text{C} \quad (6)$$

These revised estimates indicate that the membrane offers more resistance to heat transfer than either R_1 or R_4 since the estimated values that we obtained by assuming that $R_1 = R_{35} = R_4$ result in a value of T_h that is too low and a value of T_c that is too high; that is, for the particular PVDF run for which this sample calculation was done the estimated values on the Excel spreadsheet were $T_h = 52.7 \text{ }^\circ\text{C}$ and $T_c = 36.8 \text{ }^\circ\text{C}$.

Calculation of the pore diameter of the fouling layer (PVDF Membrane)

The pore diameter is determined from the value of β :

$$\beta = \frac{4\gamma V_w}{RTd} \Rightarrow d = \frac{4\gamma V_w}{RT\beta}$$

The physical properties in the above should be determined at the average value of T_h , which is $56.0 \text{ }^\circ\text{C}$ for which

$$V_w = \frac{18 \frac{\text{g}}{\text{mol}}}{\left(985 \frac{\text{kg}}{\text{m}^3} \right) \left(10^3 \frac{\text{g}}{\text{kg}} \right)} = 1.83 \times 10^{-5} \frac{\text{m}^3}{\text{mol}}$$

$$\gamma = 0.0669 \frac{\text{N}}{\text{m}} \text{ at } 56^\circ \text{C}$$

$$8.314 \frac{\text{N} \cdot \text{m}}{\text{K} \cdot \text{mol}}$$

$$d = \frac{4\gamma V_w}{RT\beta} = \frac{4 \left(0.0669 \frac{\text{N}}{\text{m}} \right) \left(1.83 \times 10^{-5} \frac{\text{m}^3}{\text{mol}} \right) \left(10^9 \frac{\text{nm}}{\text{m}} \right)}{\left(8.314 \frac{\text{N} \cdot \text{m}}{\text{K} \cdot \text{mol}} \right) (329.15 \text{ K}) (0.15)} = 11.9 \text{ nm}$$

List of symbols

C_p	Heat capacity (W·s/kg·K)
d	Characteristic diameter of pores in the fouling layer (m)
K_p	Overall mass-transfer coefficient of water vapor through the membrane (kg/m ² ·s·Pa)
k_{air}	Thermal conductivity of air (W/m·K)
k_f	Thermal conductivity of the fouling layer (W/m·K)
k_m	Effective thermal conductivity of the microporous membrane (W/m·K)
$k_{polymer}$	Thermal conductivity of the polymer in the microporous membrane (W/m·K)
N	Mass-transfer flux (kg/m ² s)
N_h	Mass flux owing to capillary suction (kg/m ² s)
p^o	Vapor pressure of water (kPa)
p_c^o	Vapor pressure of water on the distillate side of the membrane (kPa)
p_h^o	Vapor pressure of water on the feed side of the membrane (kPa)
R	Universal gas constant (N·m/K·mol)
R^2	Coefficient-of-determination for linear regression (dimensionless)
R_m	Conductive heat-transfer resistance of the microporous membrane (K·m ² /W)
R_v	Pseudo heat-transfer resistance associated with the vaporization of water (K·m ² /W)

R_1	Convective heat-transfer resistance associated with the hot feed (K·m ² /W)
R_2	Conductive heat-transfer resistance associated with MMBF layer (K·m ² /W)
R_3	Effective heat-transfer resistance associated with the resistances R_m and R_v in parallel (K·m ² /W)
R_4	Convective heat-transfer resistance associated with the cold distillate (K·m ² /W)
R_{124}	Effective resistance of the resistances R_1 , R_2 , and R_4 in series (K·m ² /W)
T	Temperature (K)
T_c	Temperature on the cold side of the membrane (K)
T_d	Temperature of the distillate (K)
T_f	Temperature of the feed (K)
T_h	Temperature on the hot side of the membrane (K)
V_w	Molar volume of liquid water (m ³ /mol)

Greek Symbols

β	Group defined by Eq. (14) that characterizes the Kelvin effect (dimensionless)
γ	Surface tension of water (N/m or kg/s ²)
ΔH_v	Heat-of-vaporization of water (W·s/kg)
ΔP	Pressure driving force owing to capillary suction (kPa)
δ_f	Thickness of the fouling layer (m)
δ_m	Thickness of the microporous membrane (m)
ε	Porosity of the microporous membrane (dimensionless)
λ	Mean free path of a water molecule in the gas phase (m)
μ	Shear viscosity (kg/m·s)
θ	Contact angle of water (degrees)

ρ Mass density of liquid water (kg/m³)

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CHAPTER 3 : ALTERING MODULE ORIENTATION AND CHANNEL GEOMETRY TO IMPROVE THE MD PROCESS

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3.1. Introduction

Despite MD being an attractive green technology, two of the primary issues that plague MD and that are areas of active research are low fluxes and pore-wetting which compromises permeate quality [1]. Pore-wetting occurs when hydrophobic or amphiphilic compounds such as oil or surfactants in the feed interacts with the membrane resulting in direct flow across the pores to the distillate. The treatment of oily wastewater via membrane-based filtration processes has not flourished due to the challenges associated with sustaining the flux and rejection rates [2, 3]. However, in view of the large amounts of oily wastewater from the three main contributing industries of oil and gas, palm oil and mining [2-4], improved membrane separation processes could have a role in cost-effectively treating these streams to mitigate the environmental impact associated with their disposal. It is notable that, despite MD being a promising green technology, studies on treating oily feeds via MD are scarce. A recent study on produced water treatment using MD suggested that MD can only be considered for treating low concentrations of oil (500 ppm) and oils with higher proportion of hydrocarbon [5]. Furthermore, another study on shale gas produced water treatment using MD suggests that pre-treatment of oil and grease is mandatory prior to MD application to improve stability, quantity and quality of permeate [6]. Yet another study indicated that pore-wetting in MD is not due to the oil itself, but to the interactions between salt, surfactant and the membrane [7]. The focus of this study is on furthering the understanding of MD in treating such oily feeds.

Advances in MD have focused on membrane development (e.g., membranes customized to have excellent anti-wetting properties, confer high flux, withstand high temperature, resistant to fouling and scaling, and improved thermal transfer efficiency) and processes designed to save energy through system hybridization [8]. The design and orientation of MD modules, despite being an economical alternative to changing the hydrodynamic conditions, have unfortunately garnered little attention [9]. A recent review on computational fluid dynamics (CFD) in MD showed the importance of coupling both heat and mass transfer transfers across and near the membrane surface [10]. The hydrodynamic conditions affecting foulant deposition add even more complexities. It should be noted that, while RO modules are standardized, MD modules have yet to be optimized for better performance. One recent study by Warsinger et al. [11] examined the effect of module orientation on the efficiency of air gap MD (AGMD) in treating saline solutions without colloidal foulants. They concluded that module orientation, because of its effect on droplet flow and film thickness on the condenser surface in AGMD systems, can be optimized to improve flux by up to 40%. In an analogous work on module design for microfiltration (MF), Zamani et al. [12] evaluated a simple tapered feed channel with channel height increasing from the entrance. This design, known as flow-field mitigation of membrane fouling (FMMF), was able to mitigate fouling during microfiltration via a transverse flow trajectory induced to counter the permeate drag towards the membrane. The critical flux of particulate foulants, namely, polystyrene, was shown to be much improved via FMMF.

In view of the gap in the knowledge base regarding the impact of module orientation, module geometry and particulate foulant density on the MD performance parameters of flux and membrane pore wetting, this study sought to bridge the gap via both experiments and simulations. The three questions addressed are described as follows. Firstly, does the module orientation matter in direct contact membrane distillation (DCMD) applications? Warsinger et al. [11] observed that optimizing the module orientation improved the flux of air gap membrane distillation (AGMD) by up to 40% due to hydrostatic effects, and further hypothesized that module orientation may not benefit DCMD. Secondly, with respect to the key feature of FMMF in countering the permeate drag in MF, is FMMF also feasible and beneficial in MD particularly when the ‘particulate’ foulant is less dense than water (as for oily feeds)? Thirdly, does the density

of the particulate foulant, particularly since oil is less dense than water, affect the DCMD performance?

3.2. Experimental setup and Simulation

3.2.1. Experimental Study

An experimental study was first carried out to evaluate the efficacy of the flow field mitigation of membrane fouling (FMMF) configuration in separating oil emulsions, which were significantly more buoyant compared to the polystyrene beads used in Zamani et al. [12], via membrane distillation (MD).

3.2.1.1. Experimental setup

The schematic diagram of the experimental direct contact membrane distillation (DCMD) setup is shown in Fig. 3.1. The membrane module was made of acrylic, and had thermocouples (PT100 Resistance Temperature Detectors) inserted for the control of the feed and permeate temperatures at 65 and 14 °C, respectively. The permeate flow channel was fitted with a spacer mesh (specifications listed in Table 3.4 in the appendix) to reduce the heat-transfer resistance and provide mechanical support for the membrane, but a spacer was absent on the feed side to enable a more straightforward comparison with the simulations. A new piece of PVDF hydrophobic flat-sheet microfiltration membrane (Durapore GVHP; nominal pore diameter of 0.22 μm) was used for each experimental run with an active area of 0.00371 m² (53 mm by 70 mm). Three peristaltic pumps (Masterflex L/S Digital Drive) were used to drive the feed and permeate recirculating loops, and also the recycling line. The feed was continuously recirculated at 750 ml/min between the membrane module and the feed tank (a 2-L round bottom flask), which was constantly agitated with a magnetic stirrer and heated by a hot plate (Heidolph MR Hei-Tec), via Masterflex Norprene tubing. The permeate was continuously recirculated through Masterflex Tygon E-LFL tubing at 300 ml/min between the membrane module and the permeate tank (a 1-L acrylic tank with a spout). The permeate tank had a conductivity meter (Eutech Instruments Alpha Cond 500) inserted to monitor the permeate quality, was cooled by a recirculating chiller (Julabo ME) and overflowed into the overflow permeate tank (a 300 mL beaker) that sat on a mass balance (Mettler-Toledo ME4002) for the measurement of permeate flux. The mass and conductivity data were logged on a computer via a National Instruments Data Acquisition (NI-DAQ) module

every five minutes. In order to maintain a constant feed concentration, between 0 to 82 mL of the permeate (depending on the flux) from the overflow permeate tank was recycled every 1 h throughout the experiment back to the feed tank by a peristaltic pump.

Figure 3.1. Schematic diagram of the experimental direct contact membrane distillation (DCMD) setup consisting of (1) a feed tank (i.e., 2-L round-bottom flask) heated by a hot plate and agitated with a magnetic stirrer, (2) three peristaltic pumps, (3) a cross-flow flat-sheet acrylic membrane module, (4) a permeate tank (i.e., 1-L acrylic tank with a spout) cooled by a recirculating chiller and with a conductivity meter inserted, and (5) an overflow permeate tank (300 ml beaker) atop a mass balance.

3.2.1.2. Membrane module

The four geometries of the feed channel of the DCMD membrane module investigated, which were similar for both the experiments and simulations, are depicted in Fig. 3.2, while the permeate channels were constant at a uniform depth of 1 mm. Specifically, the dimensions of the four geometries, as depicted in Fig. 3.3, had different cross-sections in the x - z planes. The four feed channel geometries were, namely, (a) a uniform channel depth of 1 mm; (b) a uniform channel depth of 2 mm; (c) the FMMF configuration with an inclination angle of 1.5° such that the inlet and outlet depths were 2 mm and 3.3 mm, respectively; and (d) the FMMF configuration with an inclination angle of 3° such that the inlet and outlet depths were 2 mm and 4.6 mm, respectively. The 1mm and 2mm straight channel will provide insights on varying channel depth and cross-flow velocity on the interactions between the membrane and oil droplets. While the

inclined channel studies the efficacy of altering flow field on fouling and wetting mitigation, and further probing into the effect of inclination angle on membrane-foulant interactions. Each of these four geometries was investigated via both experiments and simulations for three different module orientations, namely, horizontal with feed at the bottom (i.e., membrane atop the feed), horizontal with feed on top (i.e., membrane beneath the feed), and vertical, as shown in Fig. 3.4.

Figure 3.2. Feed channel of the DCMD modules with different x - z cross-sectional areas: (a) uniform channel depth of 1 mm; direction of flow indicated with black arrows; (b) uniform channel depth of 2 mm; (c) FMMF configuration with inclination angle of 1.5° such that the inlet and outlet depths were 2 mm and 3.3 mm, respectively; (d) FMMF configuration with inclination angle of 3° such that the inlet and outlet depths were 2 mm and 4.6 mm, respectively. The blue planes denote the membranes.

Figure 3.3. Detailed dimensions of DCMD feed channel with a uniform channel depth of 1 mm. The blue plane denotes the membrane

Figure 3.4. Three orientations of DCMD module: (a) horizontal with feed at the bottom (i.e., membrane atop the feed); (b) horizontal with feed on top (i.e., membrane beneath the feed); (c) vertical. Directions of feed flows indicated with black arrows. The blue lines represent the membranes

3.2.1.3. Materials

The initial feed solution was 35 g/L of sodium chloride (NaCl; Merck-Millipore CAS No. 7647-14-5) dissolved in DI water for the first three hours, after which the oil-in-water emulsion was added. The oil used in this study was hexadecane (Sigma-Aldrich CAS No. 544-76-3) which was dyed with oil red (Sigma-Aldrich CAS No. 1320-06-5) at a concentration of 0.1 mg/mL to improve visual observation of oil coalescence and accumulation within the membrane module. Hexadecane was used due to its widespread use for studying membrane-filtration with feeds containing oil emulsions to mimic oily wastewater, as well as its representation as a foulant with density significantly lower than water. The oil emulsion was prepared by sonicating 1.3 mL of the dyed hexadecane in 48.7 mL of the feed solution (i.e., 35 g/L NaCl) using a Branson S-450D sonifier with $\frac{3}{4}$ inch (19 mm) high gain horn at 70% amplitude for 2 min, resulting in a 20,000 ppm stock solution of oil emulsion with an average droplet size of 10 μm (measured by the Focused Beam Reflectance Measurement system (FBRM) Lasentec S400, PI-14/206). The average droplet size of the feed solution after the experiment were within 2 μm deviation from the 10 μm measured before the start of the experiment.

3.2.1.4. Experimental Protocol

The following protocol was used for each experiment. Firstly, the membrane sheet was cut into dimensions of 70 mm by 100 mm and positioned in the membrane module. Secondly, 35 g/L NaCl solution and DI water was circulated through respectively the feed loop at 750 mL/min (average crossflow velocity, CFV, ranging from 0.0674 m/s to 0.2358 m/s) and permeate loop at 300 mL/min (CFV = 0.0943 m/s). The temperatures of the feed and permeate stream of the membrane module were set at respectively 65 and 14 °C. The flux obtained at steady-state was used as a benchmark to assess the impact of the oil emulsion; specifically, the flux in the presence of oil emulsion and 35 g/L NaCl was normalized with respect to the flux in the presence of only 35 g/L NaCl, and defined as the relative flux. Finally, after three hours, 50 mL of the 35 g/L NaCl solution was removed from the feed tank and replaced with 50 mL of the 20,000 ppm oil-in-water emulsion such that the resulting feed solution had an oil concentration of 1,000 ppm. Each

experiment lasted 24 h and every experiment was repeated twice, with each error bar in the graphs denoting standard deviation of the two experimental runs.

3.2.2. CFD simulations

3.2.2.1. Simulation setup

Three-dimensional (3D) computational fluid dynamics (CFD) simulations of the feed channels of the direct contact membrane distillation (DCMD) modules in Fig. 3.2 were carried out using Comsol Multi-Physics 5.1. The simulations aimed to reinforce and extend the conclusions drawn from the experiments. The physics packages used in the simulation were Laminar Flow (justified by the Reynolds number in Table. 3.1) and Particle Tracing for Fluid Flow, of which the governing equations, namely, the Navier-Stokes and continuity equations, are provided in the Appendix. Heat transfer was not considered in the simulations and the continuous phase was set to be incompressible liquid water at 25°C. The inlet volumetric flowrate was set as 750 ml/min, which was similar to the experimental flowrate for the feed channel. The permeate flux towards the membrane was simulated using a leaking wall boundary condition, with the x - and y -axis fluid velocities set to 0, and the z -axis component set to the respective initial fluxes obtained experimentally.

Table 3.1 Reynolds number evaluated using average hydraulic diameter of the channel

Channel	Reynolds number
1mm	1042
2mm	1039
1.5° Inclination	1042
3° Inclination	1046

The oil droplets (i.e., the particulate foulant) simulated had properties corresponding to that of the hexadecane emulsion used in the experiments, specifically, density was 770 kg/m³ and droplet diameter uniformly of 10 µm (i.e., similar to the experimental value). 10,000 particles were traced, with 1,000 particles released at the inlet every 0.5 s between 0.5 s and 5 s. The droplets were subjected to a drag force proportional

to the steady-state velocity, gravitational acceleration of 9.81m/s^2 , and a buoyancy force (Eq. A7). The oil droplets were set to bounce off all the walls, except for the wall designated as membrane surface where they were set to stick; that is, a droplet that reached the membrane stayed there to simulate fouling and wetting of the membrane. The number of oil droplets sticking on the membrane DCMD feed channel were recorded throughout the study every 0.5 s.

Because different predefined mesh sizes with tetrahedral elements gave similar results, the coarse mesh (with the finest element being 0.011 mm and the largest element being 0.036mm) was selected to shorten the computation time.

3.2.2.2. Effect of buoyancy of particulate foulants

In order to study the potential effects of the buoyancy of the particulate foulant on membrane fouling, the model simulations were run with different particle densities for the different module geometries (Fig. 3.2) in the horizontal top and bottom feed orientations (Fig. 3.4). These two orientations were chosen because the different effects of buoyancy would be evident. The densities of the particles were chosen to represent the common particulate foulants studied, namely, hexadecane (770 kg/m^3), bentonite (961 kg/m^3), polystyrene beads (1040 kg/m^3) and calcium chloride (1201 kg/m^3). Thus, the simulations allowed comparison of the buoyant oil droplets (hexadecane as used experimentally), relatively neutrally buoyant particles and settling particles.

3.3. Results and Discussion

3.3.1. Experimental Results

Fig. 3.5 presents flux versus module orientation for the four different feed channel configurations for the same 35 g/L NaCl feed over 3 hours. Two interesting observations are worth highlighting. Firstly, whereas the orientation of the module had negligible impact on the flux of the FMMF feed channels, the module orientated horizontally with the feed at the bottom gave the highest flux (specifically, the means were approximately 15% higher) compared to the other two orientations for both the conventional channels with uniform depths. It should be noted that Warsinger et al. [11] reported that the horizontal orientation augmented the flux by more than 40% in some

cases relative to the vertical orientation for air gap membrane distillation (AGMD), and further stated that module orientation likely does not affect direct contact membrane distillation (DCMD) since orientation presumably only had hydrostatic effects. However, the results here on DCMD provides affirmation that module orientation does affect DCMD too, because when the hot feed was at the bottom, (i) the natural thermal convective currents caused the hotter regions to be near the feed-membrane interface, which provided additional driving forces for the permeation, and (ii) the natural convective currents associated with the salt concentration caused the lower salt concentration to be closer to the feed-membrane interface due to the lower density, which enhanced the water vapor pressure. Similar observations were made by Youm et al. [13] in crossflow ultrafiltration experiments, wherein flux increase was significant when the feed channel orientation was ‘gravitationally unstable’ (i.e., similar to the bottom feed configuration in this experiment), which caused a density gradient as the salt concentration increased near the membrane surface and thereby natural convection instability. In this study, the increase was absent for the FMMF feed channels because the induced change in the flowfield counteracted the natural convection instability effects. Also, compared to the 40% flux increment in AGMD due to differing module orientations conferring different extents of thermal bridging in and flooding of air gap, effects of which are not applicable to DCMD [11], the lower 15% increment here for DCMD for the feed channels with uniform depths indicates a lesser but non-negligible impact of module orientation. The dominance of convective currents, which affects the performance of different module orientations, will be assessed in Section 3.3.4. Secondly, higher flux magnitudes were observed for the feed channels of uniform depths (i.e., 1 mm and 2 mm) than for the FMMF configurations (i.e., 1° and 3° inclinations), which seems to contradict the results reported earlier where the FMMF configuration gave superior critical fluxes than the conventional channels with uniform depths [12]. However, FMMF is effective in mitigating the deposition on the membrane of particulate foulant whose density approximates that of water, but the feed in this case had foulants whose density was less than water. This will be further explored via simulations in the next section.

Figure 3.5. Experimental average flux magnitudes of the four feed channel configurations at different module orientations for a 35 g/L NaCl feed solution in the first 3 hours of operation

For feeds containing oil emulsions (specifically, 1,000 ppm oil and 35 g/L NaCl), the effects of channel configuration (Fig. 3.2) and module orientation (Fig. 3.4) were also investigated. Figs. 3.6a and b present respectively the relative flux (i.e., normalized with respect to the flux with a feed of 35 g/L NaCl and without oil emulsion) and permeate conductivity 21 h after the introduction of feed containing 1,000 ppm of oil and 35 g/L of NaCl. It should be noted that the values displayed were averaged over the final 21st hour, and the maximum conductivity value was 1999 $\mu\text{S}/\text{cm}$ due to the upper bound measureable by the conductivity meter used. Furthermore, for a more detailed look at pore wetting, Fig. 3.6c presents the time taken for the permeate conductivity to reach 75 $\mu\text{S}/\text{cm}$.

Figure 3.6. Experimental comparison of membrane fouling and pore wetting tendency of the four feed channel geometries and three module orientations: (a) relative flux and (b) permeate conductivity 21 h after the introduction of oil emulsion (1,000 ppm); (c) time taken for permeate conductivity to reach 75 $\mu\text{S/cm}$, with the black triangles denoting that wetting did not occur throughout the 21 h of experiment.

Four key observations are noted as follows. Firstly, among the three module orientations, the horizontal one with the feed at the bottom was the worst in terms of lowest flux (Fig. 3.6a), highest conductivity values (Fig. 3.6b) and shortest time taken to wet (i.e., permeate attained conductivity value of 75 $\mu\text{S/cm}$; Fig. 3.6c). This is in contrast to Fig. 3.5, where this orientation gave the highest fluxes for the uniform feed channels when oil emulsions were absent in the feed. Therefore, this suggests that the buoyancy of the oil droplets played a critical role in the performance of the MD process. In particular,

when the membrane was atop the feed, as was the case for the horizontal orientation with the feed at the bottom, the buoyancy of the oil droplet naturally increased the tendency for oil to deposit on the membrane, which led to the most extensive membrane fouling (Fig. 3.6a) and pore wetting (Figs. 3.6b and c). Secondly, as a further validation that the buoyancy of the oil droplets played a critical role in the impact of module orientation, the module oriented horizontally with the feed on top generally performed the best in terms of highest flux (Fig. 3.6a), lowest conductivity (Fig. 3.6b), and general lack of pore wetting (Fig. 3.6c) for all the feed configurations. Analogously, the superior performance was because the buoyancy of the oil droplets naturally propelled them away from the membrane beneath the feed stream. Thirdly, among the modules oriented vertically, the feed channel with a uniform depth of 2 mm stood out in having both a high flux and high conductivity. Fig. 3.7, which shows the evolution of flux and conductivity for this system, sheds some light. Specifically, the flux declined and the conductivity increased immediately upon the introduction of the oil emulsions at about 180 minutes, but the flux started increasing after about 300 minutes even though the conductivity continued to increase. The flux increased presumably due to extensive membrane wetting leading to the feed and permeate interacting freely through the membrane pores, then plateaued when the hydrostatic pressure equilibrated. The severe wetting issue uniquely associated with the uniform 2 mm channel among the vertically oriented modules could be tied to the lower average crossflow velocity and thereby lower surface shear on the membrane, coupled with a lack of FMMF to induce transverse velocity components [12]. Simulations were carried out to further probe this. Fourthly, among the four feed channel geometries, the uniform channel with a depth of 1 mm generally performed the best in terms of high flux (Fig. 3.6a), low conductivity (Fig. 3.6b) and longer time taken to wet (Fig. 3.6c). This is likely due to the highest crossflow velocity and thereby greater shear rate at the membrane surface to decrease the likelihood of any deposition on the membrane. The lack of performance of the FMMF feed channels compared to that reported earlier [12] could be due to the different bases (power required versus volumetric flow rate) used for comparison, the different nature of filtration (pressure-driven versus thermal-driven), and/or the different densities of the particulate foulants.

Figure 3.7. Experimental evolution of flux and conductivity for the feed channel with a uniform 2 mm depth geometry and oriented vertically

3.3.2. Simulation results

Fig. 3.8 shows the spatial velocity profiles of pure water in the x - y planes close to the membrane surface across the four different feed channels (Fig. 3.2) oriented horizontally. The channels with uniform depths gave more uniform velocity profiles (Figs. 3.8a and b) than the FMMF channels (Figs. 3.8c and d). Between the two channels of different uniform depths (Figs. 3.8a and b), the narrower channel (Fig. 3.8a) expectedly gave higher velocities and also exhibited more uniform velocities along the y -direction than the wider one (Fig. 3.8b). For the FMMF channels (Figs. 3.8c and d), the velocities were higher near the inlet then reduced progressively towards the outlet, with the x -directional velocity gradient across the channel being steeper for the channel with a larger inclination angle (Fig. 3.8d), such that a dead-zone (i.e., negligible velocities) formed near the outlet. The velocity profiles are consistent with the experimental flux results in Fig. 3.5, in that (i) the narrowest feed channel (i.e., 1 mm) with the highest, most uniform velocities (Fig. 3.8a) generally gave the highest flux, and (ii) the conventional feed channels with uniform depths had higher velocities (Figs. 3.8a and b) and thereby higher fluxes (Fig. 3.5) than the FMMF feed channels. In particular, the diminished velocities near the outlets for the FMMF channels (Figs. 3.8c and d) may be especially detrimental to membrane fouling and pore wetting in the presence of particulate foulants. It should be

noted that the flows were all in the laminar flow regime, as indicated by Reynolds numbers of approximately 1000 at the average hot feed temperature and average crossflow velocity of the channels.

Figure 3.8. Simulated flow velocity profiles (scale displayed in m/s) of the DCMD feed channels of different channel geometries: (a) uniform channel depth of 1 mm; (b) uniform channel depth of 2 mm; (c) FMMF configuration with inclination angle of 1.5° such that the inlet and outlet depths were 2 mm and 3.3 mm, respectively; (d) FMMF configuration with inclination angle of 3° such that the inlet and outlet depths were 2 mm and 4.6 mm, respectively. The feed mimicked that of water.

The behavior of the oil droplets was studied next. The simulation setup was such that the oil droplets that contacted the surface designated the membrane remained stuck to mimic membrane fouling, while those that contacted other surfaces remained in the feed without sticking. Since the inlet feed rate of oil droplets in each case was constant (i.e., 1,000 droplets fed every 0.5 s between 0.5 and 5 s), it was possible to compare the effectiveness of the fouling mitigation in each feed channel (Fig. 3.2) and at each

orientation (Fig. 3.4). Fig. 3.9 presents the fraction of oil droplets deposited on the membrane versus time. Each sub-figure represents a feed channel geometry (Fig. 3.2) and contains the trends for the different orientations (Fig. 3.4). It is clear in Fig. 3.9 that, regardless of channel geometry, the oil droplets only deposited for the horizontal orientation whereby the feed was at the bottom (Fig. 3.4a) and the vertical orientation (Fig. 3.4c).

Figure 3.9. Fraction of total droplets accumulated on the membrane surface

versus time for the different feed channel geometries: (a) uniform channel depth of 1 mm; (b) uniform channel depth of 2 mm; (c) FMMF configuration with inclination angle of 1.5° such that the inlet and outlet depths were 2 mm and 3.3 mm, respectively; (d) FMMF configuration with inclination angle of 3° such that the inlet and outlet depths were 2 mm and 4.6 mm, respectively.

3.3.3. Simulation results vis-à-vis experimental results

Comparing Figs. 3.9 (simulation results) and 3.6 (experimental results), two agreements and two discrepancies are highlighted.

The first agreement between Figs. 3.9 and 3.6 is that the horizontal module orientation with a top feed performed well in both the experimental and simulation studies, with Fig. 3.6 showing high flux and negligible wetting, while Fig. 3.9 showing lack of oil droplet deposition. The second agreement is that the horizontal orientation with a bottom feed generally performed the worst, in terms of low flux, high permeate conductivity and shortest time taken to wet in Fig. 3.6, and greatest number of oil droplets deposited in Fig. 3.9. Both agreements are rooted in the lower density of the dispersed oil droplets relative to the continuous NaCl solution phase and thus the tendency to float upwards in the feed channel, thereby membrane fouling was severe when the membrane was atop the feed but negligible elsewhere. Therefore, the simulations (Fig. 3.9) provided evidence that the experimental trends in Fig. 3.6 are tied to the deposition of the oil droplets on the membrane.

Regarding the discrepancies between the simulation (Fig. 3.9) and experimental (Fig. 3.6) results, the first is the performance of the modules orientated vertically, except for the feed channel with a uniform depth of 2 mm. Although the simulation results show that oil droplets deposited significantly to similar extents for all modules orientated vertically (Fig. 3.9), the experimental results show that pore wetting was relatively negligible except for the feed channel with a uniform depth of 2 mm (Fig. 3.6b). The agreement between the simulations and experiments for both horizontal orientations, but disagreement for the vertical orientation suggests the lack of consideration of a force that is significant in the vertical orientation in the simulations. This force is rooted in the natural convective currents induced by the thermal and salt concentration gradients. Specifically, in the case of the experimental vertical modules, the vertical thermal and concentration convective gradients spanning the length of the module generated sufficient convective currents, along with the forced convection by the CFV and the natural buoyancy of the oil droplets, such that the deposition was negligible. Fouling and wetting was only observed for the vertical feed channel with the uniform depth of 2 mm because of the lower forced convection. For the horizontal orientations, the simulations and

experiments agreed better, because the convective currents played a less important role due to the limited channel depths. It should be noted that convective currents has been reported to enhance flux in ultrafiltration before [13]. Therefore, the lack of predictive capability for the vertical modules by the simulations highlights the importance of accounting for the natural thermal and concentration convective currents in DCMD applications, which will be further discussed in Section 3.3.4. The second discrepancy is that, while the simulation results in Fig. 3.9 indicates that the 1.5° FMMF channel consistently performed the best in terms of the least deposition, the experimental results in Fig. 3.6 indicated the performance was not superior. This again must be due to a non-negligible factor not accounted for in the simulations, namely, the coalescence of the deposited oil, which has been reported before [14]. Specifically, because of the gradually decreasing CFVs along the FMMF channels, the oil tended to accumulate and coalesce, which worsened the performance due to the corresponding cake-enhanced temperature polarization. Hence, the two discrepancies between simulations and experiments underscore the importance of convective currents and oil coalescence in DCMD performance.

3.3.4. Double-diffusive convective currents

Double-diffusive convection, which is a hydrodynamics phenomenon by which convection is driven by two different gradients [15], is known to make fluid motion more erratic [16-18]. In this study, the two gradients are temperature and salt concentration. While many studies have been done on such mixed convection flows where the primary focus is heat exchange[19-22], few have been done with focus on mass transport which is of great importance in MD processes as highlighted by Wang[23]. Queslati et al. [16] showed that, when the thermal and concentration sources overlap, as is the case in the DCMD module studied here, heat and mass transfers increase as the gradients increase, and convection currents are stronger near the top of the cell. The double-diffusive convection phenomenon is further assessed here since the lack of this consideration in the simulations led to discrepancies with the experimental results, specifically with respect to the modules orientated vertically. However, (i) the orientation with the greatest gravitational instability are the horizontal channels in bottom feed orientation and (ii) the

finite wall conductivity in a vertical channel can significantly alter the critical Rayleigh number value which is used to determine the significance of natural convection[24], this section will focus on examining the extent of which mixed convection affects the flow in this orientation. The dimensionless numbers, ratio of Grashof to square of Reynolds (Gr/Re^2) and Rayleigh number (Ra), are commonly used to assess if natural convection is dominant. Theoretically, convection dominates when Gr/Re^2 is much greater than 10 or Ra is above 1708 [25]. The thermal Grashof (Gr_t) is quantified as follows [25]:

$$Gr_t = \frac{g\beta_T L^3 \Delta T}{\nu^2} \quad (1)$$

where g is gravitational acceleration, β_T is coefficient of thermal expansion, L is average channel depth, ΔT is the temperature difference between the bulk and the membrane surface, and ν is the kinematic viscosity. And the solutal Grashof number (Gr_s) is quantified by:

$$Gr_s = \frac{g\alpha L^4 J C_{avg}}{\nu^2 D} \quad (2)$$

where α is the volume expansion coefficient, J is the permeation velocity, C_{avg} is the average concentration between the bulk solution and the membrane surface, and D is the diffusivity of salt in water. The Reynolds number is described by:

$$Re = \frac{2\rho UL}{\mu} \quad (3)$$

where ρ is the density of the solution, U is the average crossflow velocity, and μ is the dynamic viscosity of the solution. Finally, the thermal and solutal Rayleigh numbers are quantified by:

$$Ra_t = Gr_t \left(\frac{\nu}{\lambda} \right) \quad (4)$$

$$Ra_s = Gr_s \left(\frac{\nu}{D} \right) \quad (5)$$

where λ is the thermal diffusivity of the salt solution.

Table 3.2. Gr/Re^2 and Ra values

Channel	Gr_t/Re^2	Ra_t	Gr_s/Re^2	Ra_s
1 mm	1.1×10^{-3}	3.3×10^3	1.4	1.8×10^8
2 mm	8.7×10^{-3}	2.6×10^4	22.7	3.0×10^5
1.5° Inclination	1.7×10^{-2}	5.2×10^4	39.4	5.2×10^5
3° Inclination	4.7×10^{-2}	1.4×10^5	149.4	2.0×10^5

Table 3.2 summarizes the Gr/Re^2 and Ra values calculated for the different channel configurations studied here. All the Ra_t and Ra_s values were above the theoretical threshold value of 1708, which indicates that both convective currents due to temperature and salt concentration were dominant in the vertical modules. However, the Gr_t/Re^2 values were less than 0.1, which indicates forced convection dominates, while the Gr_s/Re^2 values were between 10^0 and 10^2 , which suggests mixed forced and natural convection. Although the theoretical threshold Gr/Re^2 value is such that natural convection dominates at above 10 [25], it was stipulated by Youm et al. [13] that the threshold Gr/Re^2 for the ultrafiltration studied ranged a few orders-of-magnitude, from 0.9 to 8 for modules without spacer and 247 to 720 for modules with spacer, and the threshold value further decreased with increasing salt concentration [13]. Therefore, the threshold Gr/Re^2 value in this study may be much smaller than 0.9 [13], because of (i) lack of spacer and higher salt concentration, and (ii) solute diffusivity increases with temperature [26], making natural convection due to solute concentration gradient much more dominant in the MD process here compared to the ambient ultrafiltration. The Gr_s/Re^2 values in Table 3.2 may thus indicate natural convection due to the salt concentration gradient, although the Gr_t/Re^2 values are not conclusive. Nonetheless, this affirms the presence or natural convection, and thereby that the lack of consideration of convective currents in the simulations was at least in part responsible for the discrepancy with the experimental results.

In order to further prove the significance of temperature gradient induced convection, a 2D simulation of the different channels with and without heating of the feed solution were performed using the same conditions in the experimental methods using Comsol Multi-Physics 5.1. The y-axis component of velocity normalized against the x-axis component of velocity was evaluated within a section from 5cm to 6cm downstream of the channel

(Fig. 3.10). The results indicate flow pattern changes with (65°C) and without (14°C) heating of the feed solution; with more pronounced upward and downward motions near the membrane surface with the heating of the feed. Based on these 2D simulations and the calculations of Gr/Re^2 and Ra above, one could expect the salt gradient difference within the MD channel to result in a greater change in upward and downward motions in the channels.

Figure 3.10. The y-axis component of velocity normalized against the x-axis component of velocity evaluated within a section from 5cm to 6cm downstream with (65°C) and without (14°C) heating of the feed solution in feed channel with (a,

b) uniform channel depth of 1 mm; (c, d) uniform channel depth of 2 mm; (e, f) FMMF configuration with inclination angle of 1.5° such that the inlet and outlet depths were 2 mm and 3.3 mm, respectively; (g, h) FMMF configuration with inclination angle of 3° such that the inlet and outlet depths were 2 mm and 4.6 mm, respectively.

Further reinforcing the efficiency of the FMMF configurations, the 2D simulation results show that the inclined channel creates a significant downward motion, which mitigates membrane-foulant interaction (Fig. 3.10e-h).

3.3.5. Current study vis-à-vis previous study on FMMF [12]

In view of the apparent contradiction between a previous study [12] and this study regarding respectively the benefits and lack thereof of the FMMF configuration, more simulation studies were carried out to understand the underlying reasons for the discrepancy. The three main differences between the studies are (i) microfiltration (MF) versus membrane distillation (MD), (ii) the basis of constant power input versus constant volumetric flow rate, and (iii) the particulate foulant of polystyrene versus oil emulsion. Whereas (i) is not expected to cause the discrepancy as the transport phenomena, (ii) is a plausible reason tied to the cross-flow velocity and back-transport of foulants, because while the constant power input by Zamani et al. [12] implies greater cross-flow velocity and thereby greater shear rate for the FMMF configuration, the constant volumetric feed flow rate here implies the greatest shear rate at the membrane surface for the feed channel with a uniform depth of 1 mm. This was explored through Fig. 3.11. As for (iii), the effects of the different densities of polystyrene versus oil emulsion was scrutinized using Fig. 3.12.

To verify (ii), an additional set of simulations was carried out for the four feed channel configurations, with the power input kept constant at that for the uniform 2 mm feed channel by changing the volumetric feed flow rates for the other channels to account for the varying pressure drops across the channels [12]. Figs. 3.11a and b display the comparison of the rate of oil droplets deposition among the four feed channel configurations at respectively constant volumetric flow rate and constant power input. On

the same basis of constant flow rate (Fig. 3.11a), the rate of deposition was similarly fast for the feed channel with the narrower uniform depth of 1 mm and the FMMF configuration with the steeper 3° inclination, whereas the slowest for the FMMF configuration with the gentler 1.5° inclination. On the other hand, for the same basis of constant power (Fig. 3.11b), the deposition rate was fastest for the FMMF configuration with the steeper 3° inclination and slowest for the narrower uniform depth of 1 mm. Therefore, in contrast to Zamani et al. [12], the FMMF configuration of feed channels did not consistently out-perform the regular feed channels with uniform depths.

Figure 3.11. Fraction of total oil droplets accumulated on the membrane surface versus time for the different feed channel geometries in the horizontal with top feed orientation: (a) constant volumetric flow rate; (b) constant input power.

Interestingly, the results in Fig. 3.11b affirm that the FMMF configuration did not provide for better filtration performance at constant power operation compared with

that indicated in an earlier study [12]. This suggests that the reason for the poorer performance of FMMF vis-à-vis the conventional channels of uniform depths may be tied to the less dense particulate foulant used here. In order to better understand the effect of buoyancy, simulations were carried out for particulate foulants of four different densities for two module orientations, namely, horizontal with feed on top (Fig. 3.4a) and horizontal with feed at the bottom (Fig. 3.4b) at constant flow rates. The particle diameters were kept constant at 10 μm , and the four particle densities were chosen to be those of common model foulants investigated, namely, hexadecane (770 kg/m^3), bentonite (961 kg/m^3), polystyrene beads (1040 kg/m^3) and calcium carbonate (1201 kg/m^3). Fig. 3.12 presents the cumulative fraction of particles deposited on the membrane over 5 s for the four different particle densities used in all four feed channel geometries and the two horizontal module orientations, one with the feed at the bottom (Fig. 3.12a) and one with the feed at the top (Fig. 3.12b). Two noteworthy observations are described as follows. Firstly, Figs. 12a and b are in stark contrast with each other. Whereas Fig. 3.12a indicates that only the particulate foulant with density much greater than water (1000 kg/m^3) did not deposit on the membrane when the feed was below the membrane, Fig. 3.12b instead shows that only the particulate foulant with density much lesser than water did not deposit on the membrane when the feed was above the membrane. This further proves that membrane orientation does matter even for DCMD applications, in addition to the AGMD applications reported earlier [11], particularly when the buoyancy of the particulate foulant is varied. Specifically, when the feed was below the membrane (Fig. 3.12a), the three particulate foulants with lower densities ($\leq 1040 \text{ kg/m}^3$) deposited on the membrane, partially due to the natural buoyancy causing them to float upwards to the membrane. For the densest particle, the upward permeate drag towards the membrane was insufficient to counter the downward gravitational pull away from the membrane to cause deposition on the membrane. On the other hand, when the feed was above the membrane (Fig. 3.12b), the least dense particulate foulants did not deposit since the downward permeate drag towards the membrane was insufficient to counter the upward buoyancy of the particles. Furthermore, Fig. 3.12 indicates that the greater the density differential between the particulate foulant and water, the more accentuated the deposition was, which affirms the mechanistic picture that the permeate drag paled against the inherent inertia of the particulate foulants, and that the orientation of the MD module hence played a critical

role in the fouling tendency of such processes. It should be noted that the rise or settling velocities are proportional to the square of the foulant size, so in the practical feeds whereby a range of foulant sizes exist, the smaller ones are less affected by module orientation than the larger ones. Secondly, regardless of particulate foulant density and membrane module orientation, the FMMF geometry with the slighter 1.5° inclination angle consistently gave the least deposition of the particulate foulants among the feed channel configurations. However, the benefits of FMMF did not extend to the greater inclination angle of 3° . It was also noted in Zamani et al. [12] that backflows at larger inclination angles of 4.89° reduced the effectiveness of FMMF. Because the aim of FMMF is in countering the drag towards the membrane, the upper angle limit is presumably lower in MD due to the lower flux observed here, although it is noted that MD flux can exceed $50 \text{ L/m}^2\text{h}$ with a high temperature differential and sustained temperature polarization coefficient (TPC). This highlights that the design of MD modules requires more mechanistic studies, rather than relying on the past understandings acquired from pressure-driven filtration processes.

Figure 3.12. Fraction of total particles accumulated on the membrane surface over 5 s for particulate foulants with four different particle densities for the four

feed channel geometries at two module orientations: (a) horizontal with bottom feed; and (b) horizontal with top feed.

3.4. Conclusions

The impact of three module orientations and four feed channel geometries on the direct contact membrane distillation (DCMD) of a feed containing oil emulsion was investigated via both experiments and simulations. The three module orientations were horizontal with the feed on top (i.e., membrane beneath the feed), horizontal with the feed at the bottom (i.e., membrane atop the feed) and vertical; and the four feed channel geometries were two conventional ones with uniform depths of 1 mm and 2 mm, and two of FMMF configurations [12] (i.e., tapered feed channels) inclined at 1.5° (i.e., inlet and outlet depths were 2 mm and 3.3 mm, respectively) and 3° (i.e., inlet and outlet depths were 2 mm and 4.6 mm, respectively). The feed flow rate was constant in each case.

The experimental results are summarized as follows. In the absence of oil emulsions, the feed containing 35 g/L NaCl gave superior flux for the two conventional feed channels with uniform depths vis-à-vis the FMMF feed channels due to the higher cross-flow velocities for the former, and the highest flux was for the feed channels with uniform depths and module oriented horizontally with feed at the bottom due to the natural thermal convection currents and density gradient. Compared to the 40% flux increment in air gap membrane distillation (AGMD) [11], the lower 15% increment here for DCMD indicates a lesser but non-negligible impact of module orientation. In the presence of oil emulsions, three noteworthy observations are: (i) among the three module orientations, the horizontal one with the feed at the bottom performed the worst, while that oriented horizontally with the feed on top performed the best, which suggests the buoyancy of the oil droplets played a critical role; (ii) among the modules oriented vertically, the feed channel with a uniform depth of 2 mm performed the worst due to the lower average crossflow velocity, coupled with a lack of FMMF to induce transverse velocity components [12], causing increased interaction of the oil droplets with the membrane; and (iii) among the four feed channel geometries, the uniform channel with a depth of 1 mm generally performed the best due to the highest cross-flow velocities, which indicates the FMMF feed channel geometry was not advantageous.

As for the simulations, more uniform velocity profiles were expectedly observed for the feed channels with uniform depths. Regarding membrane fouling and pore wetting tendencies by the oil emulsion, two agreements and two discrepancies between the experimental and simulation results were obtained. The agreements are that the horizontal module orientation with a top feed performed well and the horizontal orientation with a bottom feed generally performed the worst, both of which are rooted in the lower density of the dispersed oil droplets relative to the continuous NaCl phase and thus the tendency to float upwards in the feed channel. The first discrepancy lies in the case of the vertical module orientations, where oil droplets were observed to deposit significantly via simulations, but severe wetting only occurred experimentally for the uniform feed channel depth of 2 mm. This is presumably tied to the lack of consideration of the natural thermal convective current in the simulations, which in turn highlight its dominant effect particularly for the vertical DCMD modules. The second discrepancy is that the simulations indicate the FMMF feed channel with the gentler inclination angle (namely, 1.5°) out-performed other channels at the same volumetric flow rate, whereas the experiments did not agree. This could be because of two reasons not accounted for in the simulations: (i) cake-enhanced temperature polarization, and (ii) oil coalescence, as clearly observed for deposited oil droplets by Tummons et al [14], which would more detrimentally affect the flux than rigid particles.

The two key highlights here provide more mechanistic understandings into the design of MD modules, showing that simple changes to the flow channel geometries and orientation could be considered to avoid fouling and wetting during MD operation. Firstly, module orientation mattered for DCMD applications, in addition to the AGMD applications reported earlier [11], particularly when the particle density of the particulate foulant differs greatly compared to the bulk continuous phase of the feed solution. Secondly, the lack of consideration of the convective currents induced by the thermal and concentration gradients, and oil coalescence and the corresponding cake-enhanced temperature polarization in the simulations caused disagreement with the experimental results, although agreement was shown for microfiltration of rigid latex particles [12]. This underscores the importance of these factors, as well as that the design of MD modules particularly for oily feeds requires more mechanistic studies, especially in view of the thermal gradients, rather than relying on analogy with pressure-driven filtration

processes. Hence, this work paves way for MD module designs which incorporates alteration of flowfield or inducing secondary flows to avoid oil fouling and wetting for oil seawater treatment.

Appendix

Table 3.3 summarizes properties of the PVDF membrane used in this study, while Table 3.4 gives the specifics for the flow channel and the mesh spacers used in the flow channels to increase the heat-transfer coefficients on the permeate side of the membrane.

Table 3.3 Properties of Polymeric Membranes

Membrane	PVDF
Specification	Durapore GVHP
Thickness (μm)	125
Nominal pore diameter (μm)	0.22
LDP mean-flow pore diameter (μm)	0.209
Porosity (%)	75
Water contact angle (degrees)	111
Polymer thermal conductivity ($\text{W/m}\cdot\text{K}$)	0.17
Air thermal conductivity ($\text{W/m}\cdot\text{K}$)	0.028
Effective membrane thermal conductivity ($\text{W/m}\cdot\text{K}$)	0.0354
Conductive heat-transfer resistance ($\text{K}\cdot\text{m}^2/\text{kW}$)	3.530
Heat-transfer coefficient ($\text{kW/K}\cdot\text{m}^2$)	0.283

Table 3.4 Channel and Spacer Specification

Channel height (permeate side) (m)	0.001
Channel height (feed side) (m)	Refer to diagram Figure 3.1
Channel width (m)	0.053
Channel length (m)	0.06

Channel cross-sectional area (permeate side) (m ²)	0.000053
Channel active membrane area (m ²)	0.00318
Spacer material	polypropylene
Spacer filament diameter (m)	0.00026
Spacer thickness (m)	0.00052
Spacer mesh size (m)	0.003
Spacer hydrodynamic angle (degrees)	90
Feed attack angle (degrees)	45
Spacer void fraction (dimensionless)	0.932

Governing equations and boundary conditions

The continuity and Navier-Stokes equations for a 3D steady-state incompressible flow used in the laminar flow stationary study are as follows:

$$\frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} + \frac{\partial u_z}{\partial z} = 0 \quad (\text{A1})$$

$$\begin{aligned} & \rho \frac{\partial u_x}{\partial t} + \rho u_x \frac{\partial u_x}{\partial x} + \rho u_y \frac{\partial u_x}{\partial y} + \rho u_z \frac{\partial u_x}{\partial z} \\ &= -\frac{\partial p}{\partial x} + \mu \left(\frac{\partial^2 u_x}{\partial x^2} + \frac{\partial^2 u_x}{\partial y^2} + \frac{\partial^2 u_x}{\partial z^2} \right) - \mu \frac{\partial}{\partial x} \left(\frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} + \frac{\partial u_z}{\partial z} \right) \end{aligned} \quad (\text{A2})$$

$$\begin{aligned} & \rho \frac{\partial u_y}{\partial t} + \rho u_x \frac{\partial u_y}{\partial x} + \rho u_y \frac{\partial u_y}{\partial y} + \rho u_z \frac{\partial u_y}{\partial z} \\ &= -\frac{\partial p}{\partial y} + \mu \left(\frac{\partial^2 u_y}{\partial x^2} + \frac{\partial^2 u_y}{\partial y^2} + \frac{\partial^2 u_y}{\partial z^2} \right) - \mu \frac{\partial}{\partial y} \left(\frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} + \frac{\partial u_z}{\partial z} \right) \end{aligned} \quad (\text{A3})$$

$$\begin{aligned} & \rho \frac{\partial u_z}{\partial t} + \rho u_x \frac{\partial u_z}{\partial x} + \rho u_y \frac{\partial u_z}{\partial y} + \rho u_z \frac{\partial u_z}{\partial z} \\ &= -\frac{\partial p}{\partial z} + \mu \left(\frac{\partial^2 u_z}{\partial x^2} + \frac{\partial^2 u_z}{\partial y^2} + \frac{\partial^2 u_z}{\partial z^2} \right) - \mu \frac{\partial}{\partial z} \left(\frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} + \frac{\partial u_z}{\partial z} \right) \end{aligned} \quad (\text{A4})$$

where u_x , u_y and u_z are the velocity components in x -, y - and z -directions, p is the pressure, μ and ρ are respectively the dynamic viscosity and density of the fluid. The two boundary conditions of the simulated flow system are listed as follows:

- a) $u_x, u_y, u_z = 0$ at the walls (i.e., no-slip condition)
- b) Outlet pressure is set as atmospheric

In the particle tracing module used in the time-dependent study, the drag force, F_D , is defined using the Stokes drag law, which uses the fluid velocity calculated in the stationary study. The equations used specified by Comsol are as follows:

$$F_D = C_D m_p u_{rel} \quad (A5)$$

$$C_D = \frac{18\mu}{\rho_p d_p^2} \quad (A6)$$

where C_D is the drag coefficient, u_{rel} is the relative velocity between the oil droplet and the water, m_p , ρ_p and d_p are mass, density and diameter, respectively, of the oil droplet

The particles experience a buoyancy force, F_B , as follows:

$$F_B = m_p g \frac{(\rho_p - \rho_{salt\ water})}{\rho_p} \quad (A7)$$

where g is the gravitational acceleration, $\rho_{salt\ water}$ is the density of salt water, m_p and ρ_p are mass and density, respectively, of the oil droplet.

List of symbols

C_D	Drag coefficient (dimensionless)
CF	Average crossflow velocity (m/s)
D	Diffusivity (m ² /s)
d_p	Oil droplet diameter (m)
F_B	Buoyancy force (N)

F_D	Drag force (N)
g	Gravitational acceleration (m/s^2)
L	Average channel depth (m)
m_p	mass of oil droplet (kg)
u_{rel}	Relative velocity between the oil droplet and the water (m/s)
u_x	Velocity component in x -direction(m/s)
u_y	Velocity component in y -direction(m/s)
u_z	Velocity component in z -direction(m/s)
Gr_s	Solutal Grashof number (dimensionless)
Gr_t	Thermal Grashof number (dimensionless)
Ra_s	Solutal Rayleigh number (dimensionless)
Ra_t	Thermal Rayleigh number (dimensionless)
Re	Reynolds number (dimensionless)

Greek Symbols

α	Volume expansion coefficient (m^3/kg)
β_T	Coefficient of thermal expansion (T^{-1})
ΔT	Temperature difference between bulk fluid and membrane surface ($^{\circ}\text{C}$)
λ	Thermal diffusivity (m^2/s)
μ	Dynamic viscosity ($\text{kg/m}\cdot\text{s}$)
ν	Kinematic viscosity (m^2/s)
ρ	Mass density (kg/m^3)

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CHAPTER 4 : MD HYBRIDIZED WITH HEAT PUMP FOR WATER TREATMENT AND SPACE COOLING

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4.1. Introduction

Worldwide climate change and population exposure as well as urbanization are triggering the human being energy-water crisis. One issue lies in the cooling system of the modern built environment. In order to cope with the high temperature and humidity throughout the year, the building sector in tropical countries accounts for approximately 30% of primary energy demand, with space cooling for the interior accounting for over 50% of total energy consumption in buildings and increasing to 80% during peak periods [1]. A significant portion of this cooling load consumed is in the form of latent heat to dehumidify air. In some systems, air dehumidification is achieved by reducing the ambient air temperature below its dew point, which is far lower than the required comfort conditions in buildings, causing more energy waste for air reheating. In other systems, desiccants or novel polymeric electrolyte membranes [2] are utilized for dehumidification, but these desiccants or new materials have to be regenerated by adding heat or electrical energy to recover the water and cooling to dew point is also necessary. In addition to the energy wastage, the heat being pumped into the surrounding environment adds to the cooling load required characterized by the well-known urban heat island effect [3].

This inefficient use of energy results in not only the wastage of resources used to generate the energy, but also the rejection of more heat into the environment, which is the very heat we need to remove to maintain a comfortable living and working environment. Water-cooled air-conditioning systems that are often found in commercial buildings with centralized cooling systems have better thermal efficiency. Chen et al. [4] showed that by

using water-cooled condensers for split-type air conditioners in residential buildings in Hong Kong, annual electricity consumption can be reduced by 8%. However, when a cooling tower is used, evaporative cooling increases the humidity of the environment outside which in turn has to be dehumidified for space cooling. To further improve the energy efficiency, this vicious cycle can be broken by coupling the heat pump used with a membrane distillation (MD) unit to provide a system for simultaneous space cooling and water treatment.

Aside from the waste heat generated, most space cooling systems to date dispose of the condensate produced to the sanitary drain, due to the small amount of condensate produced [5] and the concern of contamination with organic and inorganic contaminants [3, 4]. However, a recent research highlighted through theoretical calculations that condensate recovery system in a typical hotel on the Arab Emirates coast can produce a significant amount of water that can be used to cover a meaningful amount of the water requirements of the hotel [6]. Furthermore, inorganic contaminants from condensate contact with metal condenser surface was reported to be inconsequential [7]. Hence, the possibility of increasing the condensate recovered through the coupling of a heat-pump and MD could improve the feasibility of condensate recovery.

Many studies have been carried out on coupling MD with different processes such as forward osmosis-membrane distillation (FO-MD)[8], membrane distillation-crystallizer (MD-C)[9, 10] and membrane distillation-bioreactor (MDBR) [11], which suggests that MD is a promising process for hybrid separation technologies [12]. This is because MD confers advantages including the ability to treat highly concentrated feed [13-15], lower membrane fouling propensity [16] and lower energy consumption, as well as ease of integration due to the relatively mild operating conditions [17, 18]. Another attractive feature of MD is the ability to make use of low-quality waste heat, although the thermal efficiency is lower than multi-stage flash [19]. In some cases, heat-loss through conduction to the permeate could even be used to pre-heat the cool feed.[20-22] Most energy-conversion processes produce primarily thermal energy, most of which could be reused if the waste heat is of high enough temperature [23], while the low-temperature waste heat are simply released into the environment [24]. An example of such low-temperature waste heat generation is the membrane bioreactors that contain microorganisms that metabolize organic compounds and produce heat while doing so, thus can be coupled with MD for further water treatment [25]. Another example is in

vapor compression cycle cooling. Heat integration of heat pumps with conventional distillation is well-studied, beginning with the comparison of different heat pump assisted distillation configurations [26], moving on to increasing the efficiency such heat pump connected to a distillation unit [27], and heat integration to the overall process [28]. All of which are discussed in a recent 2018 review of recently developed heat pump assisted distillation configurations [29]. However, published work related to the coupling of MD with heat pumps only include a patent of a thermoelectric-integrated membrane evaporation system filed in 1982 [30], and also a research article on the study of a heat pump for simultaneous cooling and desalination [31]. Conceivably, the condensate from the MD system can be condensed on the cold surface of the heat pump, which releases latent heat back to the heat pump to negate some of the energy required. The feasibility of this has not been proven to date, which formed the goal of the current study.

In this study, a sweeping gas membrane distillation (SGMD) process, which combines a relatively low conductive heat loss with a reduced mass transfer resistance [32, 33], was hybridized with a thermoelectric cooler to partially relief the cooling load of the radiator in the system. Specifically, the condensate from the membrane was directed towards the cold fins of the thermoelectric cooler to be condensed and collected. A thermoelectric heat pump is used in this experiment to drastically improve the ease of integration and reduce the footprint of this lab-scale proof-of-concept. However, the system is versatile and can be modified to accommodate other heat pumps in the future. Other than evaluating the feasibility of coupling MD with heat pumps to improve energy efficiency and extend the use of SGMD for space-cooling applications, this study also explored means to improve the condensate flux along with reducing the power consumption. This study aims to pave way for a sustainable space cooling solution which could reduce waste heat rejection while improving water consumption sustainability.

4.2. Experimental setup

4.2.1. Experimental Study

Typically, in a SGMD system used for desalination (Fig. 4.1a), an external heat source is used to heat up the seawater feed, whereas the heat generated during the condensation is fully rejected to the environment, which is a waste considering one of the prime advantages of MD is its capability to make use of low-grade waste heat for water purification. To address this, a thermoelectric heat pump can be integrated into a SGMD

system (T-SGMD) to reduce the energy cost and also extend the use of SGMD for space-cooling, as shown in Fig. 4.1b. Specifically, the heat released from the condensation of the condensate is used by a thermoelectric heat pump to heat up the seawater feed, thereby negating the need for an external heater while additionally providing for space cooling as the cool air is directed outwards by the fan.

Figure 4.1. Overview of (a) a typical SGMD; and (b) a T-SGMD with heat integration and cool air generation

4.2.2. Experimental setup of the Thermoelectric Coupled Membrane Distillation (TESGMD)

The experimental setup was designed to realize Fig. 4.1. Fig. 4.2 displays the schematic diagram of the experimental T-SGMD setups with the membrane module oriented in two different orientations, in view of earlier studies that convection plays a non-negligible role in the MD performance [34, 35]. The two thermoelectric plates (Thermonamic TEC 12715; dimensions of 50 mm length $\times$ 50 mm width $\times$ 4 mm height) used were each rated at 12 V and 15 A. When an electrical potential was applied through the semiconductor in the plates, a temperature difference was generated across the plate, creating a cold and a hot surface on the two faces of the plates. The feed was continuously recirculated using a peristaltic pump (Masterflex L/S Economy Variable-Speed Console Drive) at 250 mL/min between the membrane module and the feed tank (a 3-L polypropylene beaker) via Masterflex Norprene tubing. A temperature controller

(WILLHI WK7016C1) TC1 was used to control the temperature of the feed in the tank by switching the three fans (120 mm blade-diameter) of the radiator on and off. Air was circulated through the thermoelectric cooler at 1.25 m³/min with a fan (Nidec D08T-12PU; 80 mm blade-diameter). This air can be recirculated through the cooling fins using a horizontal blower fan (Delta electronics BFB1012H; 90 mm blade-diameter). PT100 temperature sensors (HYXC TM6-1003) T1 and T2 were used to measure respectively the cold air inlet and outlet, while T3 and T4 respectively the hot water inlet and outlet of the hollow fiber membrane (PVDF; nominal pore diameter of 0.02 μm) module. The temperature sensors are connected to a Data Acquisition module (NI-DAQ; National Instruments) for temperature data acquisition every 10 minutes. A mass balance (Mettler-Toledo ME4002) was used to measure the condensate flux. The conductivity of the collected condensate was measured using a conductivity meter (Mettler-Toledo SevenGo) at the end of each experiment to check for membrane pore-wetting (results will be discarded and membranes replaced if pore-wetting occurs), and the energy consumption of the entire system except for the balance was measured using Voltcraft 3000 energy consumption meter to compare the energy consumption at different experimental conditions. Voltcraft 3000 is a plug load meter which is used to measure the total energy consumption from the main power outlet before it is split to power the difference devices used in this experiment using a power strip. The effects of the feed recirculation temperature (namely, either 30 °C or 40 °C in this study), the membrane area (namely, bypass membrane module totally, 0.00849 m² or 0.0151 m²), the activation of the recycle and the module orientation were investigated. The membrane module was flushed with DI water after every run and dried in a forced convection oven set at 40 °C for 16 h before reusing. The experiments and the respective operating parameters investigated in this study are summarized in Table 4.1.

Table 4.1 Experiments carried out using the T-SGMD system

Experiments	Feed recirculating temperature (°C)	SGMD coupling	Membrane area	Module orientation	Recycle flow
-------------	--	------------------	------------------	-----------------------	-----------------

1	Thermoelectric only	30	No	-	Upright	Off
2	Small area T-SGMD +recycle (upright)	30	Yes	Small	Upright	On
3	Small area T-SGMD (upright)	30	Yes	Small	Upright	Off
4	Small area T-SGMD +recycle (inverse)	30	Yes	Small	Inverse	On
5	Small area T-SGMD (inverse)	30	Yes	Small	Inverse	Off
6	Large area T-SGMD +recycle (upright)	30	Yes	Large	Upright	On
7	Large area T-SGMD (upright)	30	Yes	Large	Upright	Off
8	Large area T-SGMD +recycle (inverse)	30	Yes	Large	Inverse	On
9	Large area T-SGMD (inverse)	30	Yes	Large	Inverse	Off
10	Thermoelectric only	40	No	-	Upright	Off

11	Small area T-SGMD +recycle (upright)	40	Yes	Small	Upright	On
12	Small area T-SGMD (upright)	40	Yes	Small	Upright	Off
13	Small area T-SGMD +recycle (inverse)	40	Yes	Small	Inverse	On
14	Small area T-SGMD (inverse)	40	Yes	Small	Inverse	Off
15	Large area T-SGMD +recycle (upright)	40	Yes	Large	Upright	On
16	Large area T-SGMD (upright)	40	Yes	Large	Upright	Off
17	Large area T-SGMD +recycle (inverse)	40	Yes	Large	Inverse	On
18	Large area T-SGMD (inverse)	40	Yes	Large	Inverse	Off

Figure 4.2. Schematic of the experimental T-SGMD setup with the membrane module in two different orientations: (a) upright, and (b) inverse. T1-4 represent the PT100 temperature sensors and TC1 the temperature controller used to maintain the feed temperature.

4.2.3. Materials

The feed solution prepared for each experiment was 3 L of 35 g/L sodium chloride (NaCl; Merck-Millipore CAS No. 7647-14-5) in DI water. PVDF hollow fiber membranes used had a nominal pore size of 0.022 μm ; details on the membrane properties are given in Table 4.2. The lab-scale membrane module consisted of a PTFE tube (OD: 12.7 mm, ID: 9.4 mm) with a bundle of hollow fibers membranes within, with active membrane areas of either 0.00849 m^2 (made up of 10 hollow fibers each 31 cm long) or 0.0151 m^2 (made up of 12 hollow fibers each 46 cm long).

4.2.4. Experimental Protocol

The same protocol was used for each experiment. The feed of 35 g/L NaCl solution was firstly circulated through the feed loop from the 3 L feed tank at 250 mL/min for 2 min to remove air bubbles in the system and ensure that the thermoelectric plates do not overheat, after which the direct-current power supply to the thermoelectric heat pump was switched on and the temperature controller set to the required feed temperature

(namely, either 30 °C or 40 °C). The feed (in this case also the coolant) temperature was kept at a low temperature of 30°C or 40°C to ensure the thermoelectric plate provides sufficient cooling of the air to demonstrate space cooling purposes. Furthermore, making use of low-quality waste heat to perform distillation at low temperature is unique to MD, highlighting the advantage of this coupling. The system was given an hour for the temperature to stabilize before the temperature measurement started. Temperature readings were recorded every 10 minutes, while the condensate mass, conductivity and energy consumption readings were recorded at the end of each experiment. Each experiment lasted 3 h. For all the experiments carried out, the conductivity of the condensate accumulated over 3 h remained within 10 $\mu\text{S}/\text{cm}$, which is indicative that wetting did not occur during the course of the experiments.

4.2.5. Analysis of results

The three main parameters used to compare the efficacy of T-SGMD in cooling and desalination are power consumption (kW), cooling capacity per unit energy consumed (dimensionless) and the volume of water produced per unit energy consumed (mL/kWh). The power consumption was calculated by averaging the product of energy consumption and experimental duration (kWh). The cooling capacity per unit energy input was calculated by:

$$\text{Cooling capacity per unit energy input } (-) = \frac{Q_L}{W} = \frac{|\rho_a \dot{V} c_p (T_{ai} - T_{ao})|}{W} \quad (1)$$

where Q_L is cooling capacity (kW), W is power consumption (kW), ρ_a is the density of air (kg/m^3), $\dot{V}$ is the volumetric flow rate of air (m^3/s), T_{ai} and T_{ao} are respectively the air inlet and outlet temperatures (K). The volume of water produced per unit energy input can be derived by:

$$\text{Volume water produced per unit energy input } (-) = \frac{\text{Mass of water}}{\rho_w t W} \quad (2)$$

where ρ_w is the density of water and t is the time in hours.

4.3. Results and Discussion

4.3.1. Effect of membrane area and recirculating feed temperature

The effects of membrane area and recirculating feed temperature on the performance of the T-SGMD were investigated with the module in the upright position. Fig. 4.3 compares the power consumption (Fig. 4.3a), cooling capacity per unit energy input (Fig. 4.3b) and condensate produced per unit energy (Fig. 4.3c) among the three different T-SGMD configurations (namely, without a membrane module, and with small and large membrane areas). Three conclusions can be drawn. Firstly, the effect of feed temperature was such that the power consumed, the cooling capacity per unit energy input and the condensate produced per unit energy were all lower for the higher temperature of 40 °C, which indicate that operation efficiency was improved at the lower feed temperature. In particular, the higher temperature is a result of lesser heat being removed from the feed by the radiator, and hence lesser power consumed. The decrease in cooling efficiency of the T-SGMD at the higher temperature (Fig. 4.3c) suggests that a critical temperature exist above which the extent of cooling became compromised by the returning heat; this will be discussed more in Section 4.3.4. Secondly, regarding whether the T-SGMD hybrid conferred superior performance, Fig. 4.3 shows clearly that the T-SGMD hybrids consistently out-performed with respect to lower power consumption (Fig. 4.3a) and more condensate produced per unit energy (Fig. 4.3c). On the other hand, the T-SGMD hybrids performed similarly and poorer respectively at the lower and higher temperatures with regards to the cooling capacity per unit energy input due to the heat returning to the thermoelectric cooler reducing the cooling of the air. Thirdly, the T-SGMD hybrid with the larger membrane area generally performed better than that with a smaller area, which indicates that the performance can be better enhanced with more membrane fibers.

(a)

(b)

(c)

Figure 4.3. Effect of membrane area at two different feed temperatures on (a) power consumption, (b) cooling capacity per unit energy input, and (c) volume of condensate per unit energy input. ‘Thermoelectric only’ denotes the configuration without the membrane module, while ‘small area’ and ‘large area’ indicate membrane areas respectively of 0.00849 m^2 and 0.0151 m^2 . The module orientation was upright.

4.3.2. Effect of cool air recycling in T-SGMD

The effect of cool air recycling in the T-SGMD was investigated by comparing the system performance via switching on or off the recycle blower as shown in Fig. 4.2. Fig. 4.4a shows that cool air recycling reduced power consumption significantly for the upright module orientation but not for the inverse module orientation. This observation can be explained by referring to Fig. 4.4b, which shows that the inverse modules required drastically lower cooling capacities per unit energy input, resulting in less heat being removed from the membrane module, which translates into a reduction in power consumption. Furthermore, Fig. 4.4c shows that the recycling of cool air blowing towards the membrane modules improved the condensate produced per unit energy input by approximately 14.9 to 25.4%.

(a)

(b)

(c)

Figure 4.4. Effect of membrane area (0.00849 m^2 or 0.0151 m^2), feed temperature (30°C or 40°C), presence of air recycle and module orientation (upright or inverse) on (a) power consumption, (b) cooling capacity per unit energy input, and (c) volume of condensate per unit energy input.

4.3.3. Effect of module orientation

The effect of module orientation on T-SGMD performance was investigated, since convection effects have been reported to play a non-negligible role [34, 35]. In the inverse orientation (Fig. 4.2b), natural convection would move the warm air saturated with water vapor (which is less dense than cool dry air) upwards, while forced convection was through the suction pressure provided by the 80 mm fan to cause low air flow across the condenser fins. Hence, the effect seen in this section is the combination of both natural convection as well as forced convection. Fig. 4.5a shows that the small-area T-SGMD without cool air recycle showed the greatest reduction in power consumption when the module orientation was changed from upright to inverse. This is because of the drastic decrease in cooling capacity per unit energy input resulting from low air flow across the cooling fins, which led to lesser heat transferred to the cooling fins, which in turn reduced the power consumption. This low air flow across the cooling fins also reduced the temperature of the cooling fins, allowing more water vapor to condense, and thus improving the clean water produced per unit energy input by approximately 17.1 to 19.1%.

(a)

(b)

(c)

Figure 4.5. Effect of module orientation on T-SGMD performance: (a) power consumption; (b) cooling capacity per unit energy consumed, and (c) the volume of condensate produced per unit energy consumed.

4.3.4. Feasibility of coupling heat pumps with membrane distillation

The experimental results collectively indicate that the coupling of heat pumps with membrane distillation is promising for both space cooling and water treatment. However, for this hybrid MD to be useful in space cooling and water treatment, there should be little or no decrease in cooling capacity per energy input while providing an increase in condensate produced per unit energy input. In this section, the results will be summarized to gauge the feasibility of this hybrid T-SGMD system, while providing recommendations to further improve the coupled system.

In order to be beneficial in space cooling as well as water-treatment applications, this coupled system must provide an increase in condensate produced per energy input while maintaining its cooling capacity per unit energy input. Figs. 4.6a and b display respectively the cooling capacity per unit energy input and the condensate produced per unit energy input. High values in both cases indicate better energy efficiency. Fig. 4.6a indicates that the cooling capacities per unit energy input were similarly high for all four cases in the absence of the MD module (i.e., ‘thermoelectric only’), whereas the cooling was significantly more energy-efficient with the inverse module orientation vis-à-vis the

upright one, and generally slightly more energy-efficient for the larger membrane area vis-à-vis the smaller one and for the lower temperature vis-à-vis the higher one. As for the condensate produced per unit energy input, Fig. 4.6b shows that the most energy-efficient configuration involved the combination of higher temperature, larger membrane area, recycle, and the inverse module orientation, which gave a more than 3-fold increase in the condensate produced per unit energy input relative to the least energy-efficient system (i.e., thermoelectric only and at the higher temperature). Clearly, the opposite trends in Figs. 4.6a and b indicate that optimization is necessary.

(a)

(b)

Figure 4.6. Summary of T-SGMD experimental results: (a) cooling capacity per unit energy consumed, and (b) condensate produced per unit energy consumed

This coupled system, besides being able to simultaneously cool and carry out water treatment without the need of an additional condenser and at no additional power, is able to switch between maximizing clean water production or maximizing cooling capacity. This is potentially useful for example in vapor compression cycle coolers, with inverters that produce waste heat constantly, to reduce the energy consumption by switching the compressor on or off as necessary. This will result in over-cooling of the space, which would provide just the heat removal solution for condensing the condensate produced from this hybrid MD system. Vapor compression cycle coolers are susceptible to outdoor temperature changes which could result in drastic temperature fluctuations in cooled spaces, which results in discomfort for occupants in the space; this coupled with the feed can act as a buffer against sudden outdoor temperature changes, thereby dampening such drastic temperature fluctuations in the cooled space as well.

4.4. Implications and future research directions

In this study, experimental results show how the waste heat from a thermoelectric heat pump can be integrated into a SGMD system to treat a salt water feed mimicking

seawater. The results obtained confirms the feasibility of the coupling SGMD with any system with a heat pump, which may find use also in the membrane distillation bioreactor and membrane distillation crystallizer. For example, in a common vapor compression heat pump, the heat from the compression of refrigerant can be extracted by a recirculating non-potable water before the excess is rejected to the environment through the condenser. Coupling with vapor compression heat pumps will then extend the possibility of its use in many commercially available electrical appliances beyond air-conditioning systems, such as dehumidifiers and air coolers, to refrigerators and water cooler dispensers, making decentralized commercial building or household water treatment possible. Even though a salt water feed was used in this proof-of-concept, the use of this coupled system is not limited to desalination; MD is used as a secondary or tertiary wastewater treatment process as well. The process of integration could start with easier to treat wastewater such as those from the hand wash basin could be pretreated to filter solid waste and treated using heat-pump coupled SGMD. This would reduce the waste heat being rejected to the environment while obtaining clean water.

4.4.1. Case studies

Putting this into perspective, a household with 3 rooms and 3 air-conditioning unit with a total cooling capacity of 8.2 kW could potentially produce a theoretical maximum of 2.35 kg/h of water from coupling with an SGMD that could reduce the condensing temperature by 7 °C of a vapor compression cycle utilizing an R134a refrigerant. Al-Rashed presented a theoretical coefficient of performance (COP) increase from 3.13 at 38 °C to 3.99 at 45 °C for a vapor compression system using an R134a refrigerant.[36] Since the COP is the ratio of the cooling capacity over the power input, this would correlate to a 8.2 kW cooling capacity system providing an additional cooling capacity of 1.77 kW using the same amount of power. In an ideal case, with sufficient air flow across the SGMD membrane modules, evaporative cooling will saturate the air in a typical tropical country with 80 % - 100 % relative humidity (RH), then assuming dehumidification by cooling will occur at 25 °C the evaporator of the air cooler. Looking at the psychrometric chart in Fig. 4.7, it can be determined that the enthalpy change for dehumidification by the cooling of the coupled system will require 42.5 kJ/kg dry air. Fully utilizing the additional cooling capacity of 1.77 kW from the improved COP from

coupling with an SGMD, $\frac{1.77 \text{ kW}}{23.5 \frac{\text{kJ}}{\text{kg dry air}}} = 0.075 \text{ kg dry air/s}$ can be cooled to 25 °C.

Multiplied by the difference in moisture content of 0.0274 kg/kg dry air – 0.02 kg/kg dry air = 0.0074 kg/kg dry air after dehumidification by cooling, a condensate production rate of $5.55 \times 10^{-4} \text{ kg/s}$ or 2.00 kg/h can be obtained. Since the moisture content of air at 30 °C at 80 % RH is 0.0214 kg/kg dry air, the amount of moisture added to air by the evaporative cooling process is 0.0274 kg/kg dry air – 0.0214 kg/kg dry air = 0.006 kg/kg dry air, which when multiplied by the same flow rate of air into the air cooler calculated above at 0.075 kg dry air/s, 1.62 kg/h of wastewater can be treated.

Figure 4.7. Psychrometric chart [37] illustration of the SGMD hybridized with a household air conditioning unit in a typical tropical country.

4.4.2. Simplified economic assessment

Since the above case only consist the SGMD unit, similar calculations were made to include the condensate from the other indoor air conditioning units assuming 30 % fresh air circulation [38] and a total average air flow rate of 6.4 m³/min. This amounts to an additional 5.81 kg/h of condensate from the individual indoor air conditioning units.

Assuming the case study in section 4.4.1, the membrane area required to treat 1.62 kg/h of wastewater based on the average flux data at a feed temperature of 40.5 °C obtained by Khayet et al. [39] is 0.45 m². With these additional information derived, based on the calculations carried out in the supporting information SI.1, the condensate recovery cost (CRC) was determined to be 4.11 \$/m³ of condensate, approximately 4 times that of water from the tap in Singapore [40]. This is due to the fact the condensing unit is over-designed for the small amount of condensate. Understanding that a single indoor air-conditioning unit can provide up to 2.7 kW, designing the condensate recovery system to maximize the use of a single indoor air-conditioning unit led to a CRC of 3.17 \$/ m³.

However, at approximately 3 times the cost of clean water, the CRC might not be cost effective to adopt for households with smaller space cooling requirements. Large commercial buildings such as shopping malls or hotels which have larger space cooling requirements and wastewater production, would have more incentives to adopt this additional technology to improve condensate recovery, reduce wastewater treatment costs and reduce waste heat generation. Furthermore, this simplified economic assessment did account for the savings on dehumidification before cooling and the benefits from reduced waste heat generation (e.g. reduction of urban heat island effect) as well as the savings from reducing the dependency on a particular clean water source (e.g. desalination) in terms of water security, economic and environmental cost.

4.4.3. Future research

Further research could be carried out to incorporate current advancements in different areas of research, mainly MD and humidification/dehumidification (HDH) to improve flux as well as the effectiveness and efficiency of the coupled system. For example, Wu et al. [41] bubbled air into the feed in a hollow-fiber MD system to improve flux by about 50% in the bubbly flow regime, which was attributed to the humidification of the air and the higher humid air flux across the membrane. Further coupling with new membrane dehumidification system such as those designed and used by Zhao et al. which aims to supersaturate the air with water vapor at elevated temperature before condensing the water vapor at the condenser[42, 43], may prove to be very advantageous as well. This is because the heat from the membranes can help to supersaturate the air with water

vapor due the elevated temperature surrounding the membrane fibers. The potential for such a system can be extended to larger MD-HDH systems [44] for large-scale water treatment and space cooling applications, essentially making full use of energy which will anyway be used for space cooling in tropical regions for concurrent potable water generation.

Issues and challenges which needs to be addressed includes (1) the optimization of the condensate recovery system to improve cost effectiveness by changing parameters such as air flow rate across the membrane and the balance between radiator cooling and SGMD cooling, (2) the removal of the already low levels of organic and inorganic contaminants from condensate to eliminate concerns about the potability of the water and (3) design of easily incorporated and economically affordable heat exchanger system to integrate with current HDH and/or space-cooling solutions to further reduce the CRC. However, this study along with research advances made in areas of water treatment, MD and HDH systems, should lead to us to the solutions for these issues and challenges in time to come.

4.5. Conclusions

The impact of feed temperature, membrane area, presence of recycle and module orientation on the operation of a thermoelectric coupled sweeping gas membrane distillation (T-SGMD) was investigated experimentally.

The experimental results are summarized as follows. When coupled to MD, the thermoelectric cooler consumed less energy and produced more condensate due to both the increase in thermoelectric efficiency because of the cooling provided by the MD, as well as the additional condensate produced by the MD process. Condensate production can be improved by increasing the membrane area, recycling cool air back to the membrane module and/or reducing the air flow across the cooling fins.

The two key highlights here provide more understandings for the design of such hybrid MD systems. Firstly, it is possible to couple SGMD to a heat pump for space cooling without the use of an external condenser, and yet be able to produce more condensate per unit energy without a decrease in cooling capacity per unit energy. This is made possible through the improvement in thermoelectric efficiency from the evaporative cooling occurring at the MD modules. Secondly, the increase in condensate

production comes at the expense of a reduction in cooling capacity. Hence, there is a need to first optimize the membrane area for a particular cooling capacity to minimize the decrease in cooling capacity per energy while providing an increase in condensate produced per unit energy and using cool air recycle to switch between maximizing condensate production or maximizing cooling capacity per unit energy consumed. Controlling the cool air recycle to switch between maximizing clean water production or maximizing cooling capacity per unit energy input would be more feasible compared to changing the orientation in terms of implementation.

Appendix

Table 4.2 summarizes properties of the PVDF hollow-fiber membrane used in this study

Table 4.2 Properties of Polymeric Membranes

Membrane material	PVDF
Outer diameter (mm)	1.531
Inner diameter (mm)	0.872
Nominal pore size (μm)	0.022
Maximum pore size (μm)	0.183
Water contact angle ($^{\circ}$)	116
Porosity (%)	83
Water liquid entry pressure, LEP_w (bar)	3.14
Tensile modulus (MPa)	26.4
Strain (%)	126.6
Zeta-potential (mV) ^a	-52.5

^a Surface zeta-potential was measured in NaCl solution at pH 7.

Supporting information

SGMD hybridized with a household air conditioning system process cost estimation

The condensate recovery cost (CRC) is calculated using a simplified cost estimation for the annual fixed cost (AFC) and annual operating cost (AOC). The parameters necessary for this cost estimation are listed in Table 4.3. Costs were estimated based on online quotations and sources [45, 46]. Clean water and energy tariffs were obtained from Singapore utilities provider SP group [40]. All costs were converted to US dollars based on conversion rates as of 3rd August 2018. While the replacement frequencies were based on normal MD operations reported [47].

$$CRC = \frac{AFC + AOC}{f \cdot M \cdot 365} \quad (\text{Eqn. S1})$$

Where f and M represent plant availability and the daily total condensate recovery, respectively. The AFC consists of cost required for an additional condensate recovery condenser, which is assumed to be another indoor air-conditioning unit, and a condensate recovery enclosure with polypropylene tank (Eqn. S2). The operating costs (AOC) involves membrane module and replacement, electricity to power small air intake and circulator, maintenance and consumables such as air filters (Eqn. S3).

$$AFC = \frac{\Psi_{\text{membrane}} + \Psi_{\text{indoor air-conditioning unit}} + \Psi_{\text{condensate recovery enclosure \& water tank}}}{\text{Unit life time (years)}} \quad (\text{Eqn. S2})$$

$$AOC = \Psi_{\text{membrane replacement}} + \Psi_{\text{electricity}} + \Psi_{\text{mainenance}} + \Psi_{\text{consumable}} \quad (\text{Eqn. S3})$$

Where Ψ is the cost.

Table 4.3 Data and assumptions used in economic study

Clean tap water cost (\$/m ³)	1.11
Electricity cost (\$/kWh)	0.17
Availability (%)	60
Unit life time (years)	15
Air filter cost (\$)	15
Air filter replacement	15%
Membrane cost (\$/m ²)*	220
Membrane replacement	15%

Maintenance cost (\$/year)	30
Enclosure and tank for condensate recovery unit (\$)	300
Additional indoor cooling unit (\$)	600

*Membrane price for hollow fiber 0.22 μ m PVDF from Theway membrane.

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CHAPTER 5 : PHOTOTHERMAL-ENHANCED MXENE COATED MEMBRANE FOR SOLAR-ASSISTED MD

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5.1. Introduction

The increasing interest in MD is evident in the publication of more than ten reviews on this topic in the past five years [1-15], most of which highlighted the need for better membranes since the current commercially available membranes remain far from optimized for MD. With respect to optimizing membranes specifically for MD, studies have focused on increasing permeability [16, 17], mitigating fouling [18-20], increasing resistance to membrane pore-wetting [21, 22], and improving energy-efficiency [23] by altering material surface energy, pore size, thickness, porosity, tortuosity and thermal conductivity. As reviewed by Eykens et al. [5], some have chosen to confer membranes with additional functionalities through the coating of superhydrophobic TiO₂ and/or SiO₂, which may not be long-lasting in high-flow and high-pressure operations such as RO, to increase the competitive edge of MD. Such modifications result in better flux recovery after mild washing or a better solute rejection rate, but is usually accompanied with a larger flux decline due to the additional heat and/or mass transfer resistance imposed. With the emergence of novel 2D materials like MXene, which is a group of layer-structured materials composed of metal carbides/carbonitrides/nitrides [24], beneficial properties such as photothermal and anti-fouling effects can potentially be harnessed to improve MD, which formed the motivation for the current study.

Since MD is a thermal-driven process, enhancing the thermal properties of the membrane would be advantageous. A recent review by Politano et al. [25] on the incorporation of thermoplasmonics (which are materials that serve as an excellent heat receiver when irradiated under a wavelength of light corresponding to its plasmon

resonance wavelength) in membrane applications confer benefits including increase in permeance of water in nanofiltration, high-throughput separation of oil-in-water nanoemulsions, and improvements in MD or pervaporation. Subsequently, the same group [26] embedded silver nanoparticles to improve localized photothermal heating in a vacuum MD system, and demonstrated that such surface-coating of thermoplasmonics on membrane surfaces in MD allowed for localized heating and thereby a larger temperature difference across the membrane, which would reduce the footprint of MD systems. Furthermore, Boo et al. [27] recently highlighted the potential of localized heating using Joule heating [28], which is the generation of heat by passing an electrical current through a conductor, and photothermal materials [26], such as silver nanoparticles, to reduce the heating cost in desalination by MD. While on the other hand, materials with photocatalytic functionalities were developed to efficiently degrade pollutants under visible light [29, 30]. However, as nanotechnology advances, more novel materials with multiple functionalities have been developed, with their potential practical uses untapped, eliminating the need to use multiple materials for a particular application. MXene is one of such materials, with advantageous traits including good optical absorption, thermal property and tunable band gap [24], which are useful to the MD process in terms of providing photothermal-induced localized heating and possibly photocatalytic degradation. Furthermore, the possibility of forming stable MXene materials using a wide variety of metal elements (Sc, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, Mn, etc) with various composition as well as proportion and arrangement, along with the tuning of metallic conduction and active sites, provides a whole new array of coating materials that could possibly be used to significantly improve the MD process.

Hence, this study aimed to use an emerging 2D material, namely, MXene, for the first time in a direct contact membrane distillation (DCMD) process to provide the twin effects of (i) localized heating of the feed side of the membrane photothermally to reduce the heating required; and (ii) fouling mitigation. The feed contained 200 ppm of bovine serum albumin (BSA). MXene was synthesized and coated onto the hydrophobic polyvinylidene difluoride (PVDF) membrane using polydimethylsiloxane (PDMS).

5.2. Materials and Method

5.2.1. Experimental Study

An experimental study was carried out to evaluate the effectiveness of a MXene coating on a hydrophobic PVDF membrane (specifications listed in Table 5.4) in providing localized heating photothermally and fouling resistance in a DCMD process.

5.2.1.1. Experimental setup

The schematic of the experimental DCMD setup is shown in Fig. 5.1. The membrane module was operated in counter-current cross-flow mode, with an active membrane area of 0.00371 m² (53 mm by 70 mm). The membrane module was made of acrylic, which not only allowed visible light to pass through to the feed side of the membrane to enable the photothermal effects, but also minimized absorption and diffraction losses. The light source used in this experiment was a 50 W LED lamp (Huga LED) with an illuminance of 700000 lux at 4 cm away from the light source, which is seven times that of the Sun. The distillate flow channel had a spacer mesh (specifications listed in Table 5.5) to reduce the heat-transfer resistance and provide mechanical support for the membrane, but a spacer was absent on the feed side to maximize light irradiation on the feed side of the membrane.

The feed and distillate were recirculated through the membrane distillation module from their respective tanks using two peristaltic pumps (Masterflex L/S Digital Drive). The hot feed contained in the feed tank (a 2-L round bottom flask) was heated and agitated using a hotplate stirrer (Heidolph MR Hei-Tec), while being recirculated at 250 mL/min through Masterflex Norprene tubings between the membrane module and feed tank. The cold distillate contained in the distillate tank (a 1L acrylic tank with a spout) was cooled by a recirculating chiller (Julabo ME), while being recirculated at 250 mL/min through Masterflex Tygon E-LFL tubings between the membrane module and distillate tank. The overflow tank (a 300 mL beaker) was placed on a mass balance (Mettler-Toledo ME4002) for the measurement of distillate flux which was derived from the accumulated distillate which overflowed into the overflow tank per unit time. The energy consumed by the hot-plate stirrer was measured using a power meter (UNI-Trend UT230B), and the mass and conductivity of the distillate were also measured.

A virgin PVDF hydrophobic flat-sheet microfiltration membrane (Durapore GVHP; detailed specifications listed in Table 5.4) was used to provide benchmarks for comparison. The membrane of interest was the PVDF membrane coated with MXene, a group of layer-structured materials composed of metal carbides/carbonitrides/nitrides [24], using PDMS. As another benchmark, PVDF membranes with PDMS coating alone (i.e., without MXene) were also investigated. The membrane modification procedure is described in Section 5.2.1.3.

Figure 5.1. Schematic of the experimental direct contact membrane distillation (DCMD) setup consisting of (1) a feed tank (i.e., 2 L round-bottom flask) heated by a hot plate with a heating mantle and agitated with a magnetic stirrer, (2) three peristaltic pumps, (3) a cross-flow flat-sheet acrylic membrane module, (4) a 50 W LED lamp positioned 4 cm above the feed-membrane interface, (5) a distillate tank (i.e., 1 L acrylic tank with a spout) cooled by a recirculating chiller and with a conductivity meter inserted, and (6) an overflow distillate tank (300 mL beaker) atop a mass balance.

5.2.1.2. MXene synthesis and characterization

The MXene used (namely, $\text{Ti}_3\text{C}_2\text{T}_x$, a $-\text{O}-$, $-\text{F}-$ and $-\text{OH}-$ containing surface-terminated Mxene) was synthesized using the method reported in literature [31-33]. Briefly, 1 g of MAX-phase (where M represents an early transition metal, A represents an A-group (commonly group III and IV element) and X a carbon and/or nitrogen) Ti_3AlC_2 powder was immersed in 10 mL of 50 wt% hydrofluoric acid (HF, VWR

chemicals) and stirred for 20 h at room temperature to obtain a stable suspension which consists of –O-, –F- and –OH-containing surface-terminated $\text{Ti}_3\text{C}_2\text{T}_x$. The suspension was then centrifuged, followed by washing with DI water until a pH of approximately 6.0 was obtained. The obtained $\text{Ti}_3\text{C}_2\text{T}_x$ powder was dried under vacuum at 60 °C overnight. The delamination of Ti_3C_2 was carried out using dimethyl sulfoxide (DMSO, Sigma-Aldrich), after which 1 g of the previously obtained $\text{Ti}_3\text{C}_2\text{T}_x$ dry powder was stirred with 10 mL DMSO for 18 h at room temperature, followed by centrifugation at 3500 rpm for 5 min to collect the solid. The collected powder was dispersed in DI water at a mass ratio of 1:300, and subsequently sonicated for 6 h with argon gas being continuously bubbled through the DI water during the sonication, and finally centrifuged at 3500 rpm for 30 min to remove unexfoliated particles.

X-ray diffraction (XRD) patterns were obtained with a powder diffractometer (Bruker D2 phaser XRD) using Cu K α radiation. A field-emission scanning electron microscope, (FESEM JEOL JSM-6701F) operating at 5 kV accelerating voltage and high-vacuum (9.63×10^{-5} Pa) mode was used to obtain high-magnification images of the MXene powders. All FESEM samples were coated with platinum to prevent electron build-up during imaging.

5.2.2. PVDF membrane modification and characterization

The MXene powder synthesized was re-suspended in ethanol to form a 2.5 mg/mL mixture, from which 20 mL was vacuum-filtered through a virgin PVDF membrane to deposit a uniform layer of 50 mg of MXene. The PVDF membrane with MXene atop was then transferred to a convection oven (Binder FD series) to dry at 70 °C for 1 h, after which dip-coating was carried out by submerging it into a 2 wt% Sylgard PDMS in heptane solution (base to curing agent ratio of 10:1) at room temperature for 10 s. Finally, the modified membrane was dried and cured overnight in the convection oven at 70 °C. This temperature was chosen as it is high enough for PDMS to cure while being within the maximum operating temperature of 85 °C as stated by the manufacturer.

In order to carry out a more thorough comparison of the performance, two more modifications of the PVDF membranes were made, namely, PDMS-coated PVDF and MAX phase-coated PVDF. The PDMS-coated PVDF was made by dip-coating the PVDF membrane with a 2 wt% Sylgard PDMS in heptane solution (base to curing agent ratio of

10:1). As for the MAX phase-coated PVDF, it was synthesized using a similar method as that of the MXene-coated PVDF. Specifically, the MAX phase powder was suspended in ethanol to form a 2.5 mg/mL mixture, from which 20 mL was vacuum-filtered through a virgin PVDF membrane to deposit a uniform layer of 50 mg of MAX phase. The PVDF membrane with MAX phase atop was then transferred to a convection oven (Binder FD series) to dry at 70 °C for 1 h, after which it was dip-coated with a 2 wt% Sylgard PDMS in heptane solution (base to curing agent ratio of 10:1) and cured in a convection oven (Binder FD series) at 70 °C overnight.

A field-emission scanning electron microscope (FESEM; JEOL JSM-6701F) operating at 5 kV accelerating voltage and high-vacuum (9.63×10^{-5} Pa) mode was used to obtain high-magnification images of the membranes. Energy-dispersive X-ray spectroscopy (EDS) analysis was also carried out using an Oxford Instruments SDD detector in the same FESEM with the accelerating voltage set at 15 kV. All FESEM and EDS samples were coated with platinum to prevent electron build-up during imaging and elemental analysis. Contact angle measurements of water droplet on the membranes were carried out using a contact angle goniometer (Kruss; DSA25).

A capillary flow porometer (CFP 1500A, Porous Material. Inc. (PMI)), was used to measure the pore size and pore-size distribution (PSD) of the PVDF membranes. The membrane was placed into the sample holder with a contact surface diameter of 1.5 cm and wetted with a few drops of wetting liquid (GalwickTM; surface tension = 15.9 dynes/cm). The sample holder was then placed into the sample chamber with a spacer placed on top before covering the sample chamber with the top cover. Nitrogen was the inert gas used.

5.2.3. Infrared (IR) thermal imaging

A digital IR thermal imaging camera (Cat S60), equipped with a FLIR Lepton IR sensor, was used to take a thermal image of the membranes investigated in this study before irradiation and after 1 minute of irradiation with a 50 W LED lamp placed 4 cm away from the coated surface.

5.2.4. Characterization of feed

The mean BSA aggregate size, BSA aggregate size distribution and zeta-potential of the feed were measured via dynamic light scattering (DLS) using a Phase Analysis

Light Scattering Zetasizer (Brookhaven Instruments Corporation, New York, USA). Standard disposable polystyrene cuvettes were filled with 2 mL of each sample for each test. The samples were allowed thermally equilibrate to 25 °C prior to acquiring five sets of measurements.

5.2.5. Experimental protocol

The following protocol was used for each experiment. Firstly, the PVDF membrane, either with or without MXene coating on the feed side, was positioned in the membrane module. Secondly, 10 g/L NaCl (NaCl; Merck-Millipore CAS No. 7647-14-5) solution and DI water were respectively circulated through the feed and distillate loops at 250 mL/min. NaCl was added to ensure salt rejection capability of the membrane was not compromised after the membrane modifications. The temperatures of the feed and distillate streams of the membrane module were set at respectively 65 and 15 °C. To detect any membrane-wetting, the conductivity of the distillate in the distillate tank was measured at the end of every experiment using a conductivity meter (Eutech Instruments Alpha Cond 500) to ensure that the conductivity remained within 2 µS/cm (i.e., quality of the DI water used).

5.2.5.1. Photothermal efficacy

To investigate if the coated MXene was effective in enhancing the DCMD performance under light irradiation, a suite of experiments was carried out. The protocol was as follows: (1) with the 50 W LED lamp switched off, the DCMD system was started and given an hour to stabilize before the mass and heater energy consumption measurements were recorded at the start and end of three hours; and (2) the distillate produced was recycled back to the feed tank and the 50 W LED lamp was switched on, then the system was given an hour to stabilize before the mass, energy consumption and conductivity measurements were recorded at the start and end of three hours of light irradiation.

It should be noted that the energy reported here was that consumed by the heater to maintain the feed at a constant temperature of 65 °C and did not include that by the LED lamp. For a fairer comparison among the cases with different distillate fluxes, the heater energy consumed was further normalized with respect to the distillate produced:

Energy consumed by heater per unit volume of distillate

$$= \frac{\text{Energy consumption by external heater over 3 h}}{\text{Distillate produced over 3 h}}$$

(1)

5.2.5.2. Fouling mitigation

The second suite of experiments involved assessing if MXene was able to mitigate membrane fouling. Step 1 was the same except for the produced distillate being recycled once every hour to ensure a constant feed concentration. In addition, the temperature readings at the feed and distillate inlet and outlet, as well as the mass of distillate overflow, were obtained every 5 minutes, to track the flux changes with time. The flux obtained during this steady-state operation over three hours was used as a benchmark for assessing the flux declined caused by BSA fouling. In Step 2, the feed was spiked with 200 mg BSA, resulting in a BSA concentration of 200 mg/L, and the system was left to run for 21 h with the produced distillate recycled once every hour to ensure a constant concentration of BSA in the feed. This two-step procedure was carried out for experiments with and without light irradiation, as well as for both the virgin PVDF and modified PVDF membranes. A new membrane was used for every experimental run. Every experiment was repeated to check for reproducibility.

5.3. Results and Discussion

5.3.1. Characterization of MXene and modified PVDF membranes

The FESEM images and XRD patterns of the MAX-phase Ti_3AlC_2 powder and the exfoliated MXene Ti_3C_2 powder are displayed in Figs. 5.2a and 5.2b, respectively. Contrasting Figs. 5.2a and 5.2b indicate the removal of the aluminum layer from the Ti_3AlC_2 in the exfoliated MXene Ti_3C_2 powder in Fig. 5.2b, wherein the FESEM image shows intercalated MXene sheets and the XRD pattern shows the disappearance of the strongest peak corresponding to the (104) crystal plane of Ti_3AlC_2 at $2\theta = 39.2^\circ$, similar to those reported [34, 35].

Figure 5.2. FESEM image and XRD patterns of (a) MAX-phase Ti_3AlC_2 powder, and (b) exfoliated MXene Ti_3C_2 powder

After coating MXene on the PVDF, FESEM images in Fig. 5.3a show distinctly the successful coating of a MXene layer on the surface of the PVDF matrix. EDS results in Fig. 5.3b indicate no signs of titanium within the PVDF membrane matrix, which indicates that MXene was retained and coated only on the surface of the PVDF membrane. Silicon was detected both within the PVDF membrane matrix as well as the MXene coating with similar count rates (Fig. 5.3b). This suggests that the PDMS is present within the MXene coating to bind the MXene particulates to each other as well as the PVDF.

Figure 5.3. (a) FESEM image depicting EDS scan area for MXene coating and PVDF matrix; and (b) EDS spectrum for MXene coating and PVDF matrix. Platinum (Pt) peak was present due sample being sputter coated with Pt to reduce accumulation of electron charge on sample during FESEM imaging.

The photographs and FESEM images of the membranes (namely, virgin PVDF membrane, PDMS-coated PVDF membrane, MAX phase-coated PVDF membrane and MXene-coated PVDF membrane) used in this study are displayed respectively in Figs. 5.4 and 5.5. While Fig. 5.4 only shows the feed-side of the membranes, Fig. 5.5 shows both the feed surfaces and cross-sections. For the virgin PVDF membrane and the PDMS-coated PVDF membrane, Figs. 5.4a and b show that they look similar as PDMS is colorless before and after curing, whereas Figs. 5.5a - d show that PDMS reduced the

pore sizes of the membrane due to swelling of the PVDF fibers by PDMS. As for the MAX phase-coated PVDF and MXene-coated PVDF membranes, Figs. 5.4c and d indicate that the color are similar to the materials coated; the former was grey due to the presence of aluminum while the latter black after treatment with HF. The colors observed are characteristic of the Ti_3AlC_2 MAX phase and Ti_3C_2 MXene used [34, 36]. FESEM images in Figs. 5.5e - h further show similar coating thicknesses of both membranes, although Mxene exhibited a clear intercalated structure (Fig. 5.5g). Comparing Figs. 5.5a and g indicates that the MXene was deposited on the feed side of the membrane, and the thickness measured from three different FESEM images of the membrane cross-section was found to range from 7 - 10 μm (Fig. 5.5h).

Furthermore, the pore-size distributions (PSDs) of the virgin and modified PVDF membranes (namely, PDMS- and MXene-coated) were characterized. Fig. 5.6 shows that (i) the PSD of the PDMS-modified PVDF membrane was shifted leftwards relative to the other two, which agrees with the smaller pores shown in Fig. 5.5c; and (ii) the PSDs of the virgin PVDF and MXene-coated PVDF membranes were more similar, despite the latter also dip-coated with PDMS, because of the intercalated nature of MXene shown in Fig. 5.5g.

Contact angle values listed in Table 5.1 indicate that the membrane became more hydrophobic after PDMS coating. The PDMS-, MAX phase- and MXene-coated PVDF membranes, all of which had PDMS, had respective contact angle values of 10° , 17° and 36° higher than the virgin PVDF membrane. The higher water contact angles of the MAX phase- and MXene-coated PVDF are attributed to the increased surface roughness of the membrane resulting from the deposition of the unevenly sized MAX phase and MXene particulates [37]. Notably, the MXene-coated PVDF membrane that was not dip-coated with PDMS exhibited a higher water contact angle, which was unexpected because of the hydrophilicity of MXene. A closer inspection reveals that the high contact angle is due to the coating of MXene on the water droplet (Fig. 5.7a) during the contact angle measurement, which indicates that, without PDMS as a binding agent, MXene was easily removed from the PVDF membrane (Fig. 5.7b) and therefore cannot be used in the cross-flow MD operation. Further analysis of the contact angle values shows that the decrease in contact angle due to membrane surface degradation via the formation of hydrophilic

groups on the membrane after use [38] was also reduced with the coating of PDMS on PVDF or MXene-coated PVDF.

To ensure that the MXene coat persisted throughout the experiment, the MXene-coated PVDF membranes were inspected at the end of the 21 h of filtering a feed containing 200 mg/L BSA in 10 g/L NaCl. Figs. 5.4d and e show negligible difference between the two samples. Further comparing Figs. 5.5g and h with respectively Figs. 5.5i and j demonstrates no significant change in the morphology of the MXene particles as well as the thickness of the MXene coating before and after the experiment, suggesting that the MXene coating was stable throughout the MD run.

Figure 5.4. Photographs of the feed surfaces of the membranes investigated: (a) virgin PVDF membrane, (b) PDMS-coated PVDF membrane, (c) MAX phase-

coated PVDF membrane, (d) MXene-coated PVDF membrane and (e) MXene-coated PVDF membrane after 21 h of filtering a feed containing 200 mg/L BSA and 10 g/L NaCl.

Figure 5.5. FESEM images of feed surfaces and cross-sections of the membranes investigated: (a, b) virgin PVDF membrane, (c, d) PDMS-coated PVDF membrane,

(e, f) MAX phase-coated PVDF membrane, (g, h) MXene-coated PVDF membrane and (i, j) MXene-coated PVDF membrane after 21 h of filtering a feed containing 200 mg/L BSA and 10 g/L NaCl. Insets in the left column of FESEM images show the water contact angles at the membrane surfaces.

Figure 5.6. PSDs of virgin, PDMS-coated and MXene-coated PVDF membranes

Table 5.1 Mean contact angle of a water droplet on the membrane

Membranes	Mean contact angle(°)
PVDF	123.01 ± 0.16
PVDF after use	72.48 ± 0.81
PDMS-coated PVDF	133.12 ± 0.26
PDMS-coated PVDF after use	118.03 ± 0.29
MAX phase-coated PVDF	151.69 ± 1.00
MXene-coated PVDF (without PDMS)	141.33 ± 1.72
MXene-coated PVDF	158.98 ± 4.47
MXene-coated PVDF after use	139.45 ± 0.22

Figure 5.7. (a) Water contact angle image and (b) digital image after water contact angle measurement of the MXene-coated PVDF membrane without dip-coating in PDMS. Circled in red are parts of the exposed PVDF surface after the droplet of water used for the water contact angle measurement was removed.

5.3.2. Photothermal effect of modified PVDF

The photothermal effect of the modified PVDF membranes can be observed through the temperature changes of the feed surfaces before and after light irradiation. The IR thermal images in Fig. 5.8 show that, after 1 min of light irradiation, both the pristine PVDF (Figs. 5.8a - b) and PDMS-coated PVDF (Figs. 5.8c - d) membranes exhibited a slight increase in temperatures of respectively 6 and 7 °C, while the MAX phase-coated (Figs. 5.8e - f) and MXene-coated (Figs. 5.8g - h) PVDF membranes gave significant increases in temperatures of respectively 27 and 49 °C. With the MAX phase-coated PVDF as a control experiment in this IR thermal imaging experiment, it was clearly demonstrated that MXene had the best photothermal performance. Hence, the MAX phase-coated PVDF was not being used in the actual MD experiments.

To further evaluate the effect of the PDMS coating on the photothermal performance of MXene, IR thermal images of the MXene-coated PVDF membranes with and without dip-coating with PDMS were obtained. Comparing Figs. 5.8h and j show that, after 1 min of light irradiation, the PDMS coating reduced the membrane surface

temperature by a mere 1 °C, indicating that PDMS had a negligible effect on the photothermal performance of MXene.

Figure 5.8. IR thermal images of the membranes before and after 1 min of light irradiation: (a, b) virgin PVDF membrane, (c, d) PDMS-coated PVDF membrane,

(e, f) MAX phase-coated PVDF membrane, (g, h) MXene-coated PVDF membrane, and (i, j) MXene-coated PVDF membrane without PDMS.

Typically, when an additional coat is added to the membrane, the distillate flux declines due to the increased heat transfer and mass transfer resistances resulting from the increased coat thickness and/or decreased pore sizes [5, 39-41]. Fig. 5.9 shows the flux values for the three membranes (namely, pristine, PDMS-coated and MXene-coated PVDF membranes) in the absence and presence of irradiation. Two observations are worth highlighting. Firstly, vis-à-vis the pristine PVDF membrane, both the PDMS- and MXene-coated membranes expectedly gave lower fluxes due to the additional coating layer. In the absence of irradiation, the presence of the PDMS or MXene/PDMS coats lowered the flux by approximately 20%. Secondly, while the flux values were similar regardless of irradiation for the pristine and PDMS-coated PVDF membranes, the flux values were distinctly different between the absence and presence of light irradiation for the MXene-coated PDVF membrane. In the presence of irradiation, the flux of the MXene-coated PVDF membrane improved by more than 10%, which affirms the photothermal effects conferred by MXene improved the distillate flux.

Figure 5.9. Experimental flux magnitudes of the uncoated virgin and MXene-coated PVDF membranes with and without visible light irradiation. Each error bar represents the span of two repeated experiments.

Fig. 5.10 presents the heater energy consumption for the virgin, PDMS-coated and MXene-coated PVDF membranes in the absence and presence of light irradiation. Two highlights are noted. Firstly, in the absence of light irradiation, the heater energy consumption per unit volume of distillate was highest for the PDMS-coated membrane, and similar for the virgin and MXene-coated PVDF membranes. This indicates that, relative to the virgin PVDF membrane, the PDMS-coat alone imposed greater heat and/or mass resistances, but the presence of MXene negated this increased resistances with the better thermal conductivity of the MXene material, which is one to two orders-of-magnitude greater than that of PVDF [24]. Secondly, similar to Fig. 5.9, whereas the presence of light irradiation did not affect the heater energy consumed per unit volume distillate for the virgin PVDF and PDMS-modified membranes, it decreased the heater energy consumed per unit volume distillate significantly by 12% for the MXene-coated membrane. The energy savings in the presence of light irradiation for the MXene-coated membrane indicates that MXene was able to convert light energy to heat to provide localized heating at the feed-membrane interface, which thereby lowered the heating energy required for the DCMD process. This suggests the potential of the MXene-coated membrane to utilize solar energy to reduce the energy requirement for DCMD due to the beneficial photothermal properties of MXene.

The photothermal conversion was analyzed to be 5.8 kW/m^2 , which is much higher than the approximately 1 kW/m^2 value provided by the sun. It should be noted that the energy efficiency can be further improved, because (i) the photothermal conversion efficiency here was a mere 43%, compared to the 100% reported using single-wavelength laser [36], and (ii) the heater was used as-is without any optimization (e.g., reduce heat loss to the environment). Nonetheless, this study provided proof-of-concept for the potential harnessing of such photothermal properties to improve the practical feasibility of MD.

Figure 5.10. Experimental energy per unit volume distillate of the uncoated, PDMS-coated and MXene-coated PVDF membranes in the absence and presence of visible light irradiation. Each error bar represents the span of two repeated experiments.

5.3.3. Fouling mitigation

MXene has been reported to exhibit antibacterial effects and resistance to biofouling [33], thus, this study aimed at investigating the efficacy of the MXene coating on PVDF to mitigate membrane fouling in DCMD. Fig. 5.11 shows the percentage flux decline over 21 h for a feed containing 200 ppm BSA and 10 g/L NaCl. In the absence and presence of visible light irradiation, the MXene-coated PVDF membrane gave flux declines respectively of 8.3% and 6.6%, which are much lesser than that of PVDF of respectively of 18.8% and 18.2%. This indicates that MXene was effective in mitigating membrane fouling.

Three reasons that could underlie the better fouling effectiveness by MXene are (i) hydrophilic interactions between MXene and BSA, (ii) lesser electrostatics repulsion between MXene and BSA, and (iii) absorption of BSA by MXene. Regarding (i), despite MXene being hydrophilic, the contact angle results (Table 5.1) show that the dip-coating

of PDMS resulted in a more hydrophobic surface, which rules out a weaker hydrophobic interaction with the hydrophilic BSA as the cause for the reduced fouling. As for (ii), Table 5.2 indicates that MXene had a more negative zeta potential than PVDF, which implies greater electrostatic repulsion with the similarly negatively charged BSA. The enhanced repulsion between MXene and BSA aggregates presumably contributed to reduced extents of membrane fouling. With respect to (iii), in view of the significant specific surface area of MXene of 98 m²/g due to the intercalated nature [42], the increased absorption of BSA would mitigate fouling. The increased absorption is evident in the lesser decrease in contact angles (Table 5.1) after filtration of the MXene-coated membrane relative to the uncoated membrane, which suggests the absorption of BSA within the MXene coat rather than on the membrane surface. Furthermore, the hydrodynamic diameters of the BSA aggregates listed in Table 5.3 shed light on the increased absorption by MXene too. For the uncoated PVDF membranes, the hydrodynamic diameters of the BSA aggregates increased by an order-of-magnitude after filtration because of the increased aggregation of BSA at elevated temperatures [43]. However, for the MXene-coated membranes, the increase in the hydrodynamic diameters of the BSA aggregates were much lesser at two- to three-folds, which also suggests absorption of BSA by MXene. Comparing the FESEM images in Figs. 5.12a and c indicates clearly the extensive deposition of BSA on the membrane surface after filtration, relative to that of the MXene-coated membranes (compare Figs. 5.12e and g). The results here hence demonstrate that the enhanced extent of membrane fouling mitigation by the MXene coat was due to increased electrostatic repulsion with and increased absorption of BSA.

With this, the MXene coating without further modification was shown to be able to provide localized heating under visible light and reduce the extent of protein fouling. Hence, with further modification of MXene such as rearranging the surface groups relative to the metal atoms in MXene to induce photocatalytic effect [44, 45] or using TiO₂/MXene nanocomposites treated with increased concentration of NH₄F which is able to broaden the photocatalytic activity to the visible-light range [46]. Furthermore, with its large surface area from intercalation and lower cost compared to noble metal catalysts such as platinum and gold, earth-abundant MXene family materials have been proposed as a cost-effective replacement for photocatalysts [24, 47]. When used in membrane

processes such as membrane distillation, MXene's photothermal properties provide localized heating, while MXene's large surface area facilitates adsorption of organic foulant, coupled with the possibility of improving photocatalytic activity through simple modifications can confer the membrane with self-cleaning function with potential to reduce fouling.

Figure 5.11. Experimental flux decline after 21 h of filtering a feed containing 200 ppm BSA and 10 g/L NaCl using the pristine and MXene-coated PVDF membranes in the absence and presence of visible light irradiation.

Figure 5.12. FESEM images of feed surfaces and cross-sections of the membranes: (a, b) virgin PVDF membrane, (c, d) used PVDF membrane after 21 h of filtering a feed containing 200 mg/L BSA and 10 g/L NaCl, (e, f) MXene-coated PVDF before use, and (g, h) used MXene-coated PVDF membrane after 21 h of

filtering a feed containing 200 mg/L BSA and 10 g/L NaCl. Insets in the left column of FESEM images show the water contact angles at the membrane surfaces.

Table 5.2 Zeta potentials of MXene suspension and feed containing 200 ppm BSA and 10 g/L NaCl

Species	Zeta potential (mV)
Uncoated PVDF membrane	-6.25 [48]
MXene in 10 g/L NaCl solution	-27.4 ± 3.6
Freshly prepared feed containing BSA	-12.2 ± 1.3
Feed after 21 h of filtration using PVDF (without irradiation)	-12.7 ± 3.0
Feed after 21 h of filtration using PVDF (with irradiation)	-14.3 ± 2.2
Feed after 21 h of filtration using MXene-coated PVDF (without irradiation)	-13.2 ± 2.5
Feed after 21 h of filtration using MXene-coated PVDF (with irradiation)	-12.9 ± 1.2

Table 5.3 Mean hydrodynamic diameters of BSA aggregates

BSA aggregates	Hydrodynamic diameter (nm)
Freshly prepared feed	20.1 ± 6.3
Feed after 21 h of filtration using uncoated PVDF (without irradiation)	229.3 ± 4.9
Feed after 21 h of filtration using uncoated PVDF (with irradiation)	231.8 ± 8.0
Feed after 21 h of filtration using MXene-coated PVDF (without irradiation)	62.4 ± 6.2
Feed after 21 h of filtration using MXene-coated PVDF (with irradiation)	50.6 ± 5.5

5.4. Conclusions

The efficacy of MXene as a coating material on hydrophobic PVDF membranes to improve direct contact membrane distillation (DCMD) through the inherent photothermal and fouling mitigation functionalities was investigated experimentally. The successful coating of MXene was verified by FESEM and EDS.

The photothermal properties of MXene was beneficial in conferring a 12% decrease in the energy consumed by the heater per unit volume distillate. Thermal IR images showed that the MXene-coated membrane gave a temperature of 43 °C greater than the uncoated PVDF membrane after a mere 1 minute of light irradiation. The additional mass resistance imposed by the MXene coat lowered the flux by 20% vis-à-vis the uncoated PVDF membrane, but the flux was reduced by a lesser 13% in the presence of irradiation and thereby photothermal effects. The photothermal conversion was analyzed to be 5.8 kW/m², which is a few times higher than the approximately 1 kW/m² value provided by the sun. Nonetheless, since neither the MXene nor the system was optimized, the heater energy reduction demonstrated here provided proof-of-concept for the potential harnessing of such photothermal properties to improve the practical feasibility of MD.

Regarding fouling mitigation, after 21 h of continuous filtration of a feed containing 200 ppm BSA and 10 g/L NaCl, the MXene-coated PVDF membrane conferred a 56 - 64% reduction in flux decline compared to the uncoated membrane. This is attributed to both greater electrostatic repulsion and also increased adsorption of BSA by MXene because of the significant specific surface area due to the intercalated structure.

Overall, this study demonstrated the practical use of an emerging class of 2D materials, namely, MXene, for coating membranes to improve the performance of a lab-scale DCMD setup. Other than photothermal and anti-fouling effects, MXene provides a multitude of other properties, such as electrical conductivity, and chromium adsorption and reduction, which could be further employed to provide localized heating via joule heating and removal of highly toxic chromium(VI) from water, respectively. Development of such localized heating technology can be extended to other flat-sheet MD configurations to incorporate solar heating to existing processes. Furthermore, by

coupling with solar heating of the feed too [49], the MD system could potentially be self-sufficient without the need for external heating.

Appendix

Table 5.4 summarizes the properties of the PVDF membrane used in this study, while Table 5.5 gives the specifics for the flow channel and the mesh spacer used in the distillate channel to increase the heat-transfer coefficients on the distillate side of the membrane.

Table 5.4 Properties of Durapore GVHP hydrophobic PVDF membrane

Membrane	PVDF
Specification	Durapore GVHP
Thickness (μm)	125
Nominal pore diameter (μm)	0.22
Mean-flow pore diameter (μm)	0.2566
Porosity (%)	75

Table 5.5 Channel and Spacer Specifications

Channel height (cold side) (m)	0.004
Channel height (hot side) (m)	0.004
Channel width (m)	0.053
Channel length (m)	0.07
Channel active membrane area (m^2)	0.00318
Spacer material	polypropylene
Spacer filament diameter (m)	0.00026
Spacer thickness (m)	0.00052
Spacer mesh size (m)	0.003
Spacer hydrodynamic angle (degrees)	90
Feed attack angle (degrees)	45
Spacer void fraction (dimensionless)	0.932

List of abbreviations

MD	Membrane distillation
DCMD	Direct contact membrane distillation
RO	Reverse osmosis
PVDF	Polyvinylidene difluoride
PDMS	Polydimethylsiloxane
NaCl	Sodium chloride
HF	Hydrofluoric acid
DMSO	Dimethyl sulfoxide
BSA	Bovine serum albumin
XRD	X-ray diffraction
FESEM	Field emission scanning electron microscopy
EDS	Energy-dispersive X-ray spectroscopy
PSD	Pore-size distribution

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CHAPTER 6 : PHOTOTHERMAL-ENHANCED METALLIC SPACERS TO ENHANCE MD

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6.1. Introduction

Membrane distillation (MD) is a thermal-driven separation technology that is well-acknowledged to be a promising, easy-to-integrate, green (based on utilization of low-grade waste heat) alternative to the dominant water treatment processes like distillation and reverse osmosis. Despite the increasing interest in MD, as evident in the surge in the reviews on this topic over the past five years [1-15], most of the research centered on membrane fabrication and modification, since the current commercially available membranes are not optimized for MD [16-18]. Only a handful of the research efforts were targeted at understanding the effect of flow patterns on MD performance, some of which were related to module orientation and design [19-21], while others were related to the use of spacers and its design [22-25]. In particular, although the studies on spacers are not lacking [26], the tailoring of spacers specifically for MD has not been delved into much.

Typically, a spacer functions as a stationary turbulence promoter to mitigate membrane fouling and enhance permeation through lowering the boundary-layer mass-transfer coefficient through the membrane. With respect to the design of spacers in MD, recent research has shown that the shape, configuration, diameter and number of spacer filaments have significant impact on the water vapor flux [22]. Almost all of the spacers used are typically made of low-cost polymeric material (e.g., polypropylene). Because MD is unique in terms of being a thermal-driven process, on top of improving the mass-transfer coefficient through spacers, it is conceivable to improve the heat-transfer coefficient as well. Accordingly, specific for conductive gap membrane distillation (CGMD), Ma et al. [27] and Jaichanda et al. [28] proposed the use of metallic spacers to

improve performance based on the inherently higher conductivity. This suggests that proper selection of the spacer material is beneficial for enhancing MD performance. This study focused on evaluating the possible advantages in harnessing the higher thermal conductivity of metallic spacers for DCMD.

To improve the energy efficiency in the thermal-driven MD process, recent studies have demonstrated that the addition of photothermal materials [29, 30] and electrically conductive materials [31] on the membrane could provide localized heating via light irradiation and Joule heating (i.e., the generation of heat by passing an electrical current through a conductor), respectively. This localized heating serves to increase the surface temperature of the membrane and as a result the vapor flux across the membrane can be enhanced significantly [32]. So far, the modifications are mainly targeted at imbuing the membrane surface with additional functionalities to improve the MD performance, which may have adverse effects like blocking the pores and thereby causing flux declines as observed first hand from the results obtained in Chapter 4 of this thesis. In another instance, though coating of titanium dioxide (TiO₂) nanoparticles on the membrane surface could boost the flux recovery after mild washing and give a better solute rejection rate, it was accompanied by a larger flux decline [5]. To this end, the endowment of the additional functionalities on the spacer (rather than the membrane) may be feasible, which was explored in this study.

The goals of this MD study were hence twofold. Armed with the understanding that a higher electrically conductive material facilitated better heat conduction across the membrane [28], metallic spacers were investigated to assess the benefits of the higher thermal conductivity. In addition, based on previous studies that the conferring of additional functionalities on the membrane to improve performance may have adverse effects [5], the coating of the metallic spacers were attempted instead. In this study, DCMD was investigated via both simulations and experiments. The frequently used polypropylene spacer with each mesh dimension of 3 mm was used as a benchmark for comparison. Two metals were investigated, (namely, nickel and copper), along with three spacer densities (namely, 3 mm mesh, 1.5 mm mesh and foam). Furthermore, the nickel spacer was coated with photocatalytic platinum to further enhance the energy efficiency via photothermal conversion. Through simulations, surface temperatures on both the feed and distillate sides of the membrane, and velocity profiles were obtained. Through experiments, the distillate flux, heater input energy per unit volume distillate, and rate of

heat loss were obtained. Conclusions were made on the improvement to energy efficiency possible using metallic spacers and also photocatalytic-enhanced metallic spacers.

6.2. Materials and Method

6.2.1. CFD simulations

6.2.1.1. Simulation setup

Three-dimensional (3D) computational fluid dynamics (CFD) simulations of the direct contact membrane distillation (DCMD) module in Fig. 6.1 were carried out using Comsol Multi-Physics 5.1. The simulations aimed to investigate the effect different spacers have on the heat and mass transfer near the membrane surface. The governing equations used were the Navier-Stokes and continuity equations (listed in Appendix), and the physics packages in Comsol used were Laminar Flow (because Reynolds number was 149 in the 4 mm channel) and Heat Transfer. Laminar flow was used in this case to eliminate the effect of turbulence on heat transfer, to better study the effect of thermal conductivity of the different spacers on MD performance. In order to simplify the simulation, the module walls were adiabatic and heat transfer was from the hot feed to the cold distillate. This simplification will not affect the comparison of the spacers since the spacers did not have contact with the top of the acrylic cell, effectively making the heat loss to the environment similar regardless of spacers used. The thermal conductivity of the membrane ($k_{membrane} = 0.06715 \text{ W/m} \cdot \text{K}$) was calculated using Eq. 1:

$$k_{membrane} = \varepsilon k_{air} + (1 - \varepsilon)k_{pvdf} \quad (1)$$

where ε is the membrane porosity, k_{pvdf} is the thermal conductivities of PVDF ($0.19 \text{ W/m} \cdot \text{K}$) and k_{air} is the thermal conductivity of air at 100 % relative humidity (0.0262 W/m.K). The feed and permeate flowed counter-currently, with each inlet flowrate set at 250 mL/min.

Figure 6.1. Schematic of the DCMD module, whereby the feed and permeate channels were of equal dimensions, with the membrane sandwiched in between and the spacer (mesh with dimension of 3 mm on each side) on the feed side. The blue arrows denote the counter-current flows.

Because different predefined mesh sizes with tetrahedral elements gave similar results, the ‘normal’ mesh (with the finest dimension being 0.412 mm and the largest dimension being 1.38 mm) was selected to shorten the computation time.

6.2.1.2. Effect of spacer material and mesh density

In order to study the effect of spacer material and spacer mesh density, a total of 9 simulations were carried out with three different spacer materials (namely, polypropylene (Pp), nickel (Ni) and copper (Cu)), each with three different mesh densities (Fig. 6.2). Specifically, the least dense spacer was such that each grid had four equal sides of 3 mm each (with a filament diameter of 0.26 mm and a thickness of 0.52 mm; Fig. 6.2a), followed by one of intermediate density with each grid that had four equal sides of 1.5 mm each (with the same filament diameter and thickness to the less dense spacer; Fig. 6.2b), and lastly the densest one was a 1 mm thick foam (i.e., sponge-like random pores; Fig. 6.2c) simulated using the porous media sub-model in Comsol. It should be noted that the least dense spacer (Fig. 6.2a) was designed to match that of the polypropylene spacer used in the experiments. The material properties such as density, thermal conductivity and heat capacity were obtained from the Comsol material library and used as is.

Figure 6.2. Spacer mesh densities investigated: (a) 3 mm mesh density, (b) 1.5 mm mesh density and (c) foam.

6.2.1.3. Effect of spacer position

To investigate whether the positioning of the spacer in the feed or permeate channel impacts the MD performance, the Ni foam (Fig. 6.2c) was simulated in the feed channel and the permeate channel separately.

6.2.2. Experimental Study

An experimental study was carried out in parallel with the simulations to evaluate the effect of spacer material and spacer mesh density on DCMD performance (i.e., flux and energy efficiency).

6.2.2.1. Experimental setup

A schematic of the experimental DCMD setup is shown in Fig. 6.3. The membrane module was made of clear acrylic (detailed specifications listed in Table 6.2) without additional thermal insulation, allowing visible light to pass through to the feed channel with minimal absorption and diffraction losses, and thereby allowing the spacers conferred with photothermal capability to convert light to heat in the feed channel. The membrane module was operated in counter-current cross-flow mode, which was similar to that of the simulation (Fig. 6.1). The circulation of the feed and distillate streams from their respective tanks was carried out using a peristaltic pump (Masterflex L/S Digital

Drive) for each. The feed tank (2-L round-bottom flask) was heated and agitated using a hot-plate stirrer (Heidolph MR Hei-Tec), and the feed was circulated at 250 mL/min through heat-resistant Masterflex Norprene tubings between the membrane module and feed tank. The distillate tank (1-L acrylic cylinder with a spout) was cooled by a recirculating chiller (Julabo ME), and the distillate was recirculated at 250 mL/min through Masterflex Tygon E-LFL tubings between the membrane module and distillate tank. The conductivity of the distillate in the distillate tank was measured at the end of every experiment using a conductivity meter (Eutech Instruments Alpha Cond 500) to ensure that the conductivity remained within 2 $\mu\text{S}/\text{cm}$ (which was the value corresponding to the DI water used). The overflow tank (300-mL beaker) was placed on a mass balance (Mettler-Toledo ME4002) for the measurement of distillate flux, which was derived from the accumulated distillate which overflowed into the overflow tank per unit time. The energy consumption (measured using a Uni-T UT230B-UK energy meter) of the hot-plate stirrer, mass and conductivity of the distillate was measured over each 3 h experiment.

Figure 6.3. Schematic of the experimental DCMD setup, consisting of (1) a feed tank (i.e., 2-L round-bottom flask) heated by a hot-plate and agitated with a magnetic stirrer, (2) three peristaltic pumps, (3) a cross-flow flat-sheet acrylic membrane module, (4) 50-W LED lamp 4 cm above the membrane surface, (5) a distillate tank (i.e., 1-L acrylic cylinder with a spout) cooled by a recirculating chiller and with a conductivity meter inserted, and (6) an overflow distillate tank (300-mL beaker) atop a mass balance.

A virgin PVDF hydrophobic flat-sheet microfiltration membrane (Durapore GVHP; detailed specifications listed in Table 6.1) with an active membrane area of

0.00371 m² (i.e., 53 mm by 70 mm) and a new spacer were used for every experiment. Membranes and spacers were not re-used to avoid fouling effects from affecting subsequent experiments.

The spacers investigated included a polypropylene (Pp) spacer (Sterlite; each grid with equal sides of 3 mm), and Nickel (Ni) and copper (Cu) foams (Latech), with detailed specifications listed in Tables 6.3, 6.4 and 6.5 respectively. The Ni and Cu foams used in this experiment had 100 - 110 pores per inch (PPI) and were structurally similar, as evident from the SEM images in Fig. 6.4. Furthermore, to harness photothermal effects to further improve the MD performance through localized heating at the feed-membrane interface, the Ni foam was coated with platinum (Pt; modification and characterization procedures is described in Section 6.2.2.2). For the effect of photothermal materials on metallic spacers, all the spacers with and without modification were tested with and without light irradiation. The light source (50-W LED) used had an illuminance of 700000 lux (i.e., 7 times that of the sun) at 4 cm from the light emitting surface (i.e., distance between the Ni foam and light source). This strong light source was used to compensate for the small area for light irradiation in the laboratory membrane module, thus lowering the relative contribution of systematic error towards the result. The spacer in the feed channel was varied to evaluate the effect of spacer type, while that in the distillate channel was consistently a polypropylene spacer (with grids of equal sides of 3 mm) to reduce the heat-transfer resistance and provide mechanical support for the membrane.

Figure 6.4. SEM images of (a) Ni foam and (b) Cu Foam

6.2.2.2. Foam modification and characterization

To coat platinum (Pt) nanosheets (NSs) onto the Ni foam, the thermal decomposition method [33] was employed. Specifically, the Ni foam (dimensions of 5.3 cm by 7 cm, and 0.001 cm thick) was first cleaned with ethanol and de-ionized (DI) water, and then dried at ambient temperature, before being immersed into a quartz boat containing 200 mg of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in 80 mL of solvent mixture (1:1 volume ratio of ethanol:2-propanol). After that, the quartz boat was placed in the furnace and the temperature was increased at a rate of $20\text{ }^\circ\text{C min}^{-1}$ to $450\text{ }^\circ\text{C}$, and held at $450\text{ }^\circ\text{C}$ for 15 min while 95% Ar:5% H_2 gas continuously flowed through. Finally, the sample was cooled to room temperature naturally followed by cleaning using DI water then drying in the vacuum oven at $60\text{ }^\circ\text{C}$ overnight.

X-ray diffraction (XRD) patterns were obtained with a powder diffractometer (Bruker D2 phaser XRD) using Cu K α radiation. A field-emission scanning electron microscope (FESEM JEOL JSM-6701F), operating at 5 kV accelerating voltage and high-vacuum (9.63×10^{-5} Pa) mode, was used to obtain high-magnification images of the spacer samples. All FESEM samples were coated with platinum to prevent electron build-up during imaging.

6.2.2.3. Infrared (IR) thermal imaging

A digital IR thermal imaging camera (Cat S60) equipped with a FLIR Lepton IR sensor, was used to take thermal maps of the metallic foam spacers investigated in this study before irradiation and after 1 minute of irradiation with a 50 W LED lamp placed 4 cm below the metallic foam spacers. The metallic foam rested on a 6 mm thick clear acrylic, which mimicked the acrylic window of the DCMD module used in the MD experiments.

6.2.2.4. Experimental protocol

The following protocol was used for each experiment. Firstly, the PVDF membrane and targeted spacers were positioned in the acrylic membrane module, and the necessary fittings secured. Secondly, 5 g/L of sodium chloride (NaCl; Merck-Millipore CAS No. 7647-14-5) and DI water were respectively circulated through the feed and distillate loops at 250 mL/min. The temperatures of the feed and distillate streams of the membrane module were set at respectively 65 and $15\text{ }^\circ\text{C}$. Thirdly, the system was given an hour to stabilize before the mass and heater energy consumption measurements were

recorded every five minutes over three hours, with the distillate recycled back to the feed tank every hour to maintain a constant feed composition.

Furthermore, for the investigation of photothermal effects, an LED lamp was used. The additional step was such that the 50-W LED lamp was switched on, and step three above was repeated.

Since the temperature and mixing rate of the hot-plate stirrer were fixed, the energy consumed by the hot-plate was representative of the amount of energy required to sustain the feed temperature at 65 °C. Therefore, the comparison of the heater energy consumption per unit volume of distillate would reflect the energy efficiency of each test:

$$\begin{aligned} &\text{Heater energy consumption per unit volume of distillate} \\ &= \frac{\text{Energy consumed over 3 h (obtained from the energy meter)}}{\text{Distillate produced over 3 h}} \quad (2) \end{aligned}$$

Every experiment was carried out twice to check for reproducibility.

6.3. Results and Discussion

6.3.1. Effect of spacer material and mesh density

Simulations were first carried out to assess the benefits of using metallic spacers in MD. Since commercially available metallic supports come in the form of different materials and mesh densities, the first set of simulations targeted at investigating the effect of spacer material and mesh density on membrane surface temperatures, which provide the driving force for the flux across the membrane. Figs. 6.5 and 6.6 present the temperature contour maps of the feed-membrane and distillate-membrane interfaces, respectively, while Fig. 6.7 the surface-averaged temperatures and vapor pressure differences ($p_h^\circ - p_c^\circ$) across the membrane.

Figure 6.5. Simulation results: temperature contour plots of the feed-membrane interface obtained from simulations. The first, second and third columns represent respectively the polypropylene, nickel and copper spacers. The top, middle and bottom rows represent respectively the spacer with 3 mm mesh, spacer with 1.5 mm mesh and the foam spacer. The feed flow is from the right to the left.

Figure 6.6. Simulation results: Temperature contour plots of the distillate-membrane interface obtained from simulations; note that the distillate side has a polypropylene spacer with 3 mm mesh. The first, second and third columns represent respectively the polypropylene, nickel and copper spacers on the feed side. The top, middle and bottom rows represent respectively the spacer with 3 mm

mesh, spacer with 1.5 mm mesh and the foam spacer on the feed side. The distillate flow is from the left to the right.

Figure 6.7. Simulation results: surface-averaged temperature values obtained from simulations at the (a) feed-membrane, and (b) distillate-membrane interfaces for the three spacer materials and three spacer densities; and (c) vapor pressure difference between the two faces of the membrane ($p_h^o - p_c^o$).

With respect to the feed-membrane interface, three observations are highlighted. Firstly, Figs. 6.5 and Fig. 6.7a indicate that the metallic spacers (i.e., Ni and Cu) conferred higher temperatures than the polypropylene one, with the Cu spacer performing slightly better than Ni due to the relatively higher thermal conductivity. Secondly, it is evident in Fig. 6.5 that the temperatures are most uniform across the membrane surface for the densest foam, which indicates the beneficial effect in terms of the even distribution of heat and thereby the driving force along the membrane surface. Thirdly, Fig. 6.7a indicates that the surface-averaged feed-membrane interface temperature decreases monotonically with spacer density for the polypropylene spacer, but non-monotonically (i.e., decreases then increases) for the other two metallic spacers. The monotonic relationship for polypropylene is because of the low thermal conductivity, which resulted in poorer heat transfer to the membrane surface as the spacer density increased. On the other hand, the non-monotonic relationship for the metallic spacer suggests an interplay

between the heat transfer rate from the bulk fluid to the feed-membrane interface and the heat transfer rate across the membrane. While the temperature was the lowest for the spacer with intermediate density (i.e., 1.5 mm mesh) because of the enhanced heat transfer across the membrane, the temperature was the highest for the dense foam because of the greater heat accumulation associated with the highest thermal conductivity. This implies that the mesh density of the metallic spacer has to be increased beyond a certain critical value to enhance the temperature at the feed-membrane interface.

Analogously, Figs. 6.6 and 6.7b display respectively the temperature contour maps and surface-averaged temperatures of the distillate-membrane interface for the different spacers (i.e., three spacer materials and three spacer densities) on the feed side. Clearly, the variation of the temperatures caused by the different spacers on the feed side is lesser but non-negligible. It can be observed from the results that (i) an increase in the thermal conductivity of the feed-side spacer increased the surface-averaged temperatures of the distillate-membrane interface (Fig. 6.7b); and (ii) an increase in spacer density decreased then increased the temperatures of the distillate-membrane interface for all three spacer materials (Fig. 6.9b).

Fig. 6.7c displays the $(p_h^\circ - p_c^\circ)$ trends, where p_h° and p_c° are the vapor pressure of water respectively on the hot feed side and cold distillate of the membrane, because the flux across the membrane in MD is driven by the vapor pressure differential between the two faces of the membrane:

$$N = K_p(p_h^\circ - p_c^\circ) \quad (3)$$

where N is the mass-transfer flux and K_p is the overall mass-transfer coefficient of water vapor through the membrane. Specifically, the vapor pressure is calculated by:

$$p^\circ = \exp\left(23.328 - \frac{3841}{T-45}\right) \quad (4)$$

where T is the surface-averaged temperature of the membrane. Accordingly, the vapor pressures across the membrane were derived using Eq. (4), and the $(p_h^\circ - p_c^\circ)$ values were calculated and compared in Fig. 6.7c. The $(p_h^\circ - p_c^\circ)$ trends in Fig. 6.7c are similar to that for the feed-membrane temperature in Fig. 6.7a, which implies that the relative fluxes in

this study can be better predicted using the feed-membrane rather than distillate-membrane temperatures.

In parallel with the simulations, experiments were carried out to compare the effect of the different spacers. Fig. 6.8 shows the distillate flux values for the three different spacer types on the feed side, namely, 3 mm polypropylene (Pp) spacer, nickel (Ni) foam and copper (Cu) foam. Although the simulations predict larger $(p_h^\circ - p_c^\circ)$ values for the Ni and Cu foams (Fig. 6.7), and thereby higher flux per Eqs. (3) and (4), experiments indicate on the contrary that the flux values were similar for all three feed-side spacers (Fig. 6.8). The negligible variation in the experimental flux is attributed to the decrease in flow velocity near the surface of the membrane when the highly dense foam was used in the feed channel, as shown by the simulated velocity profiles in Figs. 6.9a - c. More specifically, Fig. 6.9d indicates that the surface-averaged spatial flow velocity near the feed side of the membrane surface was 36 - 38% lower for the foam (Fig. 6.9 d). Since the temperature profiles obtained from the simulation accounts for this lower flow velocity near the surface of the membrane, the membrane area coverage by the spacers and the low mass transfer near the surface of the membrane which were not considered in calculating the $(p_h^\circ - p_c^\circ)$ values, are likely to be reason for the discrepancy between the simulation and experimental results. The reduced velocity would result in a decrease in the mass-transfer or mixing near the surface of the membrane, resulting in the solute concentration near the membrane surface to increase similar to any cross-flow filtration process[34]. Given that Raoult's law states:

$$p^\circ = p_{water}^\circ x_{water} \quad (5)$$

where p_{water}° is the vapor pressure of pure water and x_{water} is the mole fraction of water. The increase in solute concentration near the membrane surface would lead to a vapor pressure reduction. Hence, this along with the greater coverage of the membrane area by the dense foams in turn negated the improvements provided by the increase in ΔT across the membrane. This implies an optimal mesh density that is closely tied to the thermal conductivity of the spacer, as reflected in Fig. 6.7a.

Figure 6.8. Experimental flux magnitudes of the 3 mm mesh polypropylene spacer, Ni foam and Cu foam. Each error bar represents the span of two repeated experiments.

Figure 6.9. Simulation results: spatial flow velocity profile at the cross-section of the feed outlet and distillate inlet for (a) Pp 3 mm mesh, (b) Ni foam and (c) Cu foam; and (d) surface-averaged spatial flow velocity at the feed side of the membrane surface.

Further analysis of the heater input energy per unit volume of distillate shows that the highest magnitude was for the Pp 3 mm mesh, followed by the Ni foam and then the Cu foam (Fig. 6.10), which indicates that the Cu foam conferred the best energy efficiency. This is tied to the reduced spatial flow velocity near the feed side of the membrane surface (Figs. 6.9c - d). As the flow velocity reduced near the feed side of the membrane surface, the boundary-layer heat transfer coefficient reduced, and thereby the heat loss across the membrane cell was reduced. Together with the even distribution of heat on the feed side as well as a low thermal conductivity of the membrane, high thermal conductivity metal spacers produce a higher feed outlet temperature. This translates to a lower rate of heat loss across the membrane cell (Q) quantified by the following equation:

$$Q = mC_p(T_{in} - T_{out}) \quad (6)$$

where m is the mass flow rate, C_p is the heat capacity of water, and T_{in} and T_{out} are the average (over 1 h) temperatures at the feed inlet and outlet, respectively. This equation takes into consideration heat loss to the environment through the acrylic module without additional thermal insulation. The measured rate of heat loss is displayed in Fig. 6.11, which shows a similar trend as that in Fig. 6.10. This affirms that the superior thermal

conductivity of the Cu foam and its dense porous structure were advantageous in reducing the heat loss (Fig. 6.11) and thereby improving the energy efficiency (Fig. 6.10).

Figure 6.10. Experimental energy per unit volume distillate for the Pp 3 mm mesh, Ni foam and Cu foam. Each error bar represents the span of two repeated experiments.

Figure 6.11. Experimental rate of heat loss across the membrane cell. Each error bar represents the span of two repeated experiments.

6.3.2. Effect of metallic spacer position

The use of metallic spacers in MD was suggested by Ma et al. [27] and tested by Swaminathan et al. [28]. Specifically, when the metallic spacer was used on the distillate side of the MD module, the heat absorbed was used to preheat the feed, which thereby improved the overall energy efficiency of the MD system [28]. Here, whether the placement of the Ni foam on the feed or distillate side of the membrane makes a difference was assessed. The presence of the Ni foam on the feed side enhanced the temperature both in terms of magnitude and uniformity on the feed side only, while that on the distillate side enhanced the temperature on the distillate side only (Figs. 6.12a - d). This indicates that, because of the superior thermal conductivity, the metallic foam provided for a more evenly distributed temperature profile at the membrane surface where it was placed at. Fig. 6.13 quantifies the surface-averaged temperatures at both surfaces of the membrane and also $(p_h^\circ - p_c^\circ)$ values when the Ni foam was on the feed versus distillate side. Clearly, the presence of the foam at either side of the membrane improved the

temperature at that side due to the high thermal conductivity. In terms of the driving force (i.e., $p_h^\circ - p_c^\circ$; Fig. 6.13c), it was greater when the Ni foam was on the feed side, which would translate into a relative flux improvement of 30.7% per Eqs. 3 and 4 (assuming a constant K_p).

Figure 6.12. Simulation results: temperature contour plots of the feed-membrane interface obtained from simulations for the Ni foam on the (a) feed side, and (c) distillate side; temperature contour plots of the distillate-membrane interface obtained from simulations for the Ni foam on the (b) feed side, and (d) distillate side.

Figure 6.13. Simulation results: (a) Surface-averaged temperature of the feed-membrane interface, (b) surface-averaged temperature of the distillate-membrane interface, and (c) $(p_h^o - p_c^o)$ when the Ni foam was on the feed and distillate sides of the membrane.

Fig. 6.14a shows that the flux was slightly higher when the Ni foam was on the feed side rather than the distillate side, which agrees with the simulated $(p_h^o - p_c^o)$ results (Fig. 6.13c). Moreover, Fig. 6.14b indicates that the heater input energy per unit volume distillate was slightly greater when the Ni foam was on the distillate side, which indicates that the Ni foam was more beneficial on the feed side. The heat loss values were similar with overlapping error bars regardless of which side the Ni foam was on (Fig. 6.14c), indicating similar effectiveness. Overall, the experimental results agree with the simulation results in that the Ni foam was slightly more beneficial on the feed side rather than the distillate side.

Figure 6.14. Experimental results comparing the difference between the placement of the Ni foam on the feed versus distillate sides of the membrane: (a) distillate flux; (b) heater input energy per unit volume of distillate; and (c) rate of heat loss across the membrane cell.

6.3.3. Photothermal effect of modified metallic foams

In view of the superiority of the metallic spacers due to the higher thermal conductivity, this study targeted at further improving the energy efficiency of the MD process. Specifically, the Ni foam was conferred with photothermal properties to harness the readily available solar energy to reduce the energy requirements from external heater. Since the metallic spacers were placed in the feed channel, the photothermal conversion leads to localized heating near the membrane surface itself, which had been reported to improve energy efficiency of MD[35-37]. To this end, noble metals like platinum (Pt) have been reported to exhibit significant photothermal effects due to the marked

plasmonic response in the visible region of the electromagnetic spectrum [38]. Moreover, Pt is known to have excellent chemical stability and catalytic activity [33, 39, 40]. In this study, Pt NSs was adhered onto the Ni foam and the improvement in MD performance or lack thereof quantified experimentally.

Fig. 6.15a shows the SEM image of the highly porous network of the pristine Ni foam, while Fig. 6.15b the TEM image of the Pt NSs, which was coated onto the Ni foam via thermal decomposition. Fig. 6.15c displays the Pt-coated Ni foam, which is clearly rougher than the pristine Ni foam (Fig. 6.15a) due to the Pt deposits, with the EDX mapping further confirming that the Ni foam was uniformly coated with Pt. EDX analysis (Fig. 6.16) further revealed that the Pt loading on the Ni foam was approximately 37 wt%. The higher-magnification SEM image in Fig. 6.15d shows the sheet-like structure of the Pt deposited the Ni foam, which provides significant surface area for photothermal conversion.

Figure 6.15. (a) SEM image of Ni foam; (b) TEM image of Pt NSs; (c) SEM image of Pt NSs grown on Ni foam with inset EDX mapping images; and (d) higher-magnification SEM image to show the Pt NSs grown on Ni foam;

Figure 6.16. EDX spectrum of the Pt-coated Ni foam

The flux results in the absence and presence of visible light irradiation (i.e., 50-W LED) for the various spacers (namely, Pp 3 mm mesh spacer, Ni foam, Pt-coated Ni foam and Cu foam) on the feed side are depicted in Fig. 6.17. Regardless of spacer type, the average flux values were similar in both the absence and presence of the light source. The greater error bars for the Pt-coated Ni foam were likely because of the variations in the extents of Pt coating. As for the heater input energy per unit volume distillate (Fig. 6.18), the benefits of the Pt-Ni spacer were apparent in terms of the lowest magnitude in the presence of irradiation, and also the metallic spacers required less energy in the presence of irradiation (relative to the absence) due to the enhanced absorption of the heat from the light source. Specifically, under light irradiation, the Ni, Pt-Ni and Cu foams gave remarkable reductions in heater input energy per unit volume of distillate of respectively 14.8%, 27.6% and 21.3% compared to that of the Pp spacer. It should be noted that the Pt-Ni gave a photothermal conversion of 5.0 kW/m², which represents 18.5 W from the 50-W light source, and thereby a photothermal conversion efficiency of a mere 37%. The

photothermal conversion efficiency can be further optimized to be even more advantageous for such solar-assisted MD processes.

Figure 6.17. Experimental flux magnitudes with various spacers on the feed side (namely, Pp 3 mm mesh spacer, Ni foam, Pt-coated Ni foam and Cu foam) in the absence and presence of visible light irradiation. Each error bar represents the span of two repeated experiments.

Figure 6.18. Experimental heater input energy per unit volume distillate of the DCMD system with 3 mm mesh polypropylene spacer, Ni foam and Cu foam, with and without visible light irradiation. Each error bar represents the span of two repeated experiments.

The photothermal effects were validated using thermal images. Fig. 6.19 shows the thermal images of the Ni and Ni-Pt spacers before and after 1 minute of irradiation to elucidate the effect of irradiation. The changes in temperatures were not significant before and after irradiation for the used Ni foam (Figs. 6.19a - b), while the temperature change after irradiation was marked for the used Pt-Ni foam (Figs. 6.19c - d), with increases of up to 22.8 °C. This clearly indicates the significant photothermal effects conferred by the Pt coat.

Figure 6.19. IR thermal images of the membrane before irradiation: (a) used Ni foam, and (c) used Pt-Ni foam; and after 1 min of light irradiation: (b) used Ni foam, and (d) used Pt-Ni foam.

6.3.4. Implications and future research directions

As a limitation, this work only studied the feasibility of using metal spacers, more specifically commercially available metal foams, in the DCMD process and imbuing metal spacers with photothermal properties to carry out solar-assisted MD. However, more research needs to be carried out to further improve our understanding and discover new potential uses of metal spacers in MD, of which a few would be briefly highlighted in this section.

Firstly, the fouling characteristics and the effect of other modifications of the metal foams are not yet understood in MD. While the foulants trapped within the dense spacer is foreseeably more difficult to remove, it is possible that the trapping or

adsorption of foulants on the metal foam instead of membrane could reduce the membrane fouling propensity [37], especially for foulants that aggregates with time at elevated temperature [41]. Such foulants could bypass feed treatment using cartridge filter and result in aggregation on the surface of the membrane. If so, potentially photocatalysts can be grown on the large surface areas of the metallic foam to degrade the deposited molecular organic foulants before they form larger aggregates [42-45], which are much more difficult to be degraded via photocatalysis. Despite having limitations such as the need to use feed which are optically transparent and the variations in solar irradiation throughout the day, photocatalysis could potentially result in loosely packed foulants which would not result in drastic flux decline due to vapor pressure depression [46].

Secondly, due to the constraints of commercial availability, spacers of similar mesh density with different materials could not be procured for the experiment. Published research using polymeric spacers with similar material and different mesh densities points to the use of spacer with coarse filaments and lower mesh density for better MD performance [22, 24, 25]. However, the opposite is true if metallic spacers are used. This opens up a new potential possibility of using metallic spacers of different mesh sizes, to identify a critical metallic spacer mesh density and analyzing how this critical metallic spacer mesh density changes with thermal conductivity of the different spacer materials.

Lastly, due to the intermittent nature of solar energy source, photothermal conversion localized heating through the use of spacer materials such as Pt NSs coated nickel foam discussed in this research could only be used to reduce the heating load of the external heater during the day, instead of replacing the external heater. However, the possibility of providing localized heating via joule heating by passing electricity through the metal spacers could also be explored to provide a stable source of heating. Development of such localized heating technology can be extended to other flat-sheet MD configurations to incorporate solar heating to existing process. Furthermore, since the improvement done on spacers are independent of the technology used to heat the feed in the feed tank and membrane modifications, by coupling solar heating of the bulk feed[47] or novel heating method such as microwave heating [48] the MD system could potentially be made much more energy efficient.

6.4. Conclusions

The efficacy of metallic foams as spacers to improve DCMD performance was investigated via CFD simulations and experiments. The frequently used polypropylene spacer with each mesh dimension of 3 mm was used as a benchmark for comparison. Two metals were investigated, (namely, nickel and copper), along with three spacer densities (namely, 3 mm mesh, 1.5 mm mesh and foam). In addition, the feasibility of coating the spacers with photocatalysts (namely, platinum nanosheets (Pt NSs), which are known to exhibit excellent chemical stability and catalytic activity) to further enhance the energy efficiency through harnessing solar energy was assessed.

The following results are noteworthy. Firstly, because of higher thermal conductivity, the metallic spacers placed on the feed side of the membrane gave higher temperatures that were more uniform along the membrane surface. Secondly, whereas the surface-averaged membrane temperature for the polypropylene material decreased with spacer density, that for the metallic materials decreased then increased with spacer density. This is due to the interplay between the heat transfer rate from the bulk fluid to the feed-membrane interface and the heat transfer rate across the membrane, and implies that the mesh density of the metallic spacer has to be increased beyond a certain critical value to enhance the temperature at the feed-membrane interface. Thirdly, although the experimental distillate fluxes were similar across all spacers used in this experiment, the heater input energy per unit volume distillate was lower for the metallic foam spacers by up to 16% relative to the polypropylene spacer, due to the lower rate of heat loss associated with the lower fluid velocity within the metallic foam spacers along with the higher thermal conductivity of the metallic spacers. This allows heat to be transferred from the bulk fluid to the surface of the membrane with less heat loss in the bulk fluid. Fourthly, the placement of the Ni foam was slightly more beneficial on the feed rather than distillate side. Fifthly, relative to the polypropylene spacer, the metallic foams gave significant reductions of up to 21% in heater input energy per unit volume of distillate under irradiation due to the absorption of the heat from the light source, while the Pt-coated Ni foam gave an even more remarkable reduction of 28% due to photothermal conversion.

Overall, this study proved for the first time the practical use of metallic spacers to improve the energy efficiency of producing distillate via DCMD. The potential for

further improvements using other commercially available metallic foams remains untapped. Furthermore, since the spacer is independent of the membrane, existing membrane modification methods may instead be applied to the spacer to avoid issues with pore plugging.

Appendix

Table 6.1 summarizes the properties of the PVDF membrane used in this study, while Table 6.2 gives the specifics for the flow channel. Table 6.3 to 6.5 gives the specifications of the spacer materials used in this study, namely, the 3 mm mesh polypropylene (Pp) spacer, Ni foam and Cu foam

Table 6.1 Properties of Durapore GVHP hydrophobic PVDF membrane

Membrane	PVDF
Specification	Durapore GVHP
Thickness (μm)	125
Nominal pore diameter (μm)	0.22
LDP mean-flow pore diameter (μm)	0.2566
Porosity (dimensionless)	0.75

Table 6.2 Channel Specifications

Channel height (cold side) (m)	0.004
Channel height (hot side) (m)	0.004
Channel width (m)	0.053
Channel length (m)	0.07
Channel active membrane area (m ²)	0.00318

Table 6.3 Polypropylene Spacer Specifications

Spacer filament diameter (m)	0.00026
Spacer thickness (m)	0.00052

Spacer mesh size (m)	0.003
Spacer hydrodynamic angle (degrees)	90
Feed attack angle (degrees)	45
Spacer void fraction (dimensionless)	0.932

Table 6.4 Ni Foam Specifications

Foam thickness (m)	0.001
Pores per inch (PPI)	110
Volumetric porosity (%)	87
Volumetric density (g/cm ³)	0.42

Table 6.5 Cu Foam Specifications

Foam thickness (m)	0.001
Pores per inch (PPI)	110
Volumetric porosity (%)	87
Volumetric density (g/cm ³)	0.45

Governing equations and boundary conditions

The continuity and Navier-Stokes equations for a 3D steady-state incompressible flow used in the laminar flow stationary study are as follows:

Continuity equation

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0 \quad (\text{A1})$$

Momentum equation

$$\rho \frac{\partial u}{\partial t} = -\nabla p + \mu \nabla^2 u \quad (\text{A2})$$

The flow through the metallic foams were simulated as flow through a porous media which can be simulated using the following equations.

Momentum equation (Brinkman equations)

$$\frac{1}{\epsilon_p} \rho (u \cdot \nabla) u \frac{1}{\epsilon_p} = \nabla \cdot \left\{ -pI + \mu \frac{1}{\epsilon_p} [\nabla u + (\nabla u)^T] - \frac{2}{3} \mu \frac{1}{\epsilon_p} (\nabla \cdot u) I \right\} - \left(\frac{\mu}{\kappa} + \frac{Q_{br}}{\epsilon_p^2} \right) u \quad (\text{A3})$$

Of which, the metallic foam permeability, κ , was found to be $9.785 \times 10^{-9} \text{ m}^2$ [49]. I denotes an identity matrix.

Continuity equation

$$\nabla \cdot (\rho u) = Q_{br} \quad (\text{A4})$$

The two boundary conditions of the simulated flow system are listed as follows:

- c) $u_x, u_y, u_z = 0$ at the walls (i.e., no-slip condition)
- d) Outlet pressure is set as atmospheric

The heat transfer energy balance equations for a 3D steady-state incompressible flow used in the heat transfer study are presented as follows:

Heat transfer in fluid

$$\rho C_p u \cdot \nabla T + \nabla \cdot q = Q \quad (\text{A5})$$

$$q = -k_{water} \nabla T \quad (\text{A6})$$

Heat transfer in porous media

$$(\rho C_p)_{eff} \frac{\partial T}{\partial t} + \rho C_p u \cdot \nabla T + \nabla \cdot q = Q \quad (A7)$$

$$q = -k_{eff} \nabla T \quad (A8)$$

$$k_{eff} = \epsilon_p k_{water} + (1 - \epsilon_p) k_{metal} \quad (A9)$$

The two heat transfer boundary conditions of the simulated flow system are listed as follows:

- a) $q = 0$ at the walls (i.e., thermally insulated)
- b) Heat transfer occurs through a simulated thin layer with a thermal resistance,

$$R_{membrane} = \frac{d_{membrane}}{k_{membrane}} \quad (A10)$$

List of symbols

C_p	Fluid specific heat capacity at constant pressure (J/kg.K)
$(\rho C_p)_{eff}$	Effective volumetric heat capacity at constant pressure (J/m ³ .K)
T	Temperature (K)
P	Pressure (Pa)
u	Velocity of fluid (m/s)
$d_{membrane}$	Membrane thickness (m)
$k_{membrane}$	Thermal conductivity of membrane (W/m.K)
k_{air}	Thermal conductivity of air (W/m.K)
k_{pvdf}	Thermal conductivity of PVDF (W/m.K)
k_{eff}	Effective thermal conductivity of metallic foam (W/m.K)
k_{metal}	Thermal conductivity of metal (W/m.K)
N	Mass-transfer flux (kg/m ² .s)

p_h°	vapor pressure of water on the hot feed side of the membrane (Pa)
p_c°	vapor pressure of water on the cold distillate side of the membrane (Pa)
K_p	Overall mass-transfer coefficient of water vapor through the membrane (kg/m ² .s.kPa)
Q_{br}	Mass source/sink (kg/m ³ .s)
$R_{membrane}$	Thermal resistance of membrane (K.m ² /W)

Greek Symbols

ρ	Mass density (kg/m ³)
μ	Dynamic viscosity (kg/m·s)
ΔT	Temperature difference between membrane surface at the feed side and membrane surface at the distillate side (°C)
ε	Membrane porosity (dimensionless)
ϵ_p	Metal foam volumetric porosity (dimensionless)
κ	Metal foam permeability (m ²)

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CHAPTER 7 : CONCLUSIONS AND FUTURE PERSPECTIVES

7.1. Conclusions

The two-pronged approach to improving the MD process proved to be successful. This shows that despite being a long discovered separation technology, there are many underlying mechanistic principles to be uncovered in order to better understand the process and optimize it along the way. A deeper understanding of the MD process was developed as we researched on the proposed new improvements, allowing us to develop more improvements based on them. These results were also published to help pave way for future research along the same direction.

Improvement of the MD process can come in the form of modifications of module design and orientation, hybridizing with other processes and the modifications of membranes and spacers. All of which will be in one way or another able to alleviate the two of the primary issues faced in MD; low fluxes or output per unit energy and pore-wetting which compromises permeate quality. Furthermore, some of the proposed improvements were able to integrate sustainable energy solutions to alleviate the energy cost associated with MD. Since all three forms of improvements in the MD process are mostly independent of each other, they could potentially be worked on in parallel and combined after completion to produce additive improvements. In this thesis work, all three forms of improvement were explored, with ideas serving not only to improve the process through the use of new materials but also to gain insights on the mechanism behind how the added functionalities affect MD process.

7.1.1. Fouling and wetting

In chapter 2, our study on the effect of humic-acid fouling on membrane distillation concluded that vapor-pressure depression has a more dominant effect on the flux decline in fouling compared to the added heat- and mass-transfer resistance. This paves way to new fouling mitigation methods to promote formation of fouling layers with big pore sizes to reduce the negative impact on flux. Moving on the chapter 3, we tried to reduce oil droplet wetting in a DCMD setup treating emulsified oil in saline solution simulating oily seawater, by applying physical changes to module orientation and channel geometry. This led to findings which would prove that buoyancy of the foulant in the feed solution is the most dominant factor affecting the foulant interaction

with the membrane which would lead to fouling and/or wetting. Despite having a lesser impact on the foulant interaction with the membrane, the mixed convection flow due to the thermal and salt concentration gradient within the MD channel was found to have a significant impact on flow patterns near the membrane. Hence, simply by changing the orientation and clever design of the channel geometry, we can direct foulants away from the membrane surface and mitigate fouling and wetting. Lastly, another solution proposed for fouling mitigation was described in chapter 5, where the large surface area present in the MXene coated on the hydrophobic PVDF membrane surface was able to adsorb the BSA present in the feed without a flux decline. This idea made use of our understanding in chapter 2, by using the intercalated and uneven stacking of the MXene particles, we were able to create a coating layer that was porous enough not to create too much of a vapor-pressure depression, thus not creating a significant flux decline. Furthermore, these MXene particles significantly increased the surface area for foulants to adsorb on, preventing the membrane pores from being fouled.

7.1.2. Improving energy efficiency and sustainability

Despite being able to use low quality waste heat to produce clean water, in order to have better control over the water throughput, external heaters are often used to supplement the required heating. Hence, energy efficiency and the incorporation of sustainable energy would improve the commercial acceptability of MD as a process for water treatment as the operating cost decreases. In chapter 4, an SGMD was hybridized with a thermoelectric heat pump to demonstrate the possibility of simultaneously providing space cooling and water treatment by improving the heat pump efficiency via the hybridization. Naturally, when sustainable heat energy is required, we would think about the hot afternoon Sun. Hence, in chapter 5, MXene coated PVDF membrane was used in a lab-scale DCMD setup to make use of sustainable solar energy for localized solar-assisted heating in MD. Understanding the potential of localized photothermal heating, in chapter 6, we extended the use of photothermal materials in MD to spacers. And since we needed the photothermal material to conduct heat towards the surface of the membrane, metallic spacers with high thermal conductivity were chosen for this purpose. This gives us an opportunity to study the effect of metallic spacers in MD, with findings showing that with the right mesh density, metallic spacers itself without any

photothermal effect is able to evenly distribute heat across the feed-membrane interface and improve MD energy efficiency.

7.2. Future Perspectives

After coming up with multiple solutions to improve the MD process, it leaves combining all of these independent solutions top in the list for the future work. However, despite sounding easy, the combination of the different solution requires further research and optimization which the current thesis work paves way for. Research could aim to discuss if the combination of the solutions produce additive or synergistic, or in worst cases produce less than optimal results. For example, it might be possible that by increasing the photothermal efficiency of the materials on the metallic spacer surface, one might get a higher temperature of on the surface exposed to light but as the thermal conductivity of metal reduces with temperature, less heat might be transferred to the surface of the membrane.

Secondly, for hybridizing MD with heat pumps, larger scale system and a more efficient vapor-compression heat pump could be used to test if the feasibility scales and ease of integration. Furthermore, the possibility of treating easier to treat wastewater such as those from hand wash basin or washing machine after surfactant removal treatment, could be tested.

Thirdly, the coating of LC-NPs could be further researched upon to find other possible coating matrix which is compatible with the LC-NPs or LC-Janus NPs while being able to expose most of the ligands to absorb metal ions for extraction and recovery of toxic heavy metal and precious metal ions. The expose ligands could also potentially be modified to make different Schiff-base ligands which can form coordinate bonds with certain metal ions to create photocatalysts that can be used to speed up certain reactions to degrade organic foulants in MD.

Last but not least, the potential of metallic spacers being used with other forms of localized heating, such as Joule or induction heating, could be investigated. Where Joule heating is the generation of heat by directly passing an electrical current through a conductor, and induction heating is the generating heat from electrical current induced by means of electromagnetic induction passing through a conductor. Prior to the discovery of improved MD performance with the use of metallic support spacer in MD, the aforementioned method of feed heating was not possible without additional heat loss

to the environment. These new methods of heating would be able replace external heating of feed and could be combined with photothermal materials for solar-assisted MD. In this case, photothermal materials increasing the temperature of the metallic spacers might produce synergistic results with Joule and induction heating, since the increase in electrical resistance will increase the heat produced. Furthermore, surface modification of metallic spacer with many different photocatalytic materials to degrade organic contaminants can be tested out within the MD process.

Reaching the end of this thesis, we have proved that despite working with MD for four years, there are still more work left to be done to improve the MD process.

CHAPTER 8 : LIST OF PUBLICATIONS

1. E.H. Ang, **Y.Z. Tan**, J.W. Chew, Three-Dimensional Plasmonic Spacer Enables Highly Efficient Solar-Enhanced Membrane Distillation of Seawater, *Journal of Materials Chemistry A*, (2019), Accepted manuscript.
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