

**A Janus-type Engineered Surface Multiple-layer
Membranes for Highly Saline Water Treatment
via Membrane Distillation**

BY

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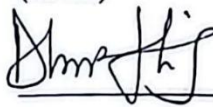

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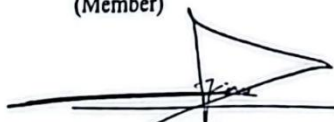

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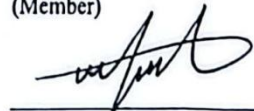



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DEDICATION

I dedicate this work to my dear country Nigeria.

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ABSTRACT

The global freshwater scarcity, exacerbated by climate change, population growth, and the increasing demand for water, has made desalination technologies significant for sustainable water treatment. Membrane distillation (MD) is an attractive technique for desalination due to its low energy consumption, especially when powered by renewable energy sources. However, the performance of membrane in MD often derives certain issues including low permeate flux, early membrane fouling, and poor membrane stability especially in the treatment of hypersaline water. This thesis addresses these challenges by fabricating Janus-type engineered surface multilayer membranes designed to enhance both the performance and durability in MD applications.

Janus membranes, characterized by having distinct hydrophobic and hydrophilic sides, offer a promising solution to the trade-offs in single-layer membranes. They can help mitigate fouling while maintaining high permeate flux, but the challenge of ensuring long-term stability remains unresolved. In this study, initially, one-sided modified Janus membranes were fabricated via electrospinning polyvinylidene fluoride (PVDF-HFP) with incorporated silica nanoparticles to create a hydrophilic gradient on one side. These membranes exhibited good initial performance, with high water flux and salt rejection, but showed a significant reduction in stability after approximately 36 hours of operation, highlighting the need for further improvements.

To enhance performance of the Janus membrane, similar structured membrane was fabricated by double sided modification with metal-organic frameworks (MOFs). Aluminum-based MOFs (MOFs-A) were embedded on the hydrophobic side, and nickel-based MOFs (MOFs-B) into the hydrophilic side. This modification improved membrane stability, extending operational life to 60 hours. Additionally, the MOFs enhanced the membranes' flux attributed to the good thermal compatibility within the membrane matrix. However, long-term testing of this membrane category revealed delamination between the hydrophobic and hydrophilic layers, which compromised the membrane's durability, rendering membrane reusability difficult.

To address the issue of this desalination, a novel interfacial engineering strategy was introduced mimicking a very similar adhesion mechanism as that in gecko-type adhesion which was found to be predominantly physical interaction without formation of covalent bonds. An optimized

composite layer of PVDF-HFP and copper oxide (CuO) nanoparticles was incorporated at the interface between the hydrophobic PVDF and hydrophilic polyetherimide (PEI) layers fabricated via phase separation and electrospinning respectively. This composite layer was designed to improve the interfacial adhesion by mimicking the strong adhesive properties found in gecko feet, which use micro- and nanoscale surface interactions strengthened by both surface polarity and polarizability to achieve better adhesion. The use of CuO nanoparticles in the composite layer significantly enhanced mechanical strength and thermal requirement especially at the hydrophilic side, thus preventing delamination and improving the long-term stability of the membranes during MD operations.

The resulting Janus membrane with the adhesion layer showed a high flux of $37.2 \text{ Kg m}^{-2} \text{ h}^{-1}$ when used in treating hypersaline brine of 70,000 ppm and $\sim 39 \text{ Kg m}^{-2} \text{ h}^{-1}$ when tested in 35,000 ppm saline with effective saline rejection of 99.98%. Structurally, the Janus membrane shows no signs of delamination even after 60 hours of MD ensuring structural integrity with reusable potentials. The findings also underscore the incorporation of hydrophobic additives in the active layer of Janus membranes considering that high performance was achieved with texturing of the PVDF surface. The findings from this research represent a significant step forward in the development of durable, high-performance Janus membranes for MD and as well, the gecko-type adhesion mechanisms from surface engineering provide a robust approach to overcoming the limitations of delamination in Janus membranes. The innovative strategies developed here offer a pathway for the next generation of Janus membranes that are both high-performing and long-lasting, addressing critical challenges in desalination and water treatment.

ABSTRACT (Arabic)

أدى النقص العالمي في المياه العذبة، الذي تفاقم بسبب تغير المناخ والنمو السكاني وتزايد الطلب على المياه، إلى جعل تقنيات

التحلية ذات أهمية كبيرة لمعالجة المياه المستدامة. يعد التقطير الغشائي (MD) تقنية جذابة لتحلية المياه نظرًا لانخفاض استهلاكها

للطاقة، خاصةً عند تشغيلها بمصادر الطاقة المتجددة. ومع ذلك، غالبًا ما ينطوي أداء الغشاء في التقطير الغشائي على مشكلات

معينة، بما في ذلك انخفاض تدفق النفاذية، والتلبد المبكر للغشاء، وضعف استقرار الغشاء، خاصةً في معالجة المياه شديدة الملوحة.

تعالج هذه الأطروحة هذه التحديات من خلال تصنيع أغشية متعددة الطبقات ذات الأسطح المهندسة من نوع جانوس، والمصممة

لتعزيز كل من الأداء والمتانة في تطبيقات التقطير الغشائي. توفر أغشية جانوس، التي تتميز بوجود جانبيين متميزين أحدهما كاره للماء والآخر محب للماء، حلاً واعدًا للمفاضلات الموجودة في الأغشية أحادية الطبقة. يمكن أن تساعد في التخفيف من التلبد مع الحفاظ على تدفق نفاذية عالٍ، ولكن التحدي المتمثل في ضمان الاستقرار على المدى الطويل لا يزال دون حل.

في هذه الدراسة، في البداية، تم تصنيع أغشية جانوس معدلة من جانب واحد عن طريق الغزل الكهربائي لبوليمر فلوريد فينيليدين (PVDF-HFP) مع دمج جزيئات السيليكا النانوية لإنشاء تدرج محب للماء على جانب واحد. أظهرت هذه الأغشية أداءً أوليًا

جيدًا، مع تدفق مياه عالٍ ورفض جيد للأملاح، ولكنها أظهرت انخفاضًا كبيرًا في الاستقرار بعد حوالي 36 ساعة من التشغيل ،

مما يسلط الضوء على الحاجة إلى مزيد من التحسينات .

لتعزيز أداء غشاء جانوس، تم تصنيع غشاء ذي بنية مماثلة عن طريق التعديل المزدوج الجانبيين باستخدام الأطر المعدنية

العضوية (MOFs). تم تضمين الأطر المعدنية العضوية القائمة على الألومنيوم (MOFs-A) على الجانب الكاره للماء، والأطر

المعدنية العضوية القائمة على النيكل (MOFs-B) في الجانب المحب للماء. أدى هذا التعديل إلى تحسين استقرار الغشاء،

وتمديد عمر التشغيل إلى 60 ساعة. بالإضافة إلى ذلك، عززت الأطر المعدنية العضوية تدفق الأغشية نظرًا للتوافق الحراري

الجيد داخل مصفوفة الغشاء. ومع ذلك، كشف الاختبار طويل الأمد لهذه الفئة من الأغشية عن حدوث انفصال بين الطبقات

الكارهة للماء والمحبة للماء، مما أدى إلى المساس بمتانة الغشاء، مما جعل إعادة استخدام الغشاء أمرًا صعبًا.

لمعالجة مشكلة التحلية هذه، تم تقديم إستراتيجية هندسة سطحية مبتكرة تحاكي آلية التصاق مماثلة جدًا لتلك الموجودة في

الالتصاق من نوع أبو بريص، والتي وجد أنها تفاعل فيزيائي في الغالب دون تكوين روابط تساهمية. تم دمج طبقة مركبة

محسنة من PVDF-HFP وجزيئات أكسيد النحاس (CuO) النانوية في الواجهة بين طبقات PVDF الكارهة للماء والبولي إيثرايميد (PEI) المحبة للماء المصنعة عن طريق فصل الطور والغزل الكهربائي على التوالي. تم تصميم هذه الطبقة المركبة

لتحسين الالتصاق بين الأسطح عن طريق محاكاة خصائص الالتصاق القوية الموجودة في أقدام أبو بريص، والتي تستخدم

تفاعلات سطحية دقيقة وناوية معززة بكل من قطبية السطح وقابليته للاستقطاب لتحقيق التصاق أفضل. أدى استخدام جزيئات

أكسيد النحاس النانوية في الطبقة المركبة إلى تعزيز القوة الميكانيكية والمتطلبات الحرارية بشكل كبير، خاصة في الجانب

المحب للماء، وبالتالي منع الانفصال وتحسين الاستقرار طويل الأمد للأغشية أثناء عمليات التقطير الغشائي .

أظهر غشاء جانوس الناتج ذو طبقة الالتصاق تدفقًا عاليًا قدره 2.37 كجم م-2 ساعة-1 عند استخدامه في معالجة المحلول

الملحي شديد الملوحة بتركيز 000,70 جزء في المليون وحوالي 39 كجم م-2 ساعة-1 عند اختباره في محلول ملحي بتركيز

000,35 جزء في المليون مع رفض فعال للملح بنسبة 98.99%. من الناحية الهيكلية، لا يظهر على غشاء جانوس أي

علامات

للانفصال حتى بعد 60 ساعة من التقطير الغشائي، مما يضمن السلامة الهيكلية مع إمكانيات إعادة الاستخدام. تسلط النتائج

الضوء أيضًا على دمج المواد المضافة الكارهة للماء في الطبقة النشطة لأغشية جانوس، نظرًا لتحقيق الأداء العالي من خلال

تشكيل سطح PVDF.

تمثل النتائج التي توصلت إليها هذه الأبحاث خطوة مهمة إلى الأمام في تطوير أغشية جانوس متينة وعالية الأداء للتقطير

الغشائي، وكذلك توفر آليات الالتصاق من نوع أبو بريص من هندسة الأسطح نهجًا قويًا للتغلب على قيود الانفصال في أغشية

جانوس. توفر الاستراتيجيات المبتكرة التي تم تطويرها هنا مسارًا للجيل التالي من أغشية جانوس التي تتميز بالأداء العالي

وطول العمر، مما يعالج التحديات الحرجة في تحلية المياه ومعالجة الم ي

CHAPTER 1

INTRODUCTION

1.1 Background

The limited availability of fresh or clean water, with only 2.5% of the Earth's water being suitable for human consumption despite covering 97% of the planet, has become a critical global concern. In response, engineered structured membranes have been developed to tackle the challenges of water scarcity by advancing water and membrane technologies that are resilient, energy-efficient, environmentally friendly, and cost-effective to manufacture [1], [2], [3]. In addition, deep subterranean water, icebergs, and glaciers constitute approximately 70% of the sources of fresh water that are now available making it challenging to access [3]. Fresh Water crisis is made even more exacerbated by environmental degradation, which also causes a decline in water quality in many parts of the world [4]. As can be seen in **Figure 1.1** Seawater desalination is a major source of freshwater production in the middle east and Arabian gulf region, where there is a severe freshwater shortage caused by limited rainfall [5][6].

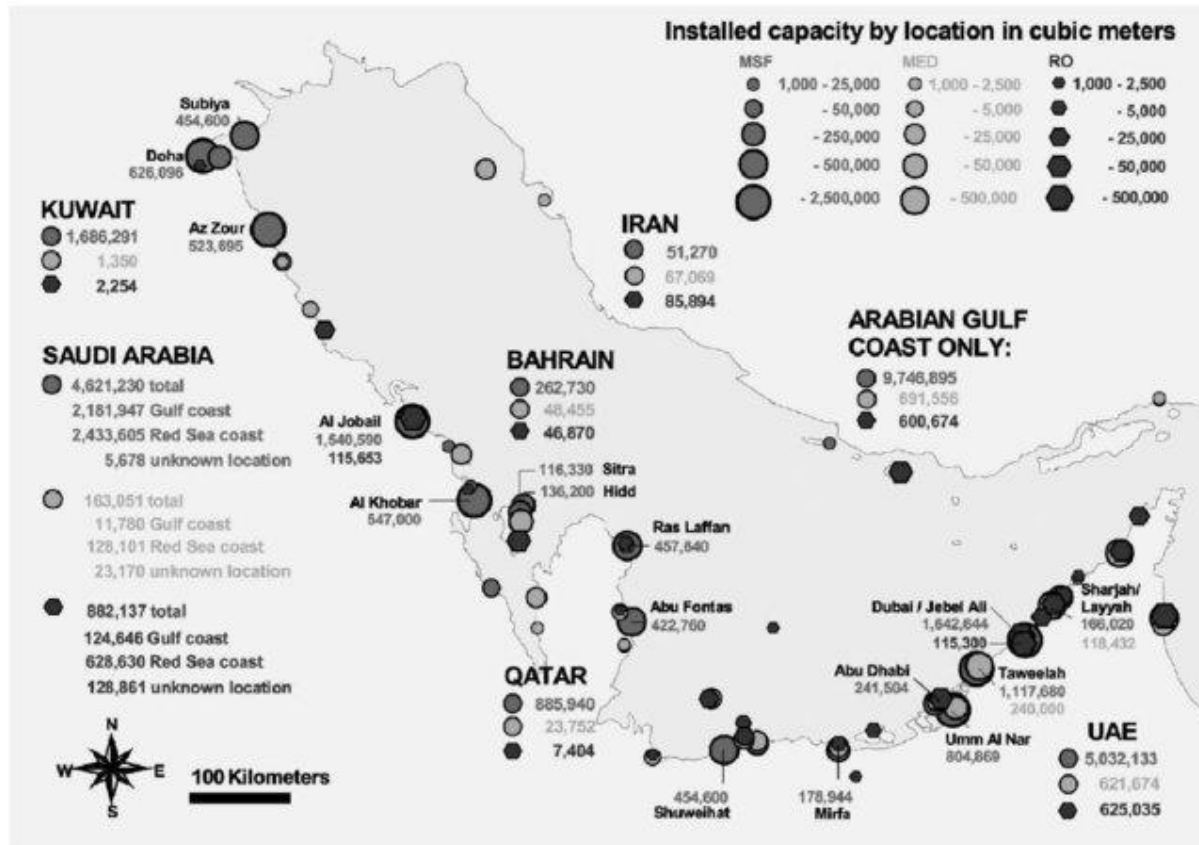


Figure 1.1: Global desalination capacity (m^3/d) and the source water type of middle east and Arabian gulf regions [7].

Membranes on the other hand are very crucial in desalination and other water treatment processes such as Reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF), thermally driven processes, new existing technologies such as electrodialysis and reverse electrodialysis and microfiltration (MF)[8]. Certain issues and limitations are reported to exist in the mentioned processes, especially when it comes to treatment of higher salinity industrial wastewater making it very difficult to meet the demand[9], [10], [11]. On the other hand, thermal techniques can be used to treat industrial wastewater, but they come with a significant energy cost that must be maintained to preserve the vapor and osmotic gradients, which are essential driving forces for successful separation. The utilization of renewable energy, such solar energy, has been rising recently to

reduce membrane separation's reliance on the burning of fossil fuels [14], [15]. In addition to membrane-based water treatment techniques, new technologies have also been developed for resource recovery and energy harvesting, such as electrodialysis (ED) and reverse electrodialysis (RED) procedures [16]. Nevertheless, the demand could not be met. In **Figure 1.2**, various desalination techniques are highlighted and grouped based on materials requirements. As can be seen, membrane-based processes outnumbered the thermal processes, a strong indication of the future trends [12].

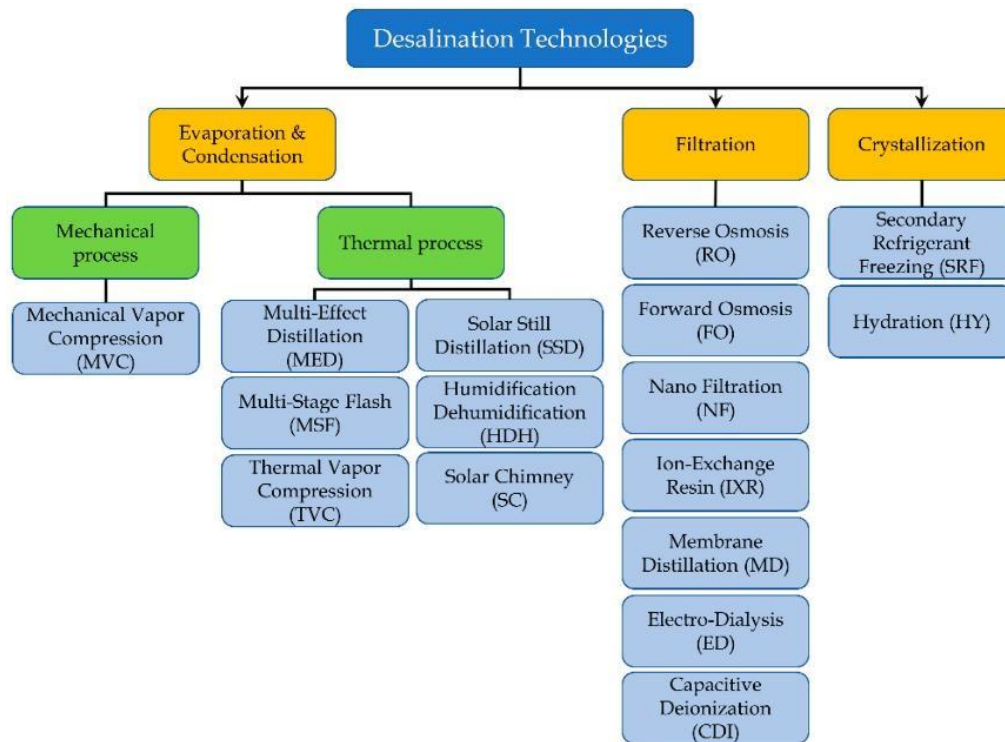


Figure 1.2: Categories of desalination technologies used for water treatment [13].

1.2 Membrane distillation

1.2.1 Principles

Basically, in MD process, a vapor pressure difference between the membrane's feed side (FS) and permeate side (PS) propels water vapor across a porous membrane in the thermally driven separation process. A temperature gradient is needed in the MD process to create a vapor on the feed side. This vapor then passes through the porous barrier to the permeate side, where it condenses to create the distillate [14]. Because the FS temperature needs are low, ranging from 40 °C to 80 °C, and the PS temperature requirement is typically 20 °C or less, the MD process has a low energy requirement. Raising the feed's temperature causes more vapor to be produced at the FS, which has a direct impact on how much vapor is carried to the PS to create the distillate [15], [16]. **Figure 1.3** displays the fundamental principles of MD process.

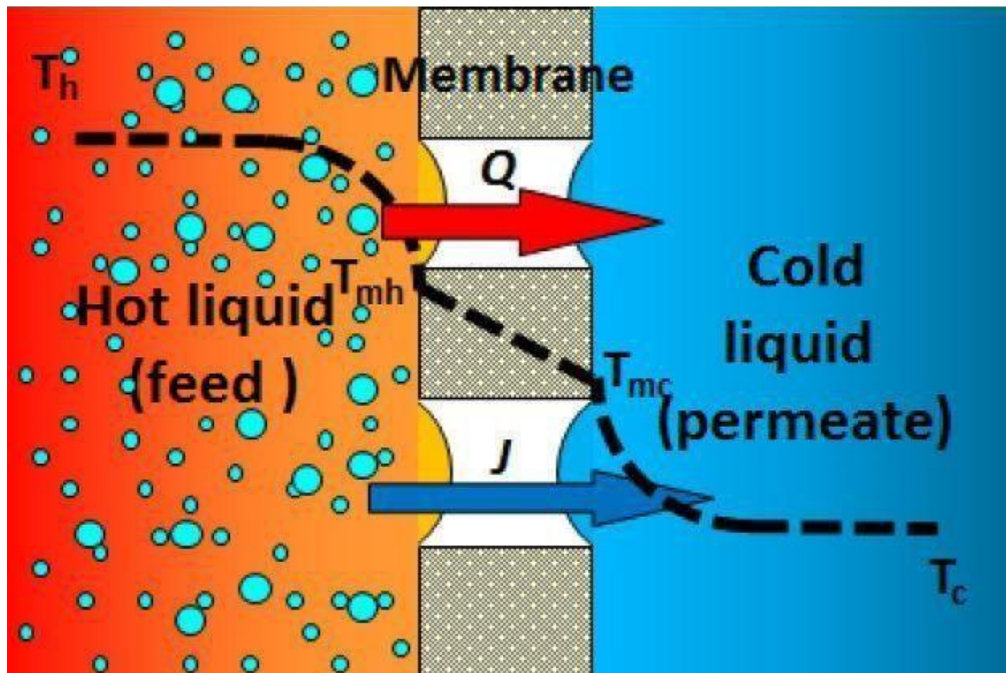


Figure 1.3: Basic principles of MD [17].

Since the MD process typically involves applying a porous barrier, which is typically a membrane, this membrane must possess certain unique qualities to guarantee increased durability and effectiveness. Nowadays, desalination, wastewater treatment, and purification which are typically applied to water bodies like seawater, municipal wastewater, or industrial wastewater are the MD applications that are given the most attention worldwide [18]. A systematic review was conducted and a schematic diagram, highlighting the requirements of membranes is illustrated in **Figure 1.4** below.

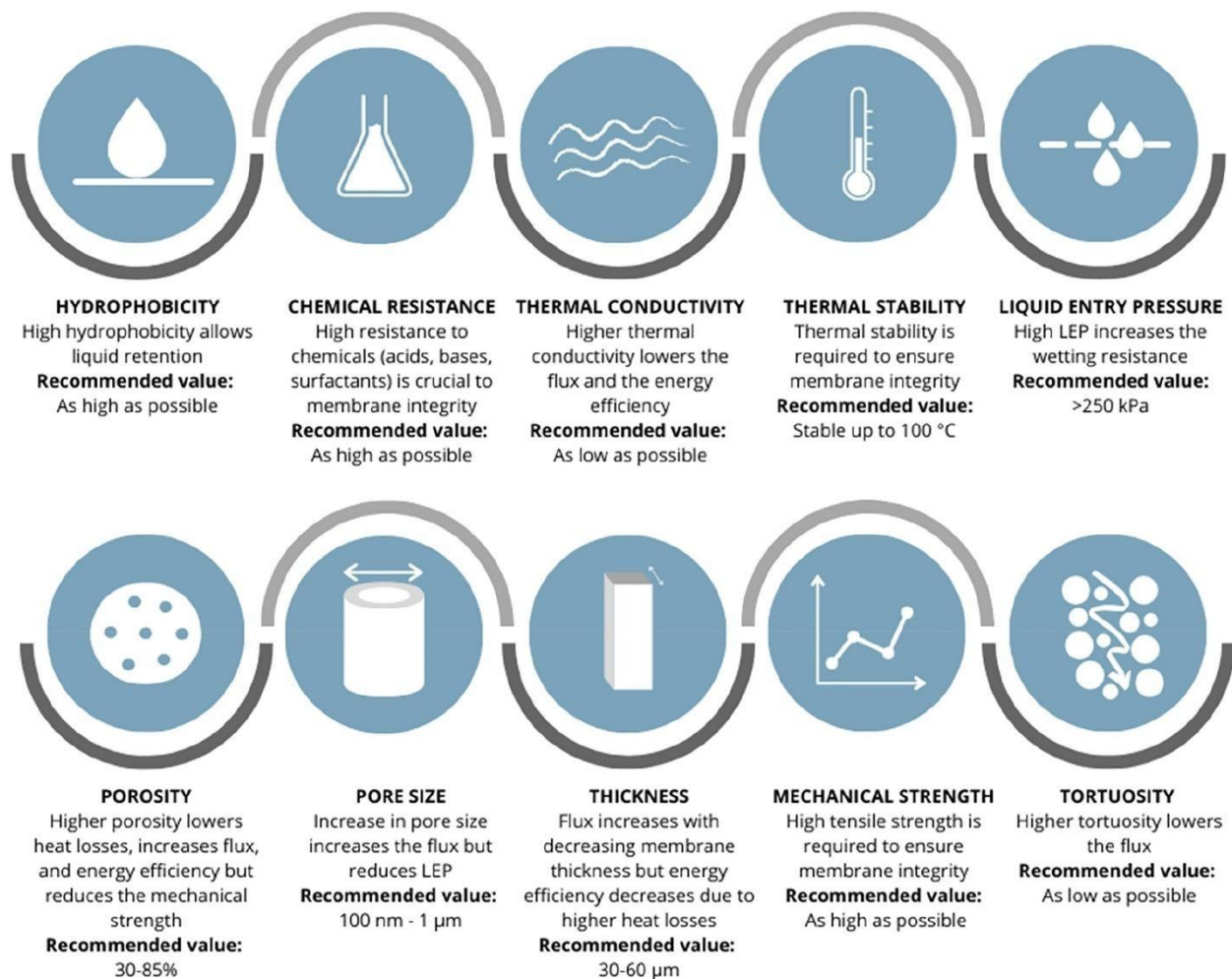


Figure 1.4: Essential parametric and properties requirements for membranes to be used in MD application [14].

1.2.2 Thermodynamic principles of MD (transport mechanisms: heat and mass transfer)

is critical for optimizing MD processes. Extensive experimental and theoretical studies, supported by advanced modeling and simulations, have highlighted significant factors influencing permeate flux and overall MD efficiency, including temperature and concentration polarization, membrane design, and module configuration [19], [20], [21], [22], [23].

In MD, mass transfer involves the convective and diffusive movement of vaporized water across the porous membrane, significantly impacting system performance [22], [24]. The two primary mechanisms molecular diffusion and Knudsen diffusion describe mass transport based on the vapor's interaction with membrane pores. Molecular diffusion dominates when pore sizes are large compared to the vapor mean free path, while Knudsen diffusion governs when pore sizes are comparable to or smaller than the mean free path [24], [25]. To integrate both effects, the Dusty Gas (DG) model was developed, extensively applied to describe mass transfer in MD processes[25] [35]. The DG model assumes that mass transfer depends primarily on the membrane's average pore size and that surface diffusion is negligible. Experimental results, however, have shown that identical membranes under different MD configurations yield varying performances, indicating that factors beyond pore size distribution significantly affect mass transfer [20], [24], [26].

According to the DG model, the total mass flux (J) across the membrane combines both viscous (J^v) and diffusive (J^d) contributions, as expressed in **Equation 1**.

$$J = J^v + J^d \dots\dots\dots 1$$

Darcy's Law relates the total flux to the vapor pressure difference (ΔP_v) and the membrane/system configuration through a coefficient B as shown in **Equation 2**.

$$J = B \cdot \Delta P_v \dots\dots\dots 2$$

As can be seen in **Equations 3 and 4**, the Knudsen number (K_n), indicating the dominant mass transfer mechanism, is defined as:

$$K_n = \frac{\lambda}{d_p} \quad \text{3}$$

$$\lambda = \frac{KT}{2\pi P\sigma} \quad \text{4}$$

where λ is the mean free path of vapor molecules, dependent on temperature (T), membrane pressure (P), collision diameter (σ), and Boltzmann constant (K) [25], [27]. Interestingly, even with consistent membrane material and pore structure, different MD configurations (e.g., DCMD vs. VMD or AGMD) exhibit distinct mass transfer behavior. This underscores the importance of module design and operational conditions in determining mass transport efficiency [28], [29].

Heat transfer

Heat transfer in MD strongly affects the vapor pressure at the feed–membrane interface, directly influencing permeate flux. Heat transport occurs via a combination of latent and sensible heat transfer mechanisms, mainly through three regions: the feed-membrane interface, the membrane bulk, and the membrane-permeate interface [24], [26] [33], [43]. As seen in **Equation 5**, total heat flux (Q) is the sum of sensible heat conduction (Q_c) and latent heat of vaporization (Q_v).

$$Q = Q_c + Q_v \quad \text{5}$$

At the feed-membrane interface, heat is transferred by convection, and the heat flux (Q_f) is related to the bulk feed temperature (T_b), membrane surface temperature (T_m), and the feed-side heat transfer coefficient (h_f) as shown in **Equation 6**.

$$Q_f = h_f(T_b - T_m) \quad \text{6}$$

Within the membrane bulk, heat transfer occurs via conduction and vapor transport, and the corresponding flux (Q_m) is defined in **Equation 7**. $Q_m = h_m(T_b - T_m) + J\Delta H_v$ 7

where ΔH_v is the latent heat of vaporization and h_m is the membrane's thermal conductivity

At the permeate-membrane interface, convective heat transfer is described in **Equation 8**. $Q_p = h_p(T_b - T_p)$ 8

where h_p is the permeate side heat transfer coefficient and T_p is the permeate side bulk temperature [30].

Different MD configurations direct contact membrane distillation (DCMD), air gap membrane distillation (AGMD), sweep gas membrane distillation (SGMD), and vacuum membrane distillation (VMD) affect both heat and mass transfer differently. In DCMD, both heat and mass transfer occur directly across the membrane, leading to significant conduction heat losses and temperature polarization. AGMD introduces an air gap, which increases thermal resistance but exacerbates temperature polarization due to a lower temperature on the permeate side. SGMD uses sweep gas to remove vapor, reducing thermal conductivity losses and improving mass transfer.

VMD uses a vacuum on the permeate side, minimizing conductive heat loss and yielding higher permeate flux [22] [31], [32], [33].

In configurations involving air gaps or vacuums (AGMD and VMD), temperature polarization effects are worsened because of the lower bulk permeate temperatures, thereby impacting vapor pressure and flux [24], [34]. Effective MD design must therefore minimize the temperature gradient between the membrane surface and the feed to improve both energy efficiency and water

recovery. A detailed schematic summarizing transport mechanisms in different MD configurations is shown in **Figure 1.5**.

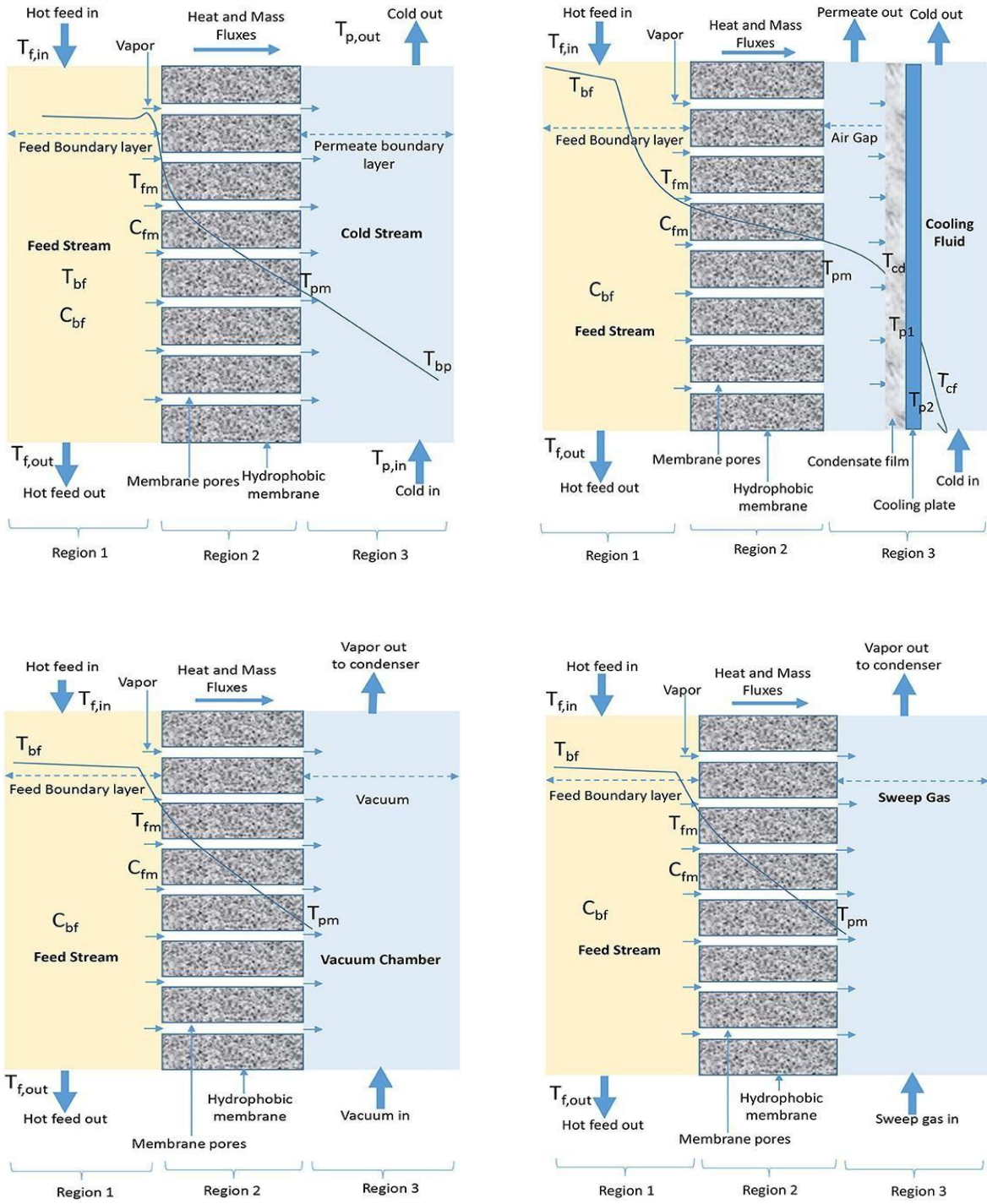


Figure 1.5: Transport mechanisms in commercial MD configurations a) DCMD b) AGMD c) VMD d) SGMD [22].

1.2.3 Operating principles in Commercial MD configurations

1.2.3.1 DCMD

Both the cold permeates, and the hot feed come into direct contact with the membrane throughout the DCMD process, with the feed side being hotter than the permeate side. A vapor pressure is created to transfer the generated vapor from the hot feed region to the cold permeate region, respectively, due to the temperature gradient created by the hot feed and cold permeate differing across the porous membrane. Three (3) regions make up the DCMD arrangement, as seen in **Figure 1.5a**, and these regions jointly decide the net mass and heat transfer effect [35][30], [36]. Condensation occurs in the permeate region as the vapor is transferred. Therefore, mass and heat transfer as well as the potential of the membrane to withstand maximum wetting and selectively allow the passage of produced vapor are all necessary for the separation efficiency of the process [37].

1.2.3.2 AGMD

Like DCMD, AGMD uses a vapor pressure gradient to transport generated water vapor to the permeate side, where it condenses. However, as seen in **Figure 1.5b**, there is a gap in the third section, which could make the temperature polarization effect from heat transfer worse. Because heat and mass transfer happened at the same time, there may be less mass transfer and a lower permeate flux as a result. In any case, AGMD is renowned for its superior thermal efficiency due to its high thermal resistance and reduced conduction of heat [31], [32], [37].

1.2.3.3 VMD

Instead of using air in the AGMD arrangement, the VMD approach uses a vacuum in the third zone. A vacuum is delivered to the cold side, as seen in **Figure 1.5c**, which strengthens vapor collecting through suction mode. Like other setups, the hot feed creates a vapor pressure that propels the water vapor through a porous hydrophobic membrane. VMD has a high permeate flux because it reduces conduction-driven heat loss when compared to other arrangements [33], [37].

1.2.3.4 SGMD

In SGMD, as seen in **Figure 1.5d**, water is used in place of an inert cold gas on the permeate side of the DCMD module, where a fixed condenser device helps condense transported vapor. The pressure gradient between the water vapor and the vapor in the cold sweep zone promotes vapor transport over the hydrophobic porous membrane, allowing condensation to occur with less thermal polarization. Due to the non-stationary nature of the gas barrier and consequently low heat loss, this structure has the important characteristics of reduced pore wetting and improved mass transfer [37].

1.3 Membrane materials

Ideal MD membranes are ensured to be hydrophobic, have high permeability, have excellent mechanical strength, low thermal conductivity, and excellent chemical and thermal stability [38]. Ceramic and polymeric membranes are suitable for MD applications; however, polymer membranes are mostly used due to their inherent hydrophobicity [39]. Ceramic membranes are known for their high resistance to harsh feed conditions but the high cost of modifying the surface has made them to be less commercially favorable. Polymeric membranes offer a cost-effective

alternative that is easily modified. The superior properties of polymers have led to a significant focus on the use of polymeric membranes for MD [40]. Hydrophobic polymers used in MD include PVDF, polyethylene (PE), polypropylene (PP), and polytetrafluoroethylene (PTFE). Many approaches have been used to improve membrane stability through the introduction of desired features to the membrane to modify the morphology and composition of with the integration of nano-scale inorganic fillers and additives into polymeric membranes such as titanium oxide, silica [41], [42], [43], [44], [45], [46].

1.4 Motivation of the study

Although single-layer and commercial hydrophobic membranes for various MD applications have been developed such as polypropylene (PP), PTFE, PE, and PVDF, these membranes not only have a high tendency to wet but also have poor permeate flow. Among various approaches, one involves creating asymmetrical wetting properties on the membrane, with one side being hydrophilic and the other side exhibiting superhydrophobic characteristics. This might be accomplished by using a variety of surface modification techniques to deposit one membrane layer on top of the other, creating what are known as Janus multiple layer membranes and these membranes possess varying wettability at both ends. However, Delamination offered a greater issue despite the numerous publications on the fabrication of Janus membranes employed in high salinity treatment which happened due to differences in the physicochemical characteristics of layers at the interface. To maximize the interaction between these layers for strong adhesion, for instance connecting the layers via covalent bonding may cause issues with heat transfer, which poses challenges to the interfacial mass transfer and results in low water flux. The solution to this problem motivates this

study, involving the development of novel techniques in the fabrication of sustainable multiple layer membranes.

1.5 Objectives

The main objectives of this thesis are as follows:

1. Fabrication of surface engineered Multiple layer membranes with improved performances involving various fabrication techniques which include non-solvent induced phase separation, electrospraying and electrospinning processes using polymeric materials. In line with surface engineering, nanofillers and other surface treatments will be employed for better compatibility and enhanced performance.
2. Characterization of the fabricated materials from various parameters to support the novelty of the fabricated membranes. These include:
 - i. Chemical and structural properties: Scanning electron microscopy (SEM) will be used in studying the surface morphology of the membranes while the crystallinity, chemical bond stretching and elemental dispersions will be studied using the x-ray diffraction (XRD), Fourier transform infra-red spectroscopy (FT-IR) and energy dispersive spectroscopy (EDS) respectively.
 - ii. Physical properties: the roughness of the membrane surface will be studied using the water contact angle (WCA) and the atomic force microscopy (AFM).
 - iii. Bulk and mechanical properties: the mechanical properties of the membranes will be studied from the liquid entry pressure (LEP) test and strain test.
 - iv. Thermal properties: the thermal stability of the membranes will be studied from the thermogravimetric analysis (TGA).

3. Assessment of WGMD performance of the fabricated membranes.

1.6 Significance of the study

The challenges stemming from the need to develop and implement integrated capacity and longterm sustainability in water and membrane technologies that are resilient, energy-efficient, environmentally friendly, and inexpensive to manufacture with increased demands of fresh water. In response to these challenges, novel surface engineered multiple layer membranes were developed with enhance performances in membrane distillation.

1.7 Thesis organization

The summary of the thesis report order is arranged into 6 chapters for easy presentation as shown below.

Chapter 1: Introduction

The worldwide freshwater dilemma is discussed in this chapter, along with membrane distillation (MD), a viable desalination technique. It describes the limits of existing membranes and talks about the fundamental characteristics needed for MD membranes. The chapter outlines the goals and importance of the work and encourages the fabrication of Janus-type engineered multilayer membranes to improve MD performance.

Chapter 2: Literature review

Here in, an in-depth literature analysis of Janus membranes for MD applications was provided, covering surface engineering approaches, fabrication processes, and application-based classification. Problems including poor long-term stability and delamination are noted. The chapter

critically evaluates the success or failure of existing designs, offering a solid basis for the ensuing experimental work.

Chapter 3: Development of one-sided modified Janus membranes

The fabrication of one-sided modified nanofibrous Janus membranes with PVDF-HFP and silica nanoparticles is covered in this chapter. Various characterization techniques were employed to study the nanofibrous membrane properties relative to the application in MD, another switchable application. In MD, however, the membrane was stable until 36 hours in WGMD which is a limitation especially considering industrial demands.

Chapter 4: Metal organic frameworks (MOFs) based electrospun nanofibrous membranes for water treatment via WGMD.

With Ni-based polyvinylidene fluoride s (MOFs-B) on the hydrophilic side and Al-based MOFs (MOFs-B) on the hydrophobic side, MOFs materials were integrated into Janus membrane's structure. The resulting Janus membranes were characterized by various performance metrics. The membrane showed excellent performance and stability even after 60 hours of WGMD analysis. However, the membrane integrity was sacrificed as some parts within the interface showed signs of delamination. Which needs further investigation.

Chapter 5: Interface engineering using Gecko-type adhesion

To solve the delamination issue, a PVDF-HFP/CuO composite interfacial layer was introduced, inspired by gecko adhesion mechanisms. This design significantly improved mechanical adhesion, preventing delamination and enhancing membrane durability. The claims made regarding the adhesion mechanism were proved by various sets of characterization metrics.

Chapter 6: Conclusion and recommendation

The final chapter summarizes the progression from basic to advanced Janus membrane designs, highlighting major achievements in stability, flux, and versatility. Recommendations for future research include exploring alternative interfacial materials, scaling up production, and extending membrane applications.

CHAPTER 2

LITERATURE REVIEW

2.1 Overview of Janus flat-sheet multiple layer membranes in hypersaline water

treatment via MD

Janus double-layered membranes are membrane categories asymmetrically designed to have different properties in both sides of the membrane. As far as MD is concerned, one side is hydrophobic[47] or omniphobic [48], [49] and the other side is hydrophilic [50], thereby generating asymmetric wetting due to adherence with water. These asymmetric water adherences of these membranes significantly mitigate the trade-off commonly made in single-layered membranes between the mechanical and mass transfer as well as that between selectivity and fouling[51], [52]. Numerous review studies were published, each addressing challenges, applications, techniques for fabricating multiple layer membranes in the water-energy nexus [53], [54], [55]. Other evaluations of the literature focused on Nano enabled membranes with a deeper understanding and attention to the state of advancements in the fabrication of membranes with superior energy harvesting and separation performance [56]. A synopsis of published research on multiple-layer Janus-type membranes spanning an 8-year period is provided in **Figure 2.1** with the x-axis representing the years and the y-axis indicating the number of publications. There was a gradual increase in Janus membrane research for MD applications from 2017 to 2021, which can be attributed to the increase interests, advancement, and developments in Janus membrane research. Innovations in Janus membrane research in various application fields other than MD in water-energy nexus is likely a reason for the dip observed in 2022 and 2024, respectively.

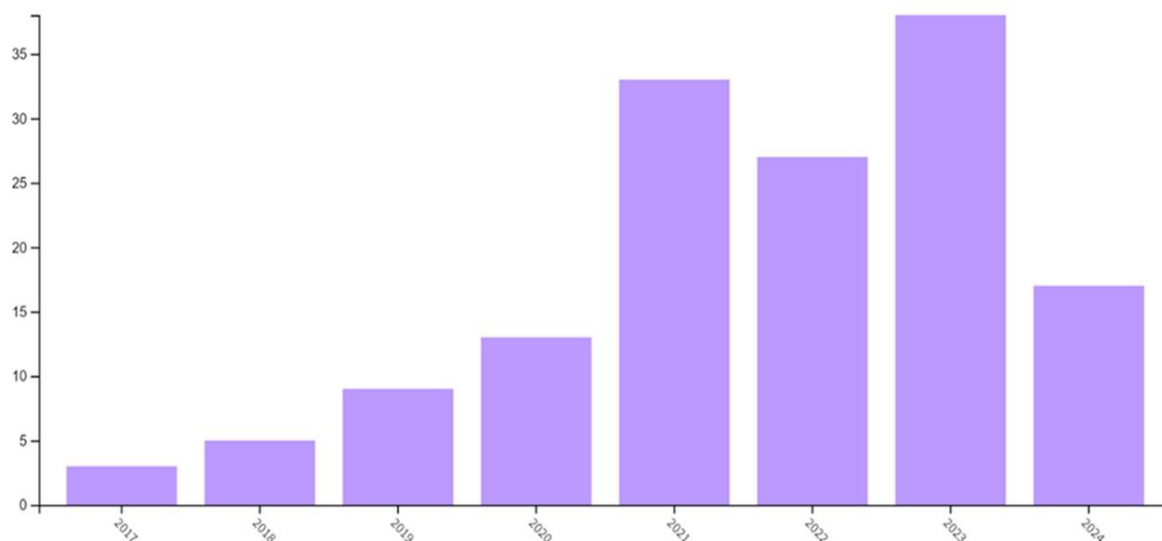


Figure 2.1: Publication counts of Janus membrane research works (Data was collected from numerous searches of Janus membrane research for Membrane distillation from Web of Science)

Conversely, **Figure 2.2** illustrated a visual analysis of maps with words in clusters associated with the fabrication and applications of multiple-layer Janus membranes in MD generated from the web of science database. Various displayed colors indicate terms and concepts associated with the advancement and application of Janus membranes in MD application while the interconnecting lines indicate the strength of relationships between the concepts. As can be seen, a large central node with the word “Janus membranes” is highly connected with various research concepts. The green clusters indicate a strong association between Janus membranes and their application areas including concepts like “water,” “nanoparticles”, “seawater desalination”, “solar desalination” and “Energy generation”. The red clusters are interconnected with concepts including “Fabrication”, “Desalination”, “oil”, “Distillation”, and “Surface modifications”, reflecting research focused on developing and enhancing Janus membranes performances for industrial applications. The blue cluster on the other hand relates the membrane performances improvements via surface

engineering modifications from the linking words “composite membranes”, “Flux”, “surface” and “resistance”.

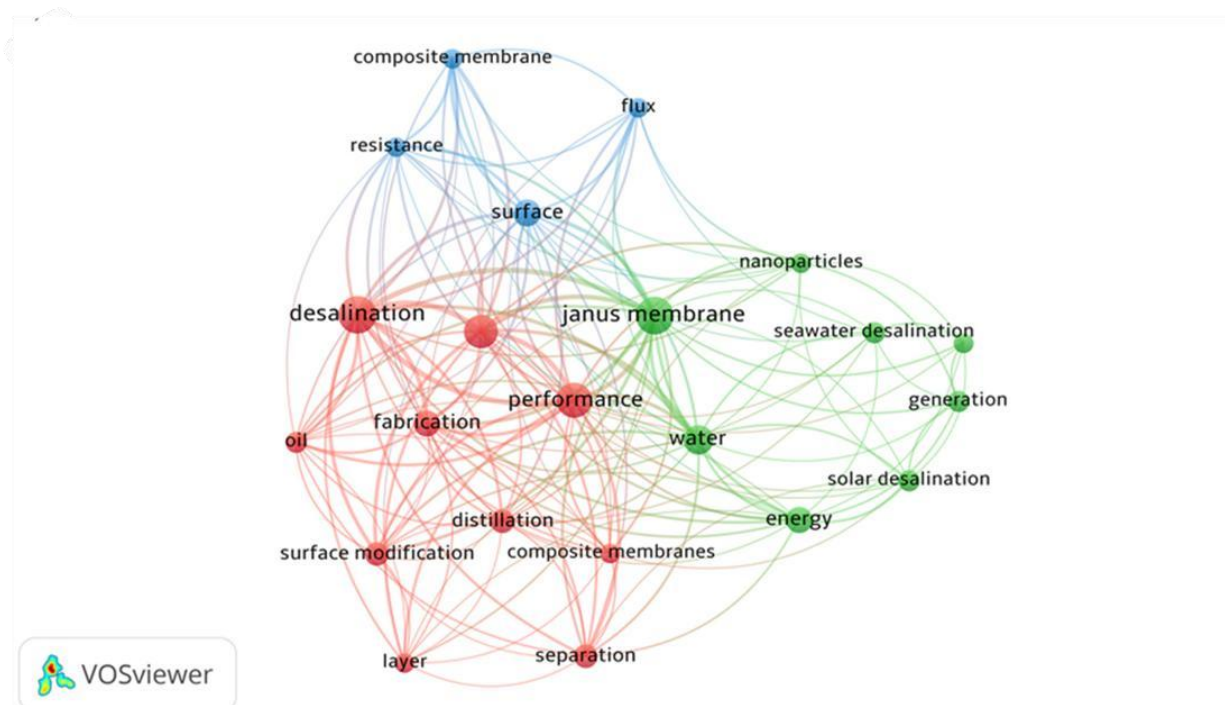


Figure 2.2: web of science generated visualization network maps with various keywords related to Janus membranes for MD applications.

2.2 Surface engineering of membranes (insights towards Janus membranes)

2.2.1 Techniques used in surface engineering

2.2.1.1 Layering

Specifically, layering is one of the easiest and most effective methods for modifying and fabricating Janus membranes via Layer-By-Layer (LBL) assembly. This technique can be applied to the deposition of nanocomposites or polymeric material in its entirety, resulting in the creation of a

surface that differs greatly from the unmodified surface in terms of both physical and chemical properties. Multi-layer films have been widely produced using LBL deposition techniques, which allow for fine control over the deposited species thickness. These films have been investigated for a variety of applications, including polymeric membranes, energy storage devices, optics, and biomedicine [57].

2.2.1.2 Coating

Coating methods have been widely explored in modification of membranes towards Janus structure design. Various techniques used in coating membrane surfaces tuned the properties of the membranes from one form to the other, rendering the creation of asymmetric features. Various cocasting and spraying techniques have been used in coating the surface of a membrane to yield multiple layers with both having asymmetrical properties. Various coating methods have been explored in literature towards modifying the surface of membranes for various applications among others which include membranes for membrane distillation [51], [53].

2.2.1.3 Functionalization

Researchers in the fields of water treatment are giving surface changes that include the use of chemicals to generate an asymmetric structure has gained a lot of attention. Several modification techniques have been employed to address feeds that are highly polluted and fouling-containing by making the surface extremely hydrophilic. For example, zwitterionic polymers, because of their high degree of hydration through electrostatic interactions, have been instrumental in addressing fouling issues in membranes. Because of this characteristic, the material can reject organic foulants very well because of the extremely dense hydrated layer that forms because of polar solvent

interactions [58]. This made these materials highly demanded in fabrications of surface engineered membranes selectively for fouling control in MD applications [59], [60], [61].

2.3 Advances in surface engineered Janus multiple layer fabrications for MD

The design of double layered membranes depends on the targeted application of the fabricated membrane. The main techniques used in fabricating the active layer, which is usually hydrophobic are phase separation and electrospinning while the hydrophilic support layer is fabricated by techniques involving deposition technique, dip-coating, spin-coating and vacuum filtration. However, in terms of fabrication, there are special categories of Janus membranes where the asymmetric wettability is created by surface modification techniques which includes the plasma treatment, layer by layer assembly modification, nanolayer modification, grafting and phototreatment modifications [62], [63].

2.3.1 Active Layer

The properties of the active layer in the fabrication of multiple-layered Janus membranes are significant as most of the performance of the membrane relies upon it. This layer must not be thermally conductive as the effect of this may lead to temperature polarization which is a great obstacle to vapor permeate flux [64], [65]. As explained by Qasim et al., several other mechanical properties and surface properties such as the hydrophobicity, surface roughness and porosity of the membranes are important, making material selection for these membranes essential and critical in membrane distillation [14]. Most common techniques used in forming this layer with desirable properties from selected materials are highlighted below.

2.3.1.1 Phase separation

For over six decades, Phase separation on has been studied in preparation of membranes and is still given much attention due to the chance of fabrication of membranes with high membrane packing density [66]. The phase separation process is a significant area of study, with extensive literature and models produced to elucidate the behaviors of polymeric materials in various phases during membrane production. In this method, the polymeric solution, also known as the dope solution, is transformed into a solid membrane by changing the dope solution's equilibrium states either by temperature [67] or by using a separate liquid phase, also known as the non-solvent [68]. NIPS technique for instance uses a solvent in which the polymer is insoluble; as a result, as previously discussed, the thermodynamics of phase-to-phase mixing caused the porous polymer membrane to precipitate. The barrier between the coagulation bath, where the membrane is mostly eluted or precipitated, and the casting solution causes this [69]. **Table 2.1** shows a literature survey of double-layered flat sheet membranes with active base layers fabricated from NIPS for salt-water treatment.

Table 2.1: Phase-inversion fabricated active layers of Janus membrane.

Active layer (hydrophobic)	Support layer (hydrophilic)	Fabrication method (active)	WCA hydrophobic	WCA hydrophilic	Water vapor flux	Salt rejection	Module type	Reference
PVDF/Hsio ₂	PDA-APTES- TEOS	NIPS	149.7	30	52.6	99.9% after 7 2 hours	DCMD	[70]
PPSU/SiNP-B	SiNP-L	NIPS/VIPS	96	82.9	42.68	94.9% after 5h	DCMD	[71]
PVDF	SiO ₂	NIPS						[72]

PVDF	PDA-PEI	NIPS	115.93	35.99	22		DCMD	[73]
PVDF/PDMS	PEI-GA	NIPS	141	8	15.7		DCMD	[74]
PVDF/PP/SMMs	PEI/DA/SMMs	NIPS	149.5	21.5	50		DCMD	[75]

2.3.1.2 Electrospinning

One of the most versatile and advanced techniques in micro and nanometer diameter non-woven fiber productions driven by electric field effect between two conducting surfaces [76]. The electrospun fibers, formed a flat layer of intrinsically interconnected fibers with high surface area and energy (for facile modifications) and high porosity, which drive them a great interest in various fields of science including filtration technology [77], textile technology [54], battery technology [78] as well as desalination in saline and wastewater treatment [79]. This advancing technology has been taken interest in desalination due to the easiness in manipulating or tuning parameters of the fibers in terms of the layer thickness, functionality, roughness and porosity which can be achieved by either varying the spinning parameters or the solution parameters [80]. Various polymeric materials were reported to yield efficient fibers in form dope formulations. One challenging feature in electrospinning of polymeric materials is the stability of the polymer in the solvent. This made it difficult to have good control of the fibers production [81], [82]. **Table 2.2** shows a list of works reporting Electro-spun fiber layer.

Table 2.2: Janus membranes with Active layers fabricated from electrospinning technique.

Active layer (hydrophobic)	Support layer (hydrophilic)	Fabrication method (active)	WCA hydrophobic	WCA hydrophilic	Water vapor flux	Salt rejection	Module type	Reference	
PVDF	Psf	Electrospinning	>140	>130	47.7	99.99	DCMD	[83]	
PVDF	PVDF@SiO ₂	Electrospinning	>130		56		DCMD	[84]	

PVDF@SiO ₂ /PDMS	PVDF@SiO ₂	electrospinning	163		27.75	99	DCMD	[85]	
PVDF-HFP	PVDF-HFP	Electrospinning	125		21	98	DCMD	[86]	
PVDF-HFP	PVA	Electrospinning	122.4		13	98.5	AGMD	[87]	
PVDF-HFP	Nylon	Electrospinning	126.3		15.5	99.3	AGMD	[87]	

2.3.1.3 Commercial membrane

Current techniques that engage membranes in water systems are being optimized to commercialize system sustainability, in which MD is among. Commercially available polymeric membranes offer greater opportunity and impacts towards this movement especially in terms of their mechanical and thermal stabilities and their socio-economic friendly properties. As cost-effective materials, commercial membranes have been used independently in desalination system in purifying higher saline water brackish water and seawater. **Table 2.3** highlighted a brief review of Janus membrane with modified commercial substrates.

Table 2.3: Janus membranes with modified commercial membrane as active layers.

Active layer (hydrophobic)	Support layer (hydrophilic)	Modification technique	WCA of hydrophobic layer (°)	WCA of hydrophilic layer (°)	Water vapor flux	Salt rejection	Module type	Janus membrane type	Referee
TC-PVDF/F-Al ₂ O ₃	PVA/Al ₂ O ₃	Sequential electrospinning	159.3	43.7	9.89	100	DCMD	PSH-JM	[88]
C-PVDF/PDMS	Mxene	Vacuum Filtration	133.0	30.2	<10	-	DCMD	PSH-JM	[89]
C-PVDF	PDA/PEI-Si	Floating coating	120	<20	19.38		DCMD	PSH-JM	[90]
C-PTFE	PDA	Coating	134	59	40.22	99.9	VMD	PSH-JM	[91]
C-PVDF	PVA/Cu-BTC MOF	Vacuum Filtration	131.9	27.4	12.30		DCMD	FSH-JM	[92]
C-PVDF	PDA/PEI-CNT	Vacuum Filtration	135	22.4	17.487		DCMD	FSH-JM	[93]
C-PVDF	Ag/PDA	In-situ co-deposition	123.5	34.0	<20	100	DCMD	FSH-JM	[94]

C-PTFE	Hydrogel (PVA-TACNC)	In-situ coating	136.6	<40	20.83	100	DCMD	FSH-JM	[95]
C-PTFE/PP	PDA	Immersion coating	145.3	30.4	16.8	-	DCMD	FSH-JM	[96]

2.3.2 Support layer

In these membranes, the hydrophilic support layer is often applied on top of the hydrophobic omniphobic membrane. The hydrophilic layer of the asymmetric Janus membranes has been created using a variety of co-casting and surface modification processes. According to numerous studies (Table 3), the support layer can be oriented toward the feed side or the permeate side. In each kind of application, certain elements like the layer's thickness and material choices must be considered. Here, several methods for creating the top hydrophilic layer are described.

2.3.2.1 Co-casting phase inversion coating

Phase inversion coating is one of the easiest ways to put a hydrophilic layer on a hydrophobic substrate. Several characteristics are considered, such as the type of hydrophobic substrate, solution thermodynamics, and material selection. Using a nano-casting coating, Yang et al. demonstrated a controlled asymmetrical wetting double layered membrane with good performance. In this study, a prepared PDMS membrane was coated with a silica-modified PVDF/PEI dope solution. The in-situ development of silica changes increased the support layer's hydrophilicity [63]. A new method for a higher flux PVDF/PVA Janus membrane using simultaneous casting and co-casting was described by Liu et al. The solvent replacement at the interface was the driving force for the adhesion between these layers [97]. Of significantly improved MD performance [98].

2.3.2.2 Coating by electrospun fibers deposition

The development of electrospinning technology has simplified the process of applying fibric materials to a surface, as previously discussed in this article. By altering the electrospinning conditions or the solution, the fibers' diameter can be readily adjusted to regulate their porosity [99]. This coating method involves spinning the fibers over a substrate, typically a flat sheet of polymeric material, that is fastened to the collecting drum. This technique produces a membrane with asymmetrical wetting and is simple and sequential. Despite the formation of interfaces, specific procedures are performed on the membrane to prevent delamination of the layers. These could involve adding nanomaterials as composites or functionalizing inorganic materials to create the spinning dope solution [100].

2.3.2.3 Vacuum filtration

Vacuum filtration is a versatile and facile method used in coating a hydrophobic or ominphobic layer with a hydrophilic one, creating asymmetric wettability in a Janus membrane. Usually, a modified dope solution is vacuum filtrated on top of a microporous flat sheet membrane, forming a coated hydrophilic layer. This method is also a sequential fabrication method, with only one side modification, leading to the formation of Janus membrane [101]. However, numerous factors were reported to be limitation to this process due to an easy detachment of the filtered layer, making the Janus membrane susceptible to delamination. This is because the adhesion is weaker due to the weak contact of the inorganic composites that were deposited, which have low surface energies. The pore size of the hydrophobic underneath membrane and the size and dispersion of the nanoparticle in the filtration layer are two factors that affect the stability of the coated layer,

according to most research on this type of simple fabrication method. These factors together affect the surface energy and, consequently, the overall separation efficiency [102].

2.3.2.4 Spray coating

Another successive technique for creating Janus membranes with asymmetric wettability is spray coating. Sprayed membranes have been shown to be good members for MD, particularly when the sprayed layer creates an interconnected pore with the active layer, producing higher flux and superior fouling characteristics. Sequential engineering in sprayed fibers involves single-sided deposition of hydrophilic or hydrophobic layer of inorganic nanomaterials like ZnO [103], SiO₂ [104], or CNTs [105], polymeric materials like PVA [106], PDMS [107] or composites. The substrate is often electrospun nanofibers or a flat sheet membrane, and the modification is typically one-sided. The coating solution will be evenly distributed in tiny droplets in this manner, creating a layer. While the composition of the sprayed solution is important, the centrifugal and electrostatic spraying forces have an impact on the deposited layer. Other factors include the spray coating cycle, coating time, and pressure. One benefit of this method is that it is simple to replace the layers by spraying the solution on the substrate a second time after they have worn out [108].

2.3.2.5 Asymmetric modification

Another simple and universal way to create asymmetric wetting between two Janus membrane sides is the asymmetric method, which involves applying a hydrophilic substance on top of a hydrophobic or omniphobic one. Song et al. reported using NIPS to fabricate an asymmetric Janus membrane by direct casting on polyester non-woven fabric. A dope solution of PVDF/DA/PEI was cast onto a polyester substrate in this innovative design, and it was then transferred into a

coagulation bath containing Tris/CuSO₄/H₂O₂, where PDA/PEI gradually migrated to one side to form a hydrophilic compact layer. This asymmetric production technique [109].

2.4 Janus membranes in MD applications

According to MD applications, constructed multiple layer Janus membranes can be classified as either permeate-side hydrophilic Janus membranes (PSH-JM) or feed-side hydrophilic Janus membranes (FSH-JM), where the support layer becomes the hydrophilic end, and the hydrophobic end is the active layer. Both single-sided and double-sided modifications may be used in the most widely developed PSH-JM and FSH-JM (**Figure 2.3**). The support layer of PSH-JM faces the permeate side, whereas the active layer faces the feed where the separation occurs. By drawing vapor and promoting faster condensation, the hydrophilic support layer effectively increases mass transfer across the membrane. The support layer of the FSH-JM is designed to come into touch with the feed stream to combat and repel foulants that could impair the base membrane's functionality. This allows for effective mass transfer by creating a vapor gradient across the base from the hot feed.

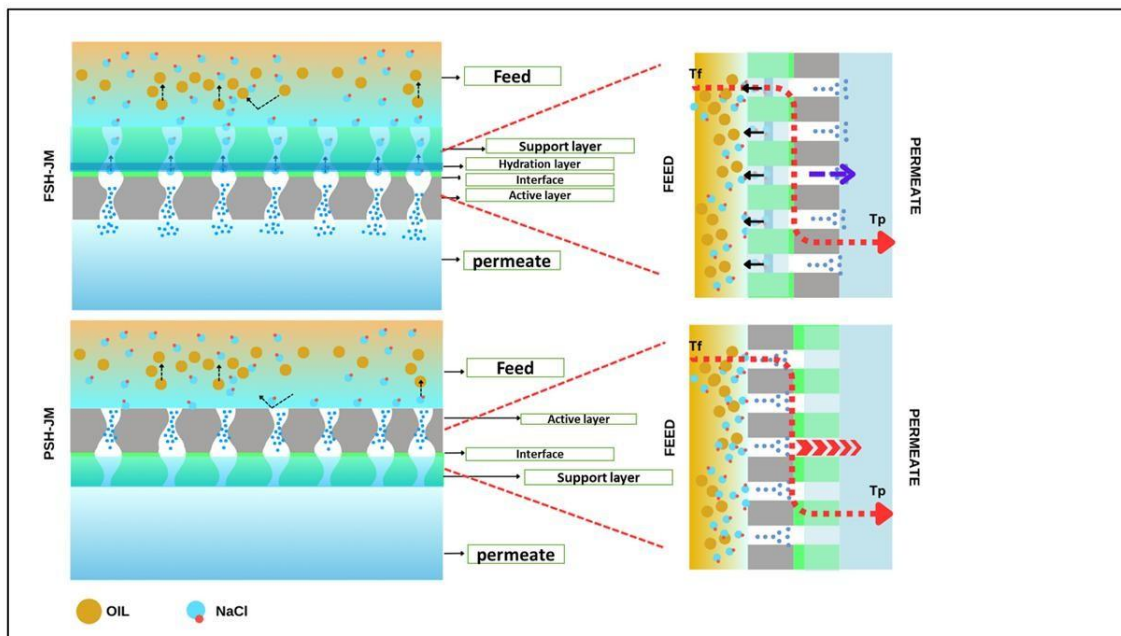


Figure 2.3: Classification of Janus Membranes based on MD applications [55].

2.5.1 PSH-JM in MD applications

These are the most fabricated double layered membranes used in MD where the active layer, which is mostly hydrophobic or omniphobic, is fixed as a substrate and the hydrophilic support is coated on top (**Figure 2.3**). Fabrication of these membranes' category is usually facile, fast and easy going with clear and straight steps [53]. Inspired by the lotus leaf's structure, a couple of research works were executed, one among which reported a Janus membrane with superior performance in high saline water treatment with a flux of $25 \text{ Lm}^{-2}\text{h}^{-1}$. In this work, the technique of electrospinning and electro-spraying were used in fabricating the superwetable double layer membrane with high fouling resistance and durability. The asymmetrically superwetable Janus skin layer of the composite membrane exhibits underwater superoleophobicity and in-air super hydrophobicity, respectively. This was accomplished by merely adjusting the concentration of the electro-spraying solution containing hydrophilic or hydrophobic silica nanoparticles (SiO_2 NPs, F- SiO_2 NPs) [110].

This research work also portrayed the significance of nanoparticles in membrane distillation technology. Similar work driven by motivation behind hydrophilic nanocomposites, Minyuan et al [111] reported a Janus membrane with functionalized MWCNTs with no compromise on the flux as reported by many works. One interesting aspect of this work showed a slight reduction in the pore sizes of the modified Janus membrane with a corresponding increase in the flux. However, this can be explained by the high-water permeability and the thermal conductivity of MWCNTs as suggested by the mass-heat transfer explanations. The high antifouling activity of this membrane is a large mark that nanoparticles modified Janus membranes are promising solutions for newgeneration membrane technology.

2.5.2 FSH-JM in MD applications

It emerged that Janus membranes might be important in MD applications that treat municipal and industrial wastewater containing higher levels of low-surface energy surfactants and foulants. MD systems with surfactant-induced feeds and oily streams can easily foul the hydrophobic side of the Janus membrane. As a result, the configuration is changed so that the hydrophilic side faces the feed, and the other side faces the permeate (**Figure 2.3**). In anti-wetting and anti-oil-fouling applications, the contact end is fabricated and modified to super hydrophilic property with a near 0° WCA. A desirable and recommended range has been specified elsewhere in the literature because the hydrophobic layer for MD applications needs to be as thick as it can tolerate the feed pressure while remaining as thin as possible to avoid mass transfer resistance. Still up for debate, though, was the necessary hydrophilic layer thickness for this application. On a PVDF substrate less than 50 nm thick, Chen et al. developed a dense, ultrathin multilayer hydrophilic coating that formed a Janus composite membrane with exceptional anti-wetting properties. This method

involved coating polyionic polymers (PSS and PEI) over an exposed side of an aluminum foilsealed PVDF substrate using the LBL technique. The LBL approach begins by PEI layering to create a reactive interface, which can facilitate the binding of subsequent species. The PEI was then coated multiple times with a solution of PSS yielding various Janus membranes with similar configuration but different hydrophilic coated layers which depends on the number of nanolayers coated per deposition. The prepared Janus membrane was then crosslinked by GA treatment to avoid sacrificial performance compromises from swelled hydrophilic layer [112].

CHAPTER 3

DEVELOPMENT OF HYDROPHILICITY GRADIENT IN A JANUS NANOFIBROUS DOUBLE LAYER MEMBRANE WITH SWITCHABLE PROPERTIES

3.1 Experimental sections

3.1.1 Materials

Polyvinylidene-co-hexafluoropropylene (PVDF-HFP, average $M_w \sim 400,000$), acetone, N, Ndimethylformamide (DMF), sodium chloride (NaCl), ethanol, hydrochloric acid (HCl) and sodium hydroxide (NaOH). It is worth noting that all chemicals were purchased from Sigma Aldrich and were used without pretreatment or adjusting their concentration. The Deionized (DI) water used throughout the research was obtained on a laboratory scale Millipore system (Milli-Q Academic).

3.1.2 Silicate bagasse ash synthesis

Silica nanoparticles were prepared from bagasse waste according to sol-gel procedures explained elsewhere in the literature [113]. In brief, bagasse waste was collected, washed and dried. 100 g of washed bagasse waste was then pre-treated by calcination up to 650 °C for a few hours. The calcined bagasse ash was then leached with 1M HCl with constant stirring at 25 °C for 2 hours. The leached ash was then filtered and washed thoroughly with pH adjusted to neutrality and oven-dried for 7 hours at 100 °C. To the washed ash residue, 1M NaOH was added with constant stirring at 100 °C for an hour. The mixture was filtered and titrated with 1M HCl to until the formation of an aqua gel. The aqua gel formed was aged 24 hours and washed thoroughly to a neutral pH which was then dried.

3.2 Nanofibrous membrane fabrication

A 5.4g of PVDF-HFP polymer was weighed and added to a 50:50 mixture solution of DMF and acetone, making a 15 wt.% electrospinning dope solution of the polymer (The ratios the solvent is maintained in all dope solutions as 50:50 without any alteration). Various other electrospinning solutions were prepared with 13 wt.% of PVDF-HFP in similar solvent mixtures with various concentrations of the synthesized silica (0.125, 0.25 and 0.5 wt.%) respectively. The prepared solutions modified with silica nanoparticles were kept for some time to let larger particles sediment which might possibly be obstruction to the fiber collections. Firstly, a single layer P0 membrane was prepared by electrospinning of 15 wt.% of PVDF-HFP solution. In doing this, the electrospinning dope solution was loaded into a 10 mL syringe and fixed on the spinneret with a tip-to-collector distance of 16 cm. the feeding rate was set at 2.6 mL/h, at high power voltage of 16.0 kV and a spinneret width of 70 mm, a uniform fibers were deposited and collected on an aluminum foil which was placed on the collection drum. Via layer-by-layer deposition method, Janus membranes P1, P2 and P3 were fabricated. In doing this the top layer was prepared similarly to M0 just that the thickness of the membranes was not the same. to create an asymmetric wettability, 10 mL solutions of each of the silica modified dope solutions were electrospun on the top layer with similar electrospinning conditions except for the electrospinning potential which was adjusted to a value of 17.5 kV. The final membranes were iron-pressed and dried at 60 °C for 24 hours to eradicate solvents. A summary of the membrane fabrication details was schematically displayed in **Figure 3.1**. In **Table 3.1**, a summary of the electrospinning dope solutions of respective membranes is illustrated.

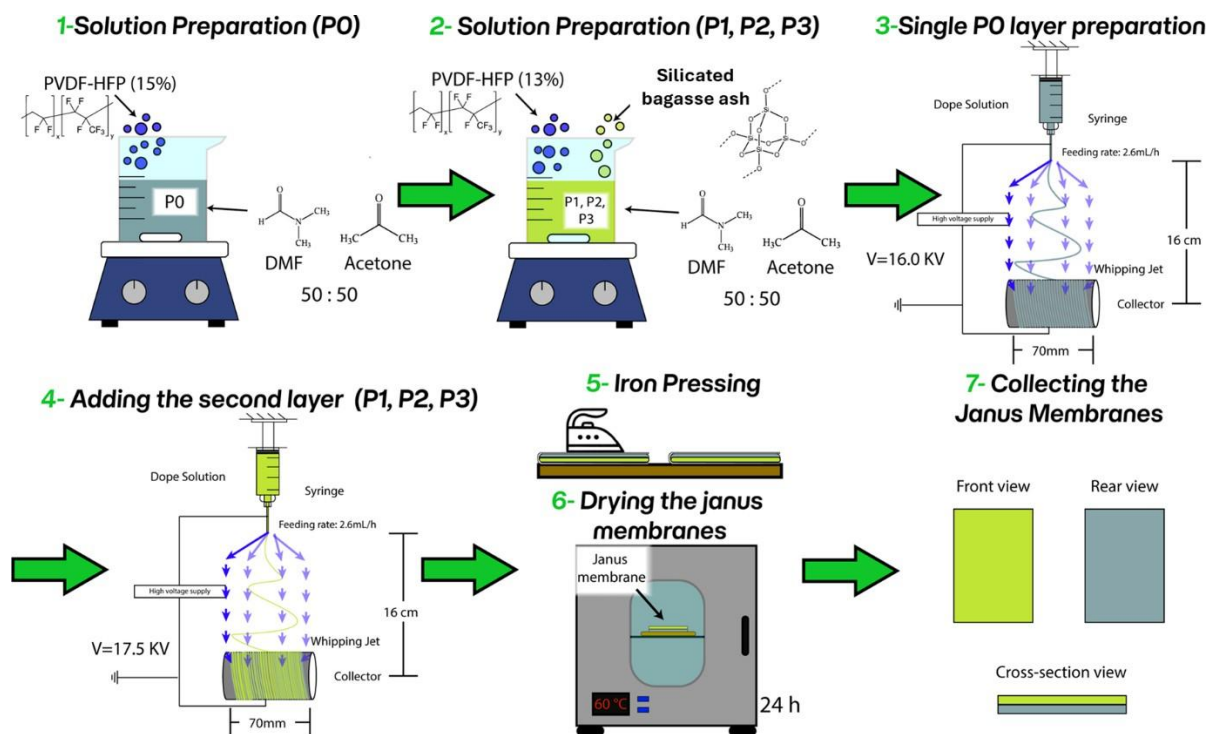


Figure 3.1: Step-by-step schematic illustration of nanofibrous Janus membranes fabrication.

Table 3.1: Compositions of pristine membrane P0 and Janus membranes P1, P2 and P3.

Membrane	Hydrophobic layer		Hydrophilic layer	
	PVDF-HFP (wt.%)	PVDF-HFP (wt.%)	Silicate bagasse ash (wt.%)	
P0	15	-	-	
P1	15	13	0.125	
P2	15	13	0.250	
P3	15	13	0.500	

3.3 Nanofibrous Janus membrane characterizations

Scanning electron microscopy (SEM, JEOL JSM-6610LV) was used to analyze the morphology of all nanofibrous membranes at a 20 kV accelerating voltage. Using a sputter coater (DII29030SCTR) with net coating thickness control, the membranes were coated with gold for 30 seconds prior to imaging which were taken at magnification of 10 μm . Using energy dispersive spectroscopy (EDX), elemental footprints were identified by examining the intensity of the distinctive X-rays that each element emitted. Atomic force microscopy (AFM) in tapping mode was used to examine surface roughness at ambient temperature. Specialized software was used to assess the average surface roughness (R_a). Within the range of 500 cm^{-1} to 4000 cm^{-1} , attenuated total reflectance Fourier transform infrared Spectroscopy (ATR-FTIR, Bruker INVENIO series) was used in analyzing the surface chemistry of the nanofibrous membranes. Thermogravimetric analysis (TGA) was carried out at heating at a rate of 10 $^{\circ}\text{C}$ per minute. The thermal sensitivity fabricated nanofibrous membranes were examined at temperatures ranging from 10 $^{\circ}\text{C}$ to 800 $^{\circ}\text{C}$.

The surface wettability of the fabricated membranes was measured via the water contact angle (WCA) measurement with a goniometer. 0.2 to 0.4 μL of water were dropped onto the membrane surface via the sessile drop method, and multiple measurements were taken to obtain an accurate average value. The pore size distribution, including mean and maximum pore sizes, was analyzed using a porometer (3Gzh, Quantachrome instrument, USA) in both dry and wet modes. The liquid penetration point of the membranes was ascertained using a liquid entry pressure (LEP) measurement apparatus on a laboratory scale. The endurance of the barrier against liquid incursion was evaluated by taking average of various readings. The thickness of the nanofibrous membranes was measured using a Litematic device (A LITEMATIC VL-50A). Measurements were taken at least 10 times along a 7 cm membrane length, and the average value was recorded.

3.4 WGMD performance evaluation

Water gap membrane distillation (WGMD) was used to assess the saline wastewater separation efficiency of the fabricated membranes with an effective surface area of $7.32 \times 10^{-4} \text{ m}^2$. The procedure used a bypassed water-filled air gap MD module. 350 g of NaCl were dissolved in 10 L of deionized (DI) water to obtain a saline feed solution with a concentration of 35,000 ppm, simulating seawater conditions. After that, the prepared feed was transferred to a water heater tank, where it was maintained at 70°C. The generated vapor passed to the permeate side, which was filled with DI water for collection, via a fixed membrane set on a rubber bed. The permeate temperature was controlled by a water chiller, which kept it at 20°C. Utilizing conveying hoses, flow meters were attached to the heater, chiller, and module to regulate the water circulation on the feed and permeate sides. The relationship in **equation 9** was used to calculate vapor flux. The weight of the condensed permeate was continually measured and recorded in kilograms at oneminute intervals using a high-precision electronic weighing balance connected to a recorder and software. **Equation 10** shows how the salt concentration (ppm) measured by a conductivity meter was used to determine the saline rejection.

$$J = \frac{m}{A \cdot t} \quad (\text{kg/m}^2\text{h}) \dots\dots\dots 9$$

$$S.R (\%) = c \frac{C_f - C_p}{C_f} \times 100 \dots\dots\dots 10$$

Where the permeate flux J was measured in $\text{Kgm}^{-2}\text{h}^{-1}$, m is the mass of permeate collected measured in Kg, A is the effective membrane area expressed in m^2 , and t is the testing duration expressed in hours (h). S.R is expressed in % and indicates the saline rejection, C_f and C_p indicates

concentration of the feed and permeate respectively. A schematic diagram of the WGMD is illustrated in **Figure 3.2**.

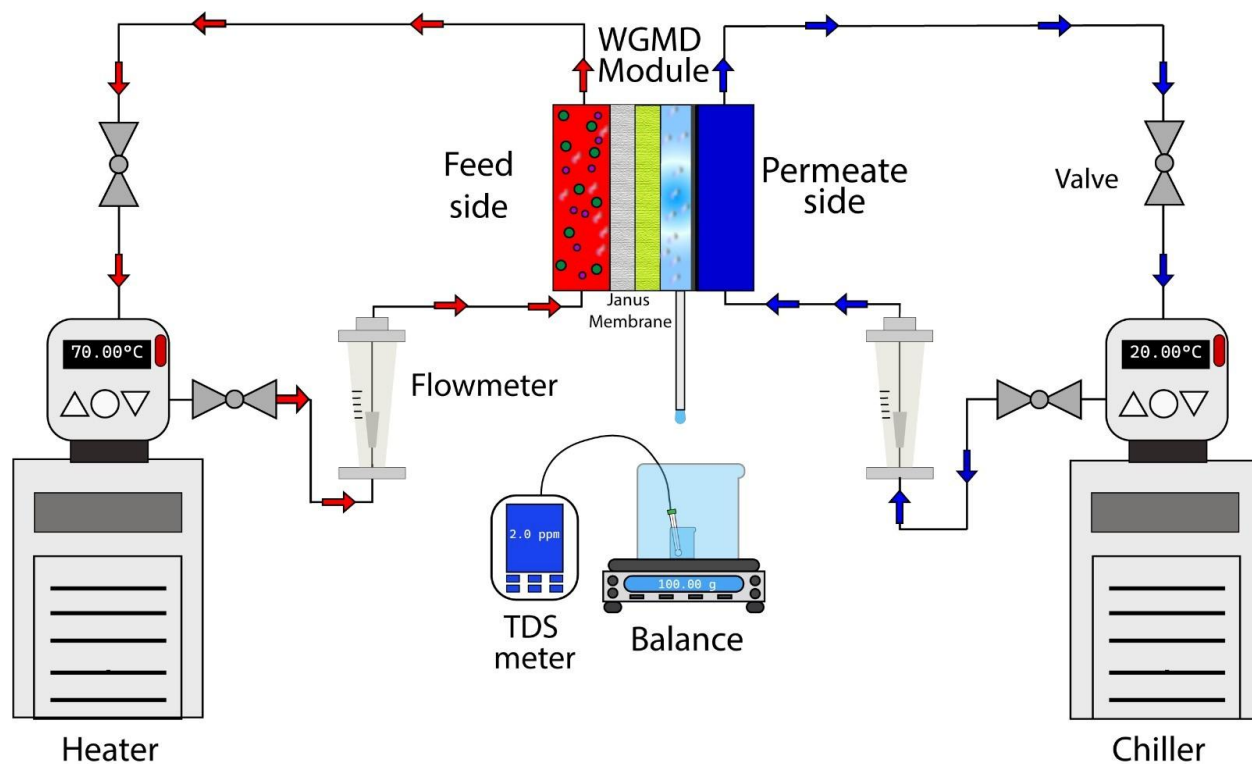


Figure 3.2: Schematic diagram of laboratory membrane distillation unit used in WGMD performance evaluation.

3.5 Results and discussions

3.5.1 Silicate bagasse ash characterization

The morphology and chemistry of the prepared nano silica prepared from the bagasse ash were studied by the SEM with elemental composition as shown in **Figure 3.3**. As can be seen in **Figure 3.3a**, various size distributions were obtained of silica nanoparticles with irregularities in accordance with the bagasse ash size which are obtained as explained elsewhere in the literature

[113]. The elemental compositions including the mapping to confirm the presence of silica nanoparticles are shown in **Figure 3.3b** and **Figure 3.3c**.

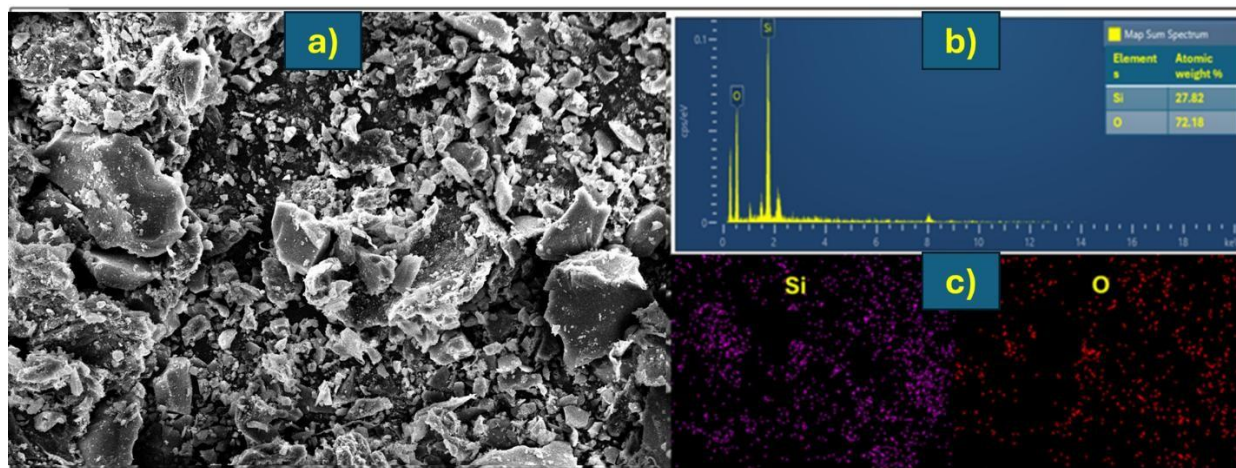


Figure 3.3: (a) SEM micrograph showing the morphology of silica particles extracted from bagasse ash, revealing irregular surface texture and diverse particle sizes. (b) EDX spectrum confirming the elemental composition, primarily indicating the presence of silicon (Si) and oxygen (O). (c) EDX elemental mapping illustrating the spatial distribution of elements, demonstrating uniform dispersion of silica across the sample surface

Figure 3.4a shows the FT-IR analysis of the prepared nano silica with prominent peaks observed at around 1067 cm^{-1} which is attributed to Si-O asymmetric stretching common in all open chain siloxane functional groups. The peak at just below 1700 cm^{-1} could be attributed to bending vibrations of O-H molecules susceptible from H_2O molecules. At higher up field region, the strong absorption at just below 3500 cm^{-1} is attributed to O-H stretching bonds of silanol groups ($\text{Si}(\text{OH})_4$). These groups have high affinity for water molecules and could be a point of intermolecular hydrogen bonding and as such influenced the hydrophilic nature of surfaces and membranes and can influence materials performance in water treatment analysis. To confirm the presence of the SiO_2 in the synthesized material, the XRD was taken and as illustrated in **Figure 3.4b**, the identified 2θ value at 22° confirmed the presence of the silica nanoparticles[113].

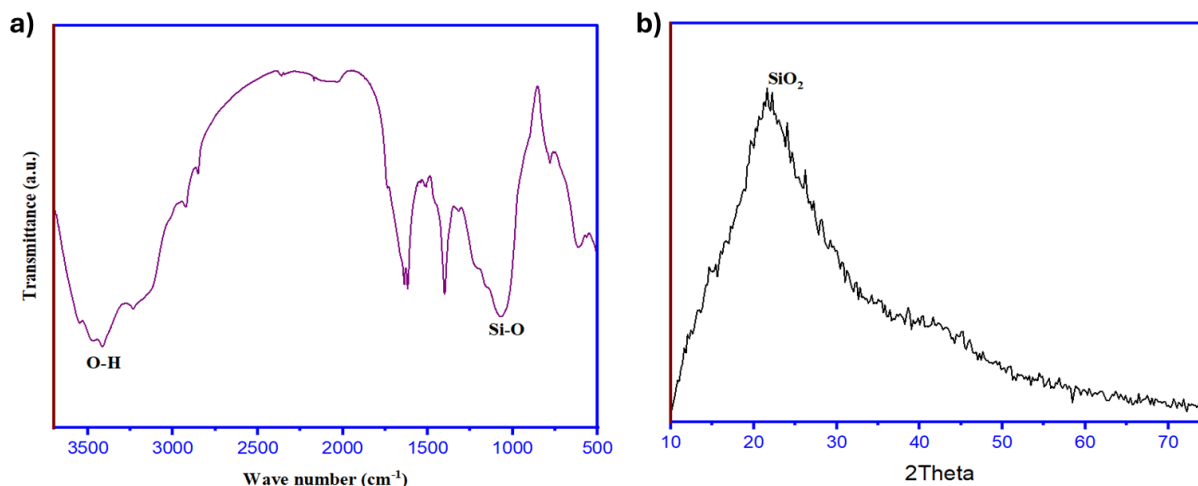


Figure 3.4: (a) FT-IR spectrum of silica extracted from bagasse ash, showing characteristic peaks around 1067 cm^{-1} (Si–O asymmetric stretching), $\sim 1700\text{ cm}^{-1}$ (O–H bending), and $\sim 3500\text{ cm}^{-1}$ (O–H stretching from silanol groups), confirming the presence of hydrophilic silica functionalities (b) XRD pattern of the silicated bagasse ash, exhibiting a broad diffraction peak near $2\theta \approx 22^\circ$, characteristic of amorphous silica.

3.5.2 Nanofibrous membranes characterization

3.5.2.1 Surface morphology

As the main aim of this study is to enhance the separation efficiency of membranes with multifunctional properties, a double layer membrane was created with Janus structure with wettability and porosity gradient. This gradient was created by varying the electrospinning solution condition by incorporating various silica concentration on one side of the Janus membrane, thereby creating a gradient in surface properties with enhanced performance in brine and emulsion treatment. As shown in **Figure 3.5a**, the active surfaces of the membranes which were denoted by P0 showed a uniform bead-free fiber. This was like the findings of Chen et al., [114] and could be attributed to the absence of an additive in the electrospinning dope solution. On the other hand, **Figures 3.5b, c & d** illustrate the surfaces of the silica modified fibers in which the additive was uniformly dispersed in the electrospinning dope solution achieved by probe sonication. As could

be observed, microbeads appeared on the surfaces which could be attributed to two factors including reduced PVDF-HFP concentration in the dope solution and as well, incorporating silica nanoparticles as was described elsewhere in the literature [115][116]. The density of the membranes on the fiber sizes remained similar with not much disparity, only that the presence of agglomerated particles could be noticed especially in P3 membrane. In the P2 membrane surface, a point embedment was observed on the microbeads observed with some agglomerated entanglements within the polymer chain. The presence of the beads in the silica modified layers as seen in P1 to P3 membranes could affect various factors. For instance, at higher bead concentrations on the membrane surface, the interconnected pore structure could be jeopardized which might hinder the penetration of permeates. With optimized quantity of the additive, the embedment of nanoparticles around the polymeric beads could enhance wettability due to synergistic hydrophilic property of the additive. This disparity in surface morphology characterized by uniform surface nanofibers and beaded structured nanofibers with embedment creates a gradient in porosity and wettability across the double layer membrane and Janus structure, and as such, improved membrane performance for the targeted application.

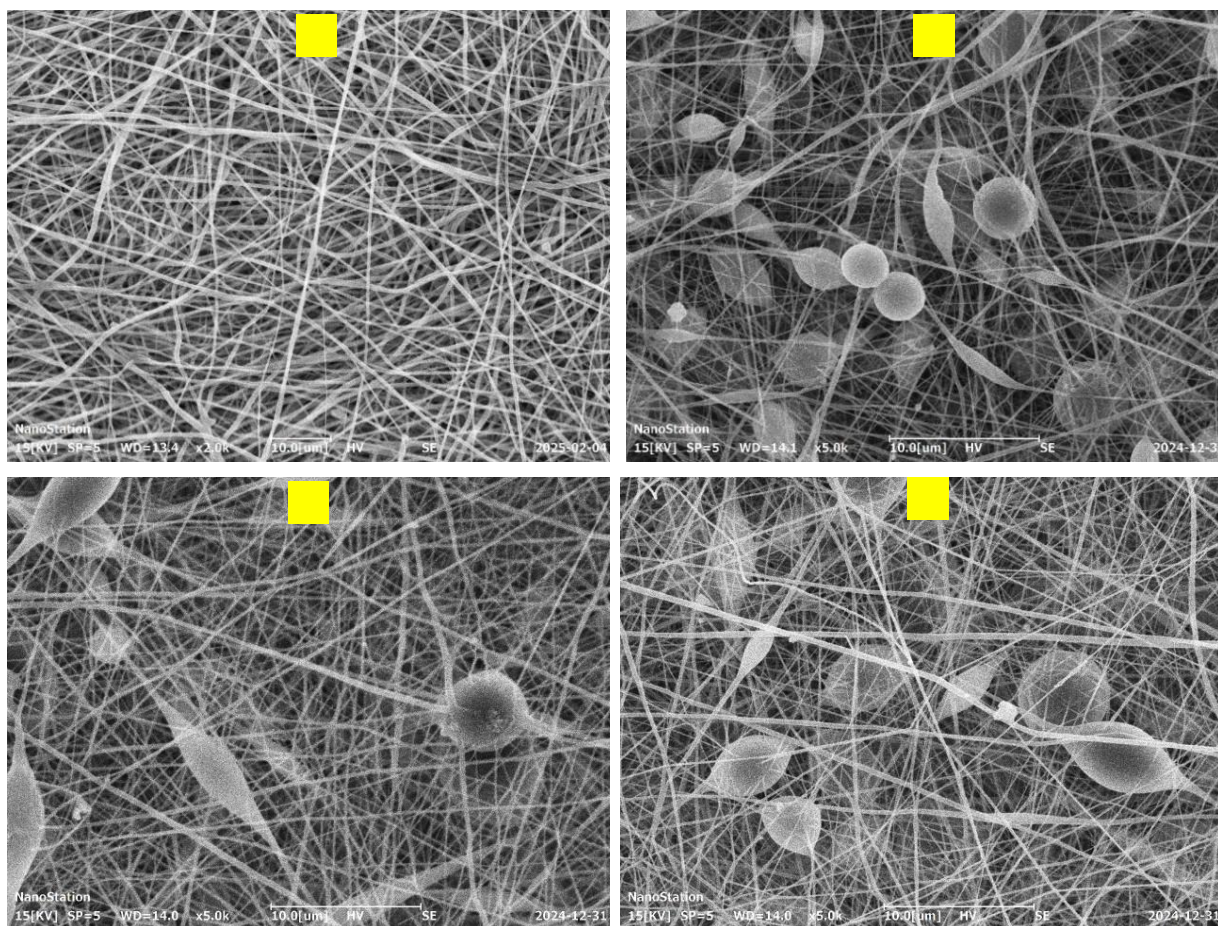


Figure 3.5: SEM images of fabricated nanofibrous membranes in pristine membrane a) P0 and Janus membranes b) P1 c) P2 d) P3 respectively.

3.5.2.2 Fibers size distribution

The influences of bagasse ash derived silica on the nanofibrous membranes fibers sizes were thoroughly and systematically investigated and illustrated in **Figure 3.6** (this was achieved by using the Image J software). As can be seen, membrane fabricated with no additive (P0) demonstrated relatively larger fibers with a broad distribution and mean fibers size of approximately $0.571 \mu\text{m}$. This reflects a stable electrospinning condition as many fibers plateaued withing the similar fiber size range. With the incorporation of nanoparticles and polymer concentration, the fibers sizes decrease significantly in almost all modified membranes. However,

P1 membrane showed a mean fiber size of 0.229 μm with broad size distribution, even though most fibers size counts between 0.1 to 0.3 μm . In P2 membranes, an approximate mean size of 0.21 μm was obtained almost like that of P1 and with highest fibers size counts within the range of 0.1 to 0.3 μm on comparison. On the other hand, P3 membrane showed an approximate mean size of 0.348 μm which is higher than those of P1 and P2 membranes respectively. The broader size distribution of P3 membranes also shows fibers size counts at the range of 0.1 to 0.6 μm . Overall, larger particles loadings might susceptibly lead to particles agglomeration and could influence the fibers sizes as seen in the fiber's morphology in **Figure 3.5**. It's worth stating that equal numbers of counts were taken for both membranes to ensure accuracy and precision in the data.

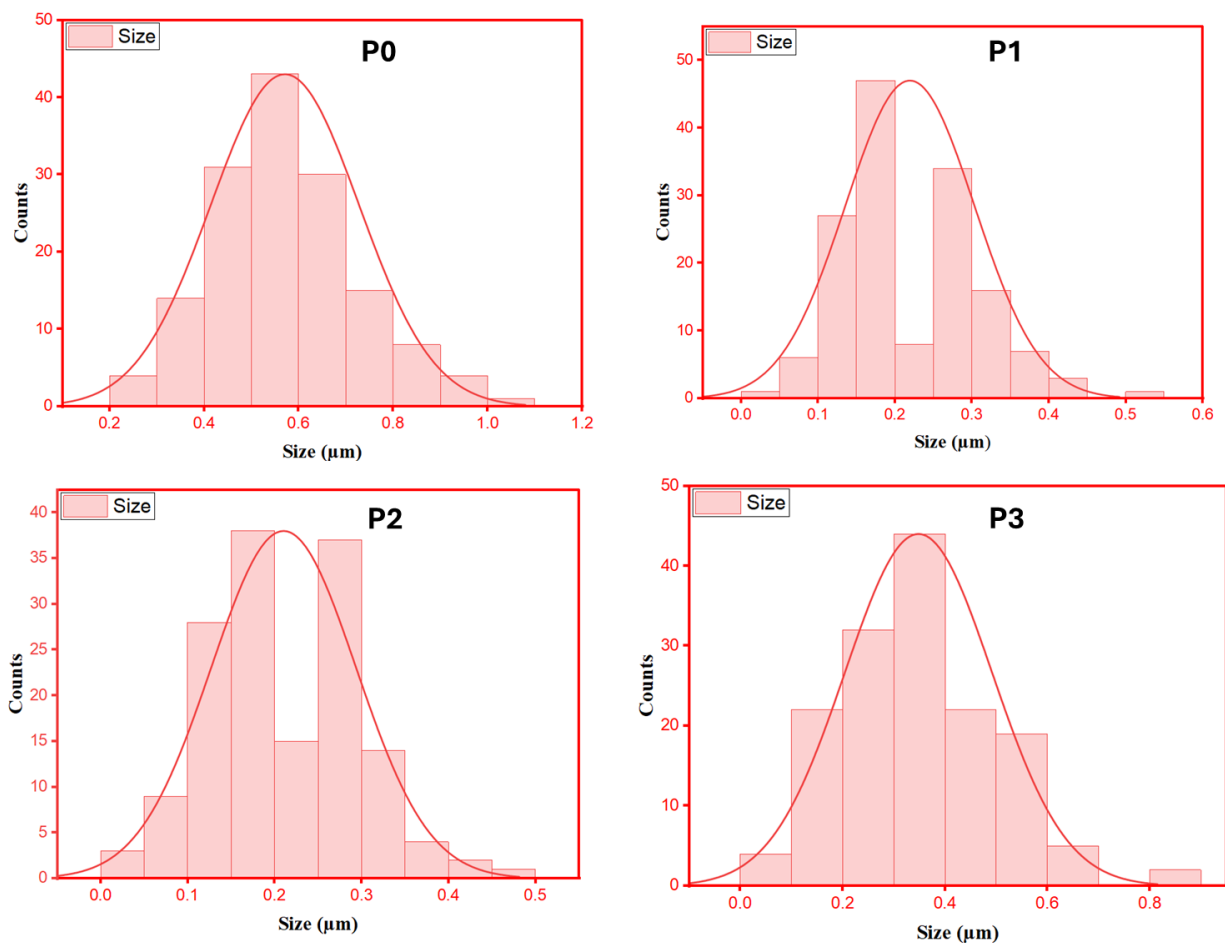


Figure 3.6: Nanofibrous membranes fibers sizes analysis of pristine membrane (P0) and Janus membranes P1, P2 and P3 respectively.

3.5.2.3 Surface chemistry

The surface chemistry of the fabricated membranes was analyzed from the FT-IR spectra illustrated in **Figure 3.7**. At lower wavenumber, a peak attributed to the α -phase was observed at 615 cm^{-1} which was absent in pristine membrane P0 but in all other silica modified membranes P1 to P3. The peaks at 761 and 840 cm^{-1} are attributed to α - and β -phases respectively [117]. PVDF-HFP are characterized by C-C bonds occurring at around 875 cm^{-1} which was also noticed in both fabricated membranes [118]. C-F bonds were influenced by the presence of silica into the PVDFHFP matrix as could be seen from the shifting of the peak from 1170 cm^{-1} in P0 to 1177 cm^{-1} in both modified

membranes. The observed shift could be attributed to the interaction of the dipoles of the polymer matrix and the incorporated silica, which is like the shift observed elsewhere in the literature [119]. The peak observed at 1400 cm^{-1} in both membranes is attributed to the methylene carbon in PVDF-HFP backbone. This peak is common for both fabricated membranes.

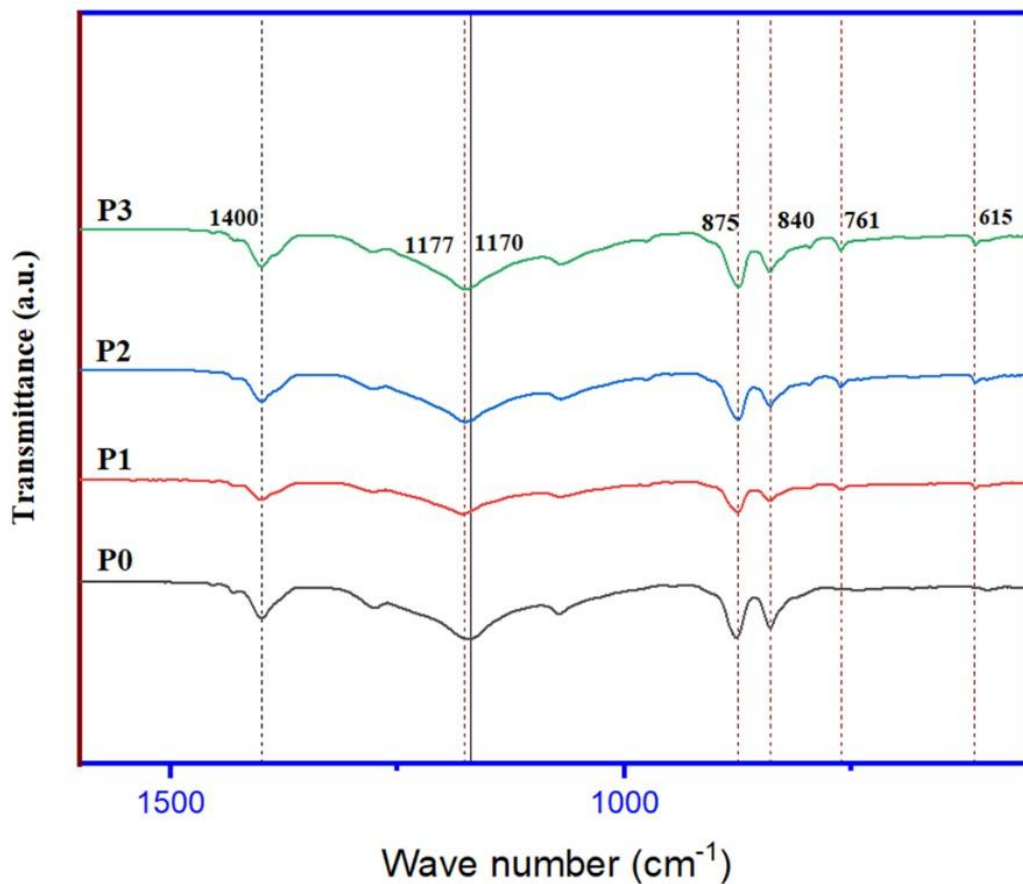


Figure 3.7: Surface chemistry analysis from FT-IR spectra of pristine membrane (P0) and Janus membranes P1, P2 and P3 respectively.

3.5.2.4 Surface wettability

The wettability of membrane surface is of paramount significance in water treatment. For instance, membrane distillation (MD) application requires a highly hydrophobic membrane with

hydrophobicity parameter defined by water contact angle (WCA) of more than 90° . for emulsion treatment in gravity-based pressurized systems, hydrophilic surface is required with WCA of less than 90° . Engineering a Janus membrane with multifunctionality an enhancement of performance in both stated applications require optimization in the surface wettability. The water contact analysis of fabricated membranes was evaluated from the sessile drop of DI water on the membrane surfaces. inherent hydrophobicity of PVDF-HFP membrane was achieved by high voltage electrospinning. As illustrated in **Figure 3.8**, the unmodified surface of the membrane P0 shows a high WCA value of 136.2° which maintained a value of 134.4° after 30 minutes. The synergistic effects of the incorporated silica on the rough membrane surface could be explained from the water contact angles of the modified membranes P1 to P3. After 5 seconds, the WCA of P1, P2 and P3 membranes show values of 101.1° , 109.2° and 112.4° respectively. After 5 mins, the membrane surface of P1 showed a dramatic decrease in WCA value to 88.71° . After 10 mins the WCA plateaued at a value of 78.3° , which sloped down to 20.2° after 15 minutes. P2 membrane over similar timing range of 5 mins, 10 mins and 15 minutes showed a WCA of 95.6° , 88.4° and 58.8° respectively. in similar vein, P3 membrane showed a WCA of 105.8° , 92.1° and 55.2° after 5, 10 and 15 minutes respectively. After 20 minutes, all membrane surfaces showed WCA of 0° , illustrating the potential of the hydrophilic surfaces to yield higher performances in targeted applications.



Figure 3.8: Surface wettability analysis of pristine membrane P0 and Janus membranes P1, P2 and P3.

3.5.2.5 Membrane thickness

Membrane thickness influences various properties of the membrane associated with the net membrane performance in targeted applications especially in water treatment. For instance, membrane thickness influences competition between mass transfer and conductive heat loss which are important parameters that affect the net performance of membranes especially in MD applications [120]. In Oil-in-water separation application, the membrane thickness influences the directional transport ability of the permeate and as such proper optimization is needed [121]. As illustrated in **Table 3.2**, general membrane thicknesses of P0, P1, P2 and P3 were found to be within the range of 70 to 80 μm which is acceptable in accordance with the fundamental principles of membranes for MD applications as explained elsewhere in the literature [14], [122].

Table 3.2: Membrane bulk properties.

Membranes	Thickness (μm)	LEP (bar)	Mean P.S. (μm)	Max. P.S (μm)
P0	80.2 ± 2.31	1.0 ± 0.05	1.178 ± 0.15	1.219 ± 0.10
P1	76.81 ± 1.87	0.9 ± 0.01	1.315 ± 0.20	1.374 ± 0.22
P2	72.4 ± 2.44	0.9 ± 0.05	1.857 ± 0.33	1.932 ± 0.29
P3	78.54 ± 0.31	0.8 ± 0.50	2.505 ± 0.29	2.6832 ± 0.35

3.5.2.6 Pore size distribution (PSD) analysis

The performance of membranes in water treatment processes is significantly influenced by pore size and membrane wetting resistance, which directly impact both Knudsen and viscous flow mechanisms. Hence analyzing the PSD of the fabricated membranes is essential for optimizing the performances of the membranes. Nanofibrous membranes, characterized by highly interconnected fibers and a narrow PSD, are particularly required for this application. To achieve such structures, various optimization studies were conducted and implemented during the electrospinning fabrication process. As can be seen in **Figure 3.9** and summarized in **Table 3.2**. The pore sizes of the membranes generally increased with an increase in the percentage of Silica in modified membranes P1 to P3. It was also noticed that the distribution of the pores widens from P1 to P3. Generally, membranes showed higher pore sizes compared to the pristine membrane P0.

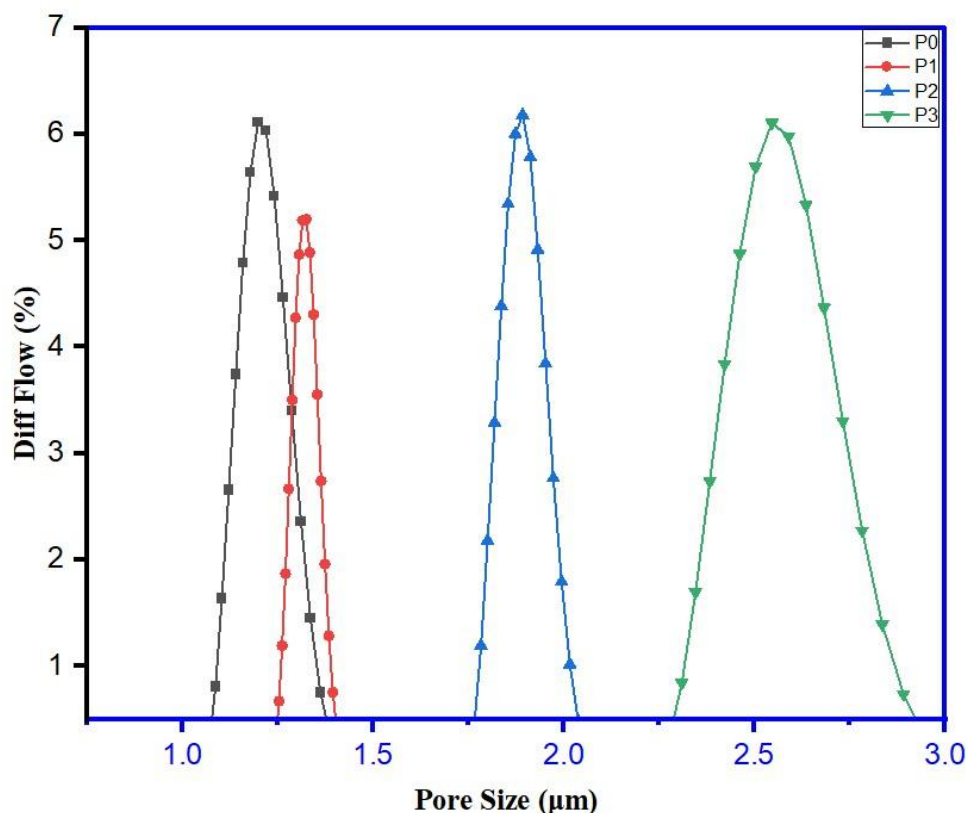


Figure 3.9: Pore size distribution analysis of P0 and Janus membranes P1, P2 and P3.

3.5.2.7 Liquid entry pressure (LEP)

Liquid entry pressure is a critical parameter in MD process and determines extent of membrane failure in operation. As listed in **Table 4.2**, both membranes show a similar trend with LEP values of 0.9 bar except for the pristine which shows an LEP of about 1 bar which might be due to lower pore sizes compared to modified membranes. For lower pressure requirement processes such as MD this value might favor stability of fabricated membranes over a range period without failure.

3.5.2.8 Thermal analysis

The thermogravimetric analysis (TGA) presented in **Figure 3.10** showed the thermal stability of the fabricated nanofibrous membranes. The unmodified membrane P0 represents a single-layer

membrane composed of PVDF-HFP without any additives, serving as the baseline material. P1, P2, and P3 are Janus membranes with a modified bottom layer containing varying concentrations of silica nanoparticles. Specifically, P1 is modified with 0.125 wt.% silica, P2 with 0.25 wt.%, and P3 with 0.5 wt.%. The curves obtained indicate that all membranes exhibit a significant weight loss in the temperature range of approximately at just below 500 °C which corresponds to the thermal degradation of PVDF-HFP. However, as can be observed, the residual weight at higher temperatures increases with the silica concentrations from P1 to P3, suggesting enhanced thermal stability due to the presence of silica. The addition of silica is likely to improve the thermal resistance of the modified layer, reducing polymer decomposition and enhancing membrane durability at elevated temperatures.

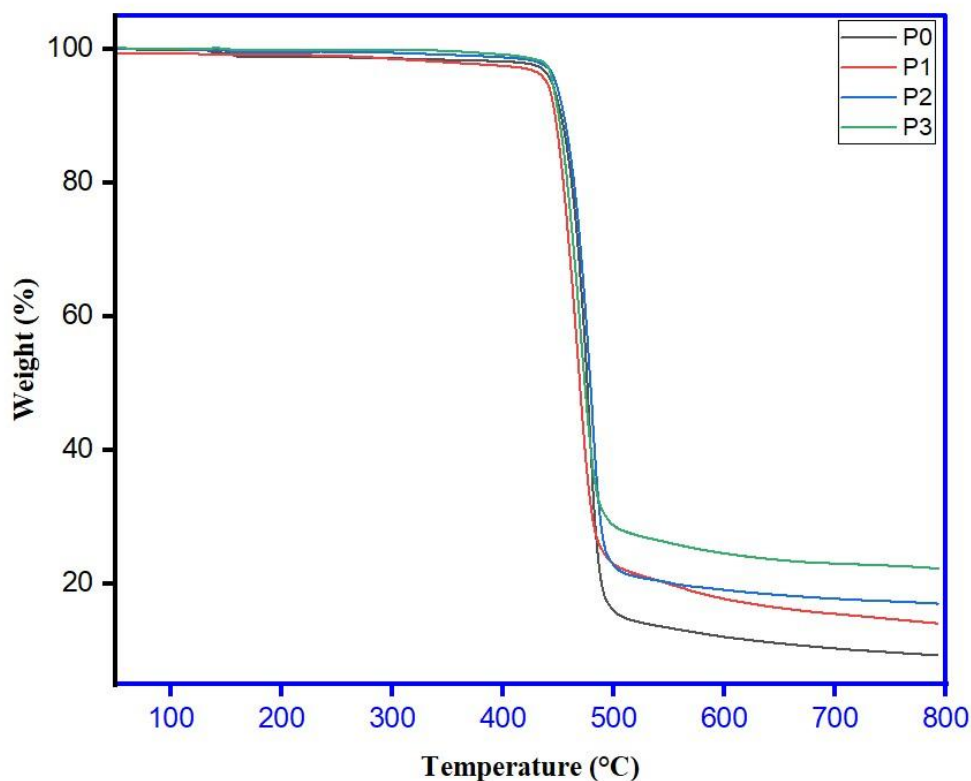


Figure 3.10: Thermal analysis from TGA curves of P0 and Janus membranes P1, P2 and P3.

3.5.3 Membrane distillation evaluation

To increase the performance of a pristine membrane the addition of a hydrophilic layer on a hydrophobic active or omniphobic surface has been explored recently which leads to fabrication of multilayer membrane with Janus structure. Successful processes have been explored in the literature including dopamine coatings, co-casting and deposition techniques. Layering techniques which involve deposition of a hydrophilic on top of hydrophobic layers have been achieved using the advanced membrane fabrication techniques including electrospinning via Layer-by-layer engineering method. Various literature works highlighted the significance of this approach in fabricating membranes used in membrane distillation and in water-oil separation intuitively. Yet the exploration of this approach in fabricating membranes with multifunctionality in MD techniques and other processes have not been explored yet or in an early stage of development. This work aims to lay a foundation for fabrication of membrane with functional parameters favorable to the mentioned process.

The performance of this membrane in membrane distillation was assessed using water gap module with the hydrophobic side of the membrane facing the feed and the hydrophilic side the permeate. The feed which was made to mimic similar concentration to sea water was made up to 38,000 ppm was heated to 70 °C to generate a vapor and the permeate was held fixed at 20 °C which in all resulted in temperature gradient. As a result of this, the vapor moves across the membrane due to pressure gradient and was condensed and collected in the permeate side of the membrane. The net flux was calculated as weight per the effective membrane and time respectively. As can be seen in **Figure 3.11**, both dual layer membranes (P1, P2 and P3) showed superior performance compared to the pristine membrane P0. The superior performance in dual layer membranes could be

attributed to both hydrophilic modification and the matrix gradient (from the concentration of dope solution during electrospinning). However, to explain the disparity in the performance of the P1, P2 and P3 membranes, P2 membrane demonstrated superior performance with a flux of 42.73 $\text{Kgm}^{-2}\text{h}^{-1}$ compared to P1 and P3 with Permeate fluxes of 36.32 $\text{Kgm}^{-2}\text{h}^{-1}$ and 39.96 $\text{Kgm}^{-2}\text{h}^{-1}$ respectively. This disparity might be attributed to various factors including membrane morphology and the pore structures. Although P3 demonstrated larger pore size, M2 membrane morphology as explained demonstrated uniform beads distributions with packets or drops of silica groups. On the other hand, due to higher nanoparticle compositions, P3 membrane morphology showed higher bead density which susceptiblely disrupts the interconnected structure and as a result affects the penetration of materials across the membrane. which is also a possible reason for having flux lower than P1 membrane also. However, all dual-layer membranes showed uniform rejection up to 99.98 after 36 hours of MD which is slightly higher than the pristine membrane (P0), which showed a rejection of 99.92% after similar testing conditions. A comparative study of nanofibrous Janus membranes was conducted and the results are tabulated as shown in **Table 3.3** below. This further highlights the significance of this study towards better understanding of Janus membranes for water treatment applications.

Table 3.3: Literature comparisons of previously reported Janus membranes in comparison with Janus membranes reported in this study.

Hydrophobic/ Janus membrane	Fabrication techniques	Flux ($\text{kgm}^{-2}\text{h}^{-1}$)	Saline Rejection (%)	Feed conc. (ppm)	Testing duration	Membrane distillation type	Reference
PVDF-Psf	Electrospinning/ Electrospinning	53.6	99.99	30,000	-	DCMD	[83]

PVDF-SiO ₂	Electrospinning/ Electrospinning	24.6	99.99	35,000	40	DCMD	[84]
PH-PVA/PAN	Electrospinning/ Electrospinning	15.5	99.99	35,000	20	AGMD	[87]
PVDF-PVA/PAA	Electrospinning/Electrospraying	27	100	35,000	36	DCMD	[73]
PVDF-HFP/ PVDF-HFP@SiO ₂	Electrospinning/ Electrospinning	42.73	99.92%	35,000	36	WGMD	This work

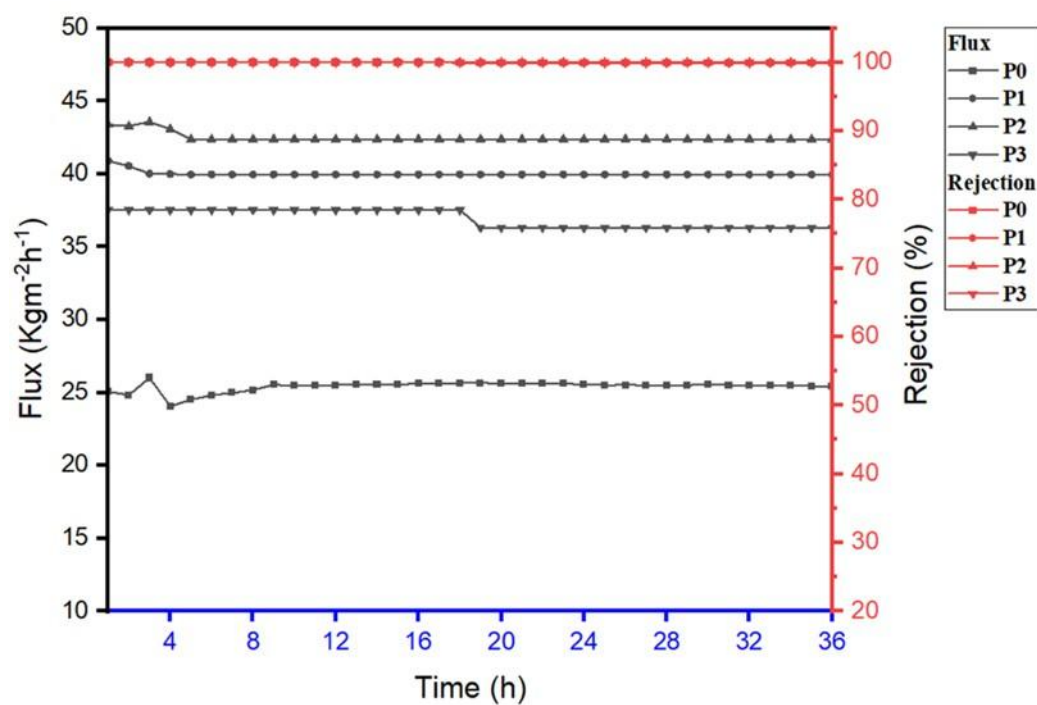


Figure 3.11: WGMD performance evaluation of P0 and Janus membranes P1, P2 and P3.

3.5.4 Switchable properties of fabricated Janus membranes (oil-water emulsion treatment)

3.5.4.1 Evaluation method

The separation efficiency of the manufactured Janus nanofibrous membranes was evaluated using a crossflow system at a constant pressure of 0.04 MPa in a laboratory setting. A water-in-oil emulsion with an oil content of 2000 ppm served as the feed solution. To create the emulsion, 4g of weighed lubricating oil was added to a two-liter DI water tank. After that, a shear mixer (MODEL) was used to vigorously stir the mixture for two hours at 4500 rpm until a stable emulsion was formed. The Janus membrane's hydrophilic side encountered the feed fluid during the separation procedure. The permeate flux (F) in $\text{Lm}^{-2}\text{h}^{-1}$ was calculated using **equation 11**, while the separation efficiency (R) in percentage was determined using **equation 12**. This was evaluated using Hanna model turbidity meter. A schematic laboratory crossflow system used in this analysis is highlighted in **Figure 3.12**.

$$F = V / (A \cdot t) \quad \dots\dots\dots 11$$

$$R = c \frac{f - C_p}{C_f} \times 100 \dots\dots\dots 12$$

Where V is the volume of collected permeate expressed in L, A is the effective membrane surface ($5.65 \times 10^{-4} \text{ m}^2$), and t is the total separation duration expressed in h. C_f and C_p represent the concentration of the feed and permeate respectively and are expressed in ppm.

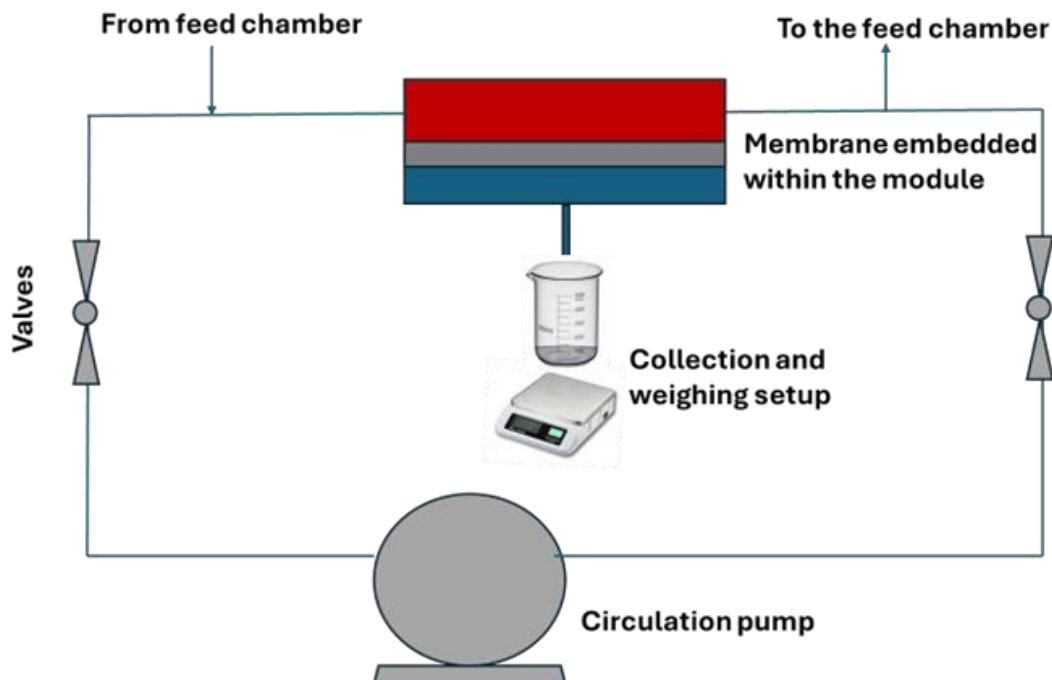


Figure 3.12: Laboratory scale crossflow system schematic used in the oil-in-water evaluation.

3.5.4.2 Analysis and findings

To test the performances of modified membranes in oil/water emulsion treatment, 2,000 ppm feed was prepared with lubricating oil and distilled water. The membrane was swapped for this purpose by exposing its hydrophilic side to the feed and its hydrophobic side to the permeate. Both membranes were compacted at higher pressures with distilled water and various cycles were run to ensure stabilization. An optimized pressure condition was fixed and used for all other cycle measurements. For each membrane P1, P2 and P3, 10 cycles were taken, and the performances are shown in **Figure 3.13a to 3.13c**. The flux of P1 membrane as shown in **Figure 3.13a** declined after the first four cycles from 565 LMH to 476 LMH which maintained a steady flux after the 8th cycle. After 10 consecutive cycles the membrane maintained a steady flux of 450 LMH. P2 membrane showed a steady flux over the entire 10 cycles with a slight reduction of flux from a value 1204 LMH in the first cycle to almost 1130 LMH in the last cycle. The P3 membrane showed a similar

trend to P1 as can be seen in **Figure 3.13c**. Significant reduction was observed after the first five cycles of performance testing from 795 LMH 700 LMH which was maintained at 690 LMH after the last cycle. However, considering the separation efficiencies of P1, P2 and P3 membrane in, both membranes display excellent separation efficiencies of > 99.9% making them suitable for this application. The P2 membrane, which gives the best performance out of the tested membranes, was further tested for various intervals of time to assess its stability. As highlighted in **Figure 3.13d**, P2 demonstrated a steady performance over the entire testing period with excellent separation efficiency. In general, a membrane's ability to separate water from oil may be impacted by its surface hydrophilicity. This is because the development of a hydration layer at the feedmembrane interface readily stops oil droplets from slipping and preferentially allows water molecules to flow.

This collectively leads to higher permeate flux and superior separation efficiency. After several cycles of operation, oil droplets in microemulsions typically develop an oily layer at the membrane's surface, resulting in flux sacrifice. However, the improved flux performance in this work may be due to the intrinsic superhydrophilicity of silica nanoparticles. Even so, the beaded morphology of the membranes has an impact on how rough their surface is when these particles are added. The compaction and distilled water cycling carried out prior to the membranes testing could be a reason worthy of stating to have influenced the formation of the hydration layer prior to the oil-water separation analysis.

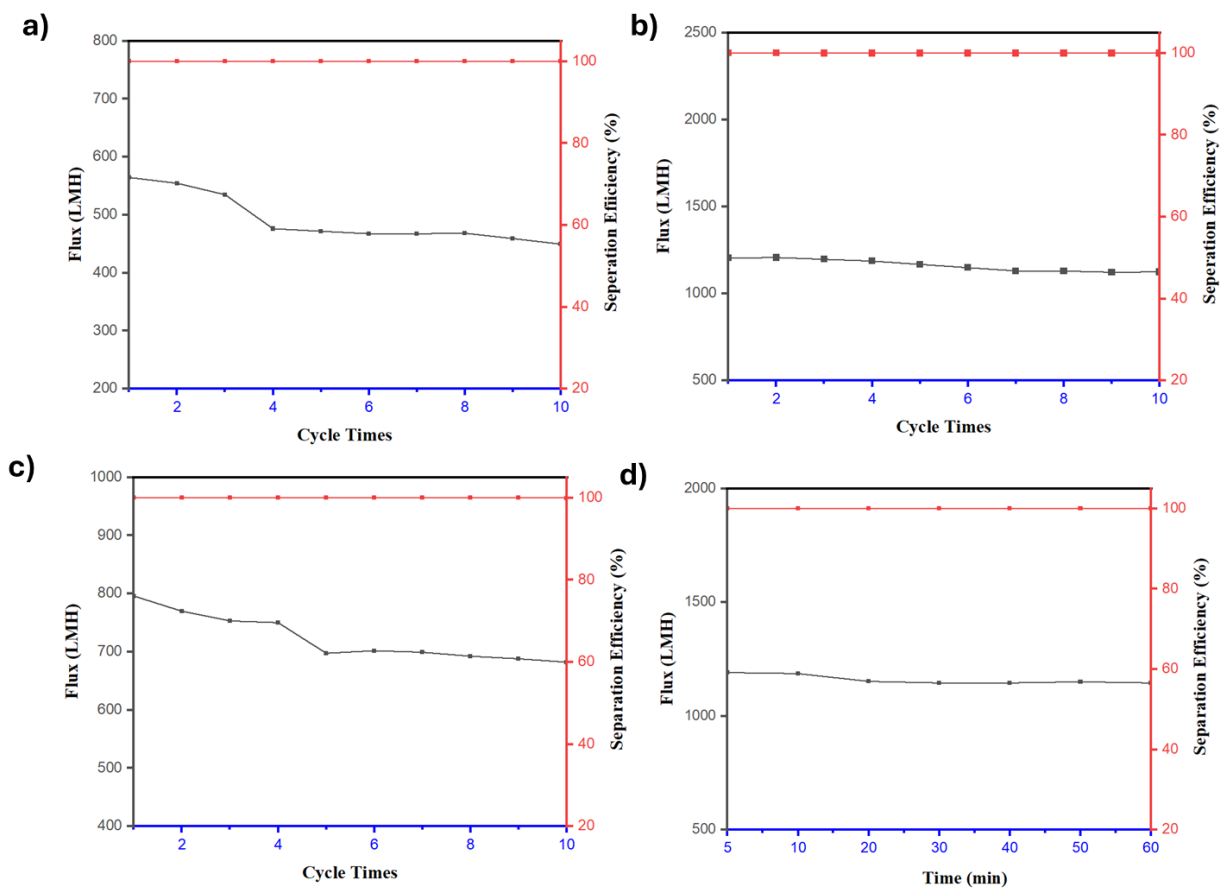


Figure 3.13: performance metrics evaluation of fabricated Janus membranes a) P1 b) P2 c) P3 d) evaluation of cycling stability of Janus membrane P2 over a certain period.

To study the particle size distributions in the feed and permeates of from the tested membranes after the 10th cycle, optical microscopies of both feed and permeated were taken and presented. As seen in **Figure 3.14a**, various particles were present in the feed in various size range from 0.5 μm to 7.0 μm . However, no particle was noticed in all the permeates collected from either P1, P2 and P3 as demonstrated in **Figure 3.14b**, indicating enhanced performances of the fabricated Janus membranes.

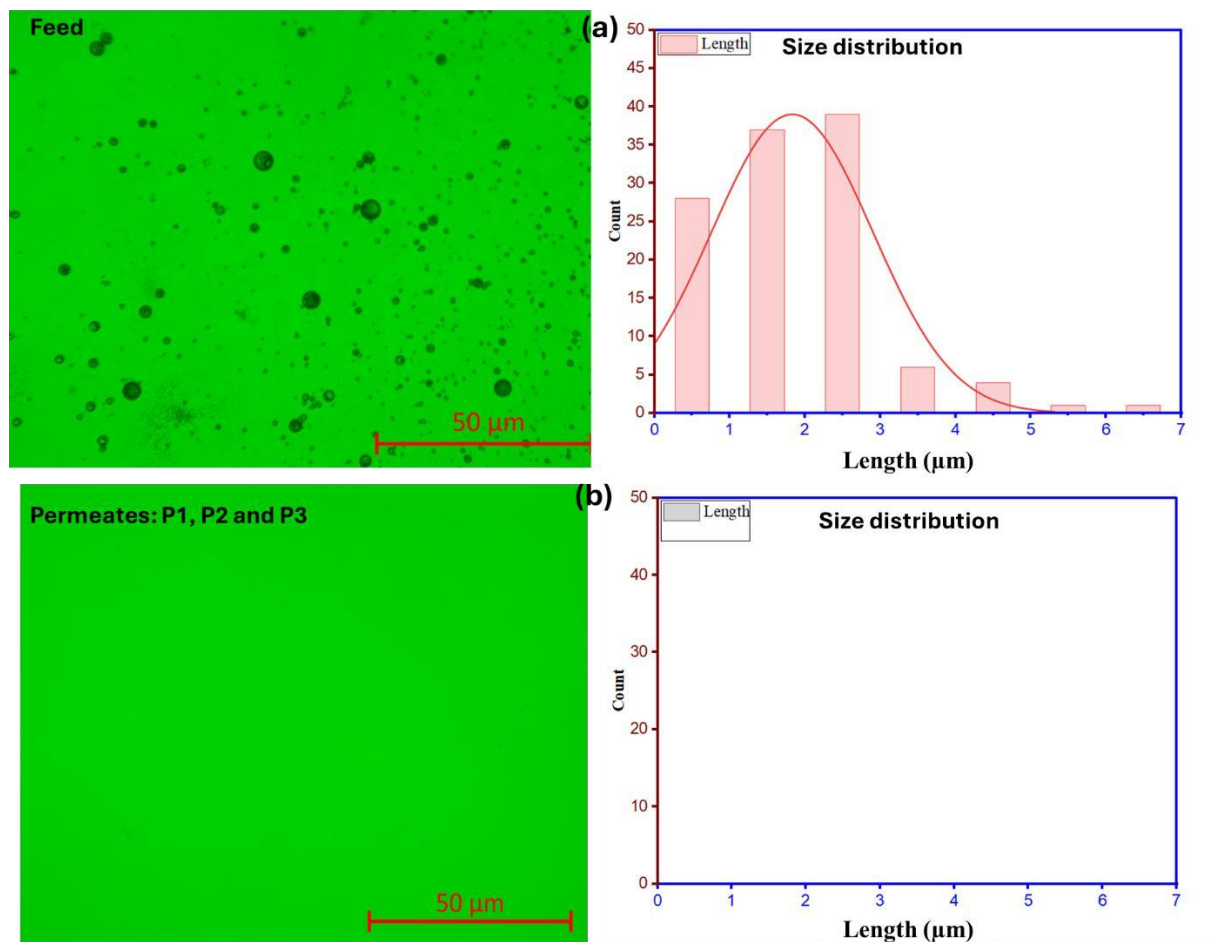


Figure 3.14: (a & b) optical microscopies of both feed and permeate respectively and the fibers size analysis were studied using the ImageJ software. The permeate after the 10th cycle was used for this analysis.

Total organic carbon (TOC) analysis of the permeates obtained from the membranes during water oil separation provides critical insight into their separation efficiency. The TOC values recorded for membranes P1, P2, and P3 were 4.755 mgL⁻¹, 3.902 mgL⁻¹, and 6.837 mgL⁻¹ as seen in **Figure 3.15**. It can be observed P2 membrane displays the lowest TOC value, suggesting superior oil rejection performance compared to P1 and P3, which also reflects the separation efficiencies of both membranes as shown in **Figure 3.13** above. The enhanced separation efficiency of P2 can be attributed to various factors including the optimal silica bagasse ash concentration (0.25 wt.%),

which appears to strike a balance between fiber uniformity and surface roughness, as evidenced by the SEM images and fibers size analysis. In contrast, P1, containing a lower additive content (0.125 wt.%), displayed moderately higher TOC, implying a slightly reduced separation performance. Membrane P3, with the highest additive concentration (0.5 wt.%), recorded the highest TOC value, indicative of the poorest separation efficiency. The formation of larger bead sizes and density as observed might likely result in heterogeneity in pore sizes and thereby slightly lower barrier to slipping of oil contents as appeared in the separation efficiency. Overall, both membranes displayed efficient separation performances.

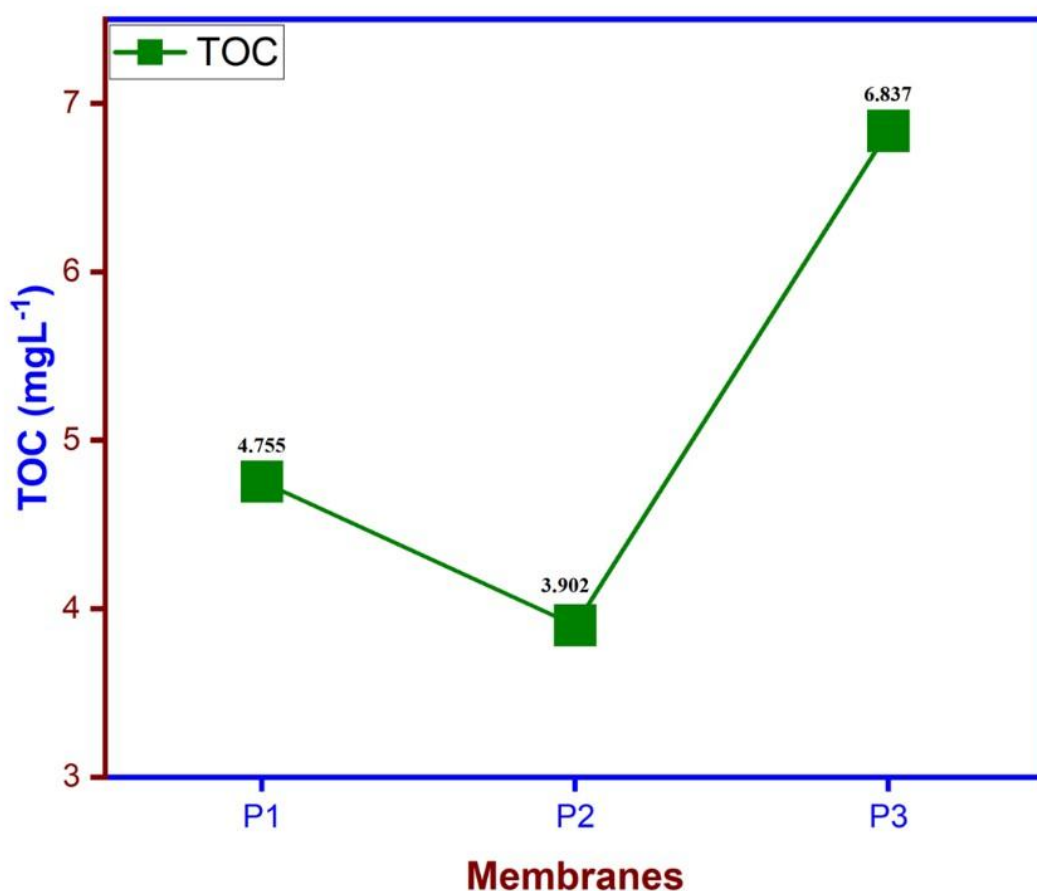


Figure 3.15: TOC results of 10th cycle permeate from oil-water emulsion separation of fabricated membranes P1, P2 & P3.

CHAPTER 4

METAL ORGANIC FRAMEWORKS (MOFS)-BASED NANOFIBROUS DUAL LAYER MEMBRANES WITH ENHANCED MULTIFUNCTIONAL WATER TREATMENT EFFICIENCY

4.1 Materials and Methods

4.1.1 Materials

Polyvinylidene-co-hexafluoropropylene (PVDF-HFP, 400,000 MW), dimethylformamide (DMF), acetone (Ac), sodium trioxocarbonate (IV) (Na_2CO_3) calciumchloride (CaCl_2), Sodium chloride (NaCl), sodium dodecyl sulphate (SDS).

4.2 Membrane fabrications

Table 4.1. Fabricated membranes compositions.

Membrane	Category	Active layer		Support layer	
		PVDF-HFP (wt.%)	MOFs-A (mg)	PVDF-HFP (wt.%)	MOFs-B (mg)
A0	Single layer	15	0		
A1	Single layer	15	60		
A2	Single layer	15	120		
A3	Single layer	15	240		
A4	Single layer	15	360		
B1	Dual layer	15	120	15	60
B2	Dual layer	15	120	15	120
B3	Dual layer	15	120	15	240

B4	Dual layer	15	120	15	360
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The general membrane fabrication process is represented by the schematic diagram illustrated in **Figure 4.1**. In the first step of the Janus membranes fabrication process, various weights of MOFs category A (60, 120, 240, and 360) were added into a 50:50 weight ratios of solvent mixture consisting of acetone and DMF and probe sonicated until uniform dispersion is achieved. To this mixture, specific amount of PVDF-HFP (15 wt.%) was added and stirred to a dope solution at 40°C and 170 rpm. The obtained solutions were loaded into a 10 mL syringe and with spinneret speed of 60 mm/s, the dope solution electrospun on an aluminum foil collector on a rotating drum of an electrospinning machine which was set at a speed of 50 mm/s. Collected membranes were folded in a paper and thermally pressed to improve the fiber packing and enhanced the mechanical properties. It's worth stating that all the membranes were prepared with the same electrospinning condition which also includes an ejection potential of 17.5 kV, a feed rate of 3.6 mLh⁻¹ and spinneret width of 75 mm. The membranes were named A1, A2, A3 and A4 membranes corresponding to the order of MOFs addition. A pristine membrane A0 was fabricated with the same polymer concentration and free MOFs and was used for comparisons in further analysis.

To fabricate the Janus membranes, A2, which was found to display superior properties, was set as a substrate and various solution compositions of PVDF-HFP with MOFs category B were electrospun in the same condition as those of the A-series membranes. The dope solution was formulated in a similar category to the A-series membranes containing various loadings of MOFs including 60, 120, 240 and 360 mg. The Janus membranes labelled B1, B2, B3 and B4 according to the order of the added MOFs were mechanically and thermally pressed and kept for further

analysis. A summary of the compositions of both single- and double-layer membrane were highlighted in **Table 4.1**.

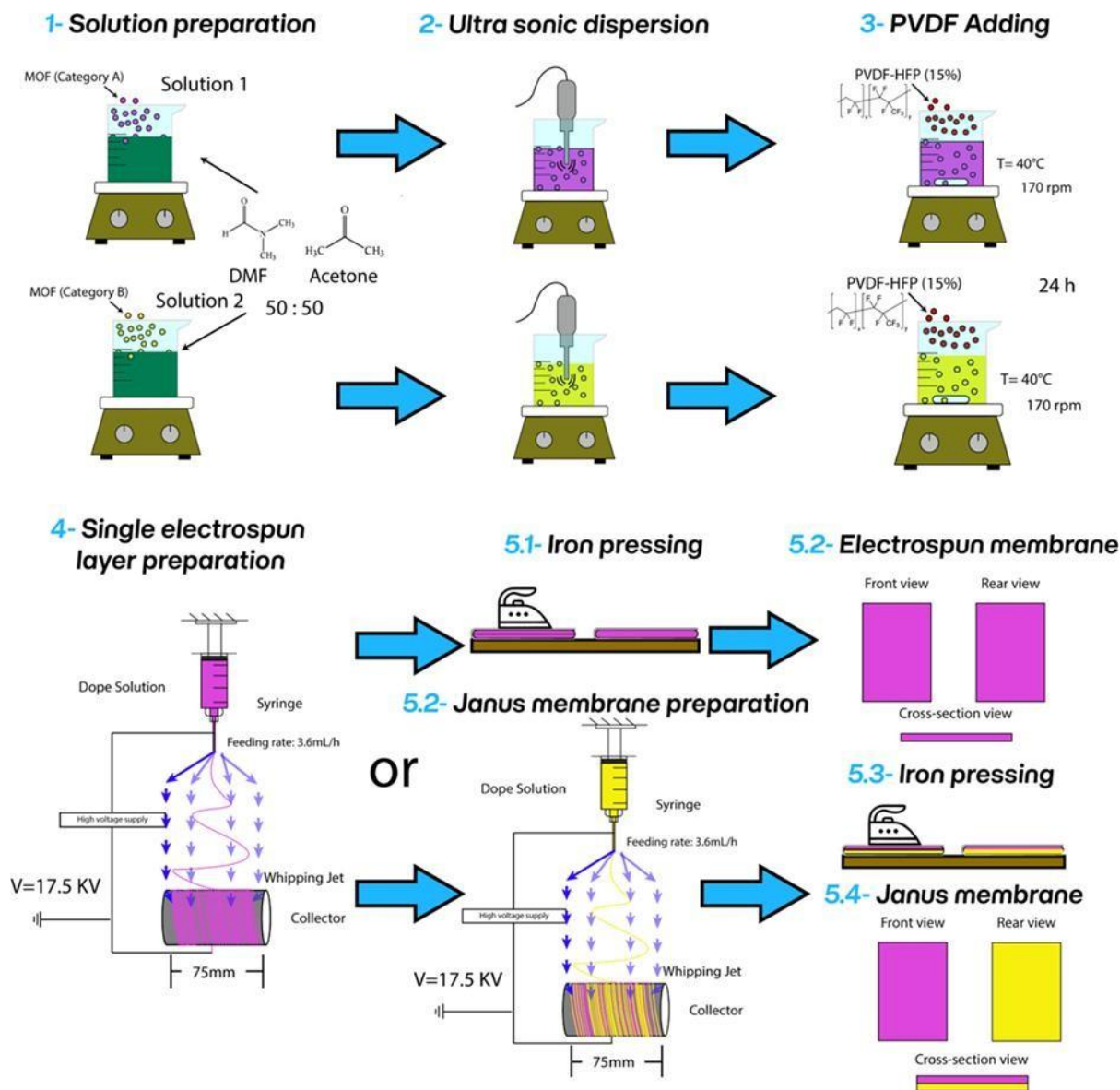


Figure 4.1: Janus Membranes fabrication details.

4.3 Membrane characterizations

Surface morphology of membranes was studied using scanning electron microscopy (SEM, JEOL

JSM-6610LV). DII-29030SCTR smart coater was used to gold-coat the sample to ensure surface conductivity. This was carried out at a controlled coating period to avoid overcoating. Various image magnifications were taken at a fixed acceleration voltage of 20 kV which were used to study nanofibrous morphology and as well, the fibers sizes distribution. To study the surface roughness contributions to the membrane's performances, the atomic force microscopy (nanosurf model) was used in tapping mode with fixed scanning are in both membranes. The surface chemistry was generally studied the Fourier transform infrared radiation (FT-IR, Bruker INVENIO series) and was used to examine the samples at wavenumbers range from 4000cm^{-1} to 400cm^{-1} . To study the crystalline phases of the fabricated membranes, the x-ray diffraction was conducted using the (XRD, Rigaku Ultima IV model). The thermal stability of the fabricated membranes was studied from the thermogravimetric analysis, which was conducted using TGA, Q600 SDT instrument. The mechanical stability of the membranes was evaluated from a lab scale rheometer. A fixed size was used for all samples at the same conditions of temperature, pressure and humidity. The surface wettability of the membranes was evaluated from the WCA measurements conducted with Goniometer. Sessile drop experiment was used for this measurement with a distilled water droplet volume of 0.2 to 0.4 μL . The readings reported were on average of a minimum of four readings taken at various portions of the membrane's surfaces. The liquid penetration point was studied from the LEP which was studied using a laboratory scale setup following the process described elsewhere in the literature [123]. The membrane thickness was measured with a precision measurement device (LITEMATIC VL-50A Mitutoyo, Japan). Measurements at a minimum of 10 points on a 7 cm by 1 cm membrane were averaged and expressed in micrometers (μm). The membranes pore size distribution (PSD) was determined by a laboratory scale porometer (3Gzh, Quantachrome Instruments, USA) with similar methods explained elsewhere in the literature.

4.4 MD performance tests

The MD performance of fabricated membranes was evaluated using a water gap module. This was formed by filling the gap in the Air gap module with DI water and extending the outlet to a beaker which was placed on high precision weighing balance (Ohaus PR200 Model) and conductivity meter connected to a recorder. The feed solution was prepared with 35,000 ppm saline prepared by dissolving 350g of table salt in 10 liters of DI water. After transferring into the water heater tank (JULIABO model), the feed was set to 70°C and was made to pass through the module via connection hoses. A DI-water filled chiller was used in the permeate side and was maintained at 20°C, thereby establishing a temperature gradient across the membrane. to ensure constant and efficient circulation, set of flow meters were connected to the heater and chiller which regulates the amount of water flowing in and out of the module. A schematic representation of the setup is illustrated in **Figure 4.2**.

The permeate flux (PF) and Saline Rejection (SR) were evaluated based on the relationships given in equations 13 and 14.

$$PF = \frac{m}{A \cdot t} \quad (\text{kg/m}^2\text{h}) \quad 13$$

$$SR (\%) = c \frac{f - c_p}{c_f} \times 100 \quad 14$$

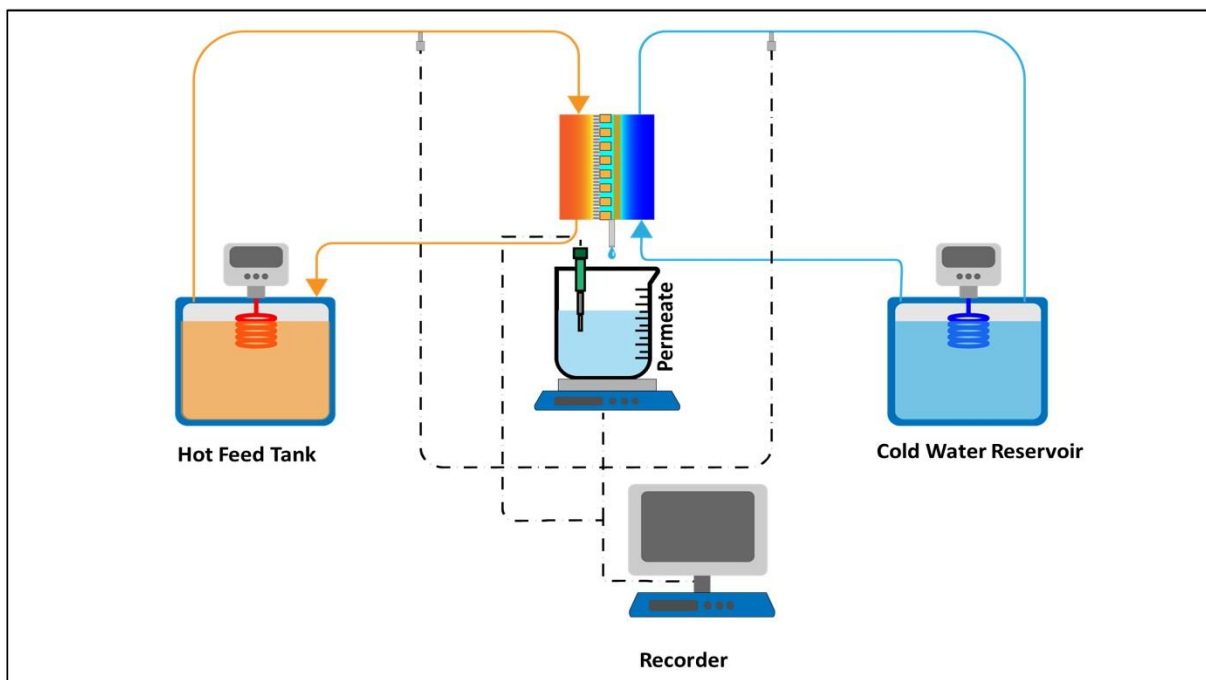


Figure 4.2: Schematic diagram of distillation unit used for the WGMD evaluation of fabricated membranes.

4.5 Results and discussion

4.5.1 Surface and structural analysis

4.5.1.1 Surface morphology

This work reported the development of materials gradient towards Janus membranes fabrication for water treatment applications. Practically, a high-voltage electrospinning was applied to fabricate these membranes which were explained in earlier sections. A hydrophobic Al-based MOF-A material was first incorporated into PVDF-HFP dope solution in various concentrations in which the best performing membrane with optimized properties was modified. This modification towards Janus membranes development was achieved via electrospinning codeposition of PVDF-

HFP dope solutions with incorporated Nickel-based MOFs named MOFs-B at various concentrations. The surface morphology of the fabricated nanofibrous membranes was studied from the SEM image displayed in **Figure 4.3**. As reported in earlier sections, the fabrication process involves high positive voltage with optimized electrospinning dope solutions. As the contents of these solutions changes, certain properties must be affected which include the electrospun fibers structural orientation and sizes resulting all from electrospinning instabilities [124]. For instance, as seen in **Figure 4.3a**, the pristine membrane which was prepared from high voltage electrospinning of 15 wt.% PVDF-HFP showed highly interconnected fibers with uniform sizes. These fibers are bead-free with no physical defects, which are susceptible to higher pore sizes and optimum surface roughness. With the addition of 0.25 wt.% MOF-A into the dope solution, the morphology of the nanofibers changed with the appearance of beads on string and reduction of fibers sizes which might influence the fibers roughness. A2 membranes to A4 (**Figures 4.3c to 4.3e**) membranes respectively showed smaller fibers sizes compared to the pristine membrane which might be attributed to the increase in the MOFs-A additive in the membranes. However, the appearance of point droplets which are secondary nano-scale roughness on the morphologies of these membranes increases with increase in MOFs concentration [125]. As can be seen in, the nano-scale secondary roughness increases the physical roughness of the nanofibrous membranes which might influence the surface roughness and wettability of the membranes.

As A2 membrane was found to have optimum properties, various solutions of PVDF-HFP with incorporated MOF-B were deposited on A2, making the hydrophilic support layer of Janus membranes and was named B1 to B4 shown in **Figure 4.3f to 4.3i** respectively. As can be seen, the physical roughness of the nanofibers increases with an increase in the concentration of MOFsB in the dope solution. Comparatively, the collection of the nanofibrous membranes was significantly

different from the surfaces of nanofibers modified with Al-based MOFs. One reason to support this observation can be attributed to the conductivity of the central elements in the MOFs. As Al emanates higher conductive than Ni, the electrospinning of the Top hydrophobic nanofibrous membranes (A1 to A4) will likely result in formation of thinner fibers because of axisymmetric deformation and whipping instability induced by electric field from the high electrospinning voltage. B1 to B4 Membranes show varying fibers physical properties, especially B1 which show more uniform fibers than B2 to B4 membranes which was attributed to the low viscosity of the solution. As the viscosity of dope solutions increases with an increase in MOFs-B, the collection of fibers becomes more uniform with the combination of both thinner and thicker fibers [126].

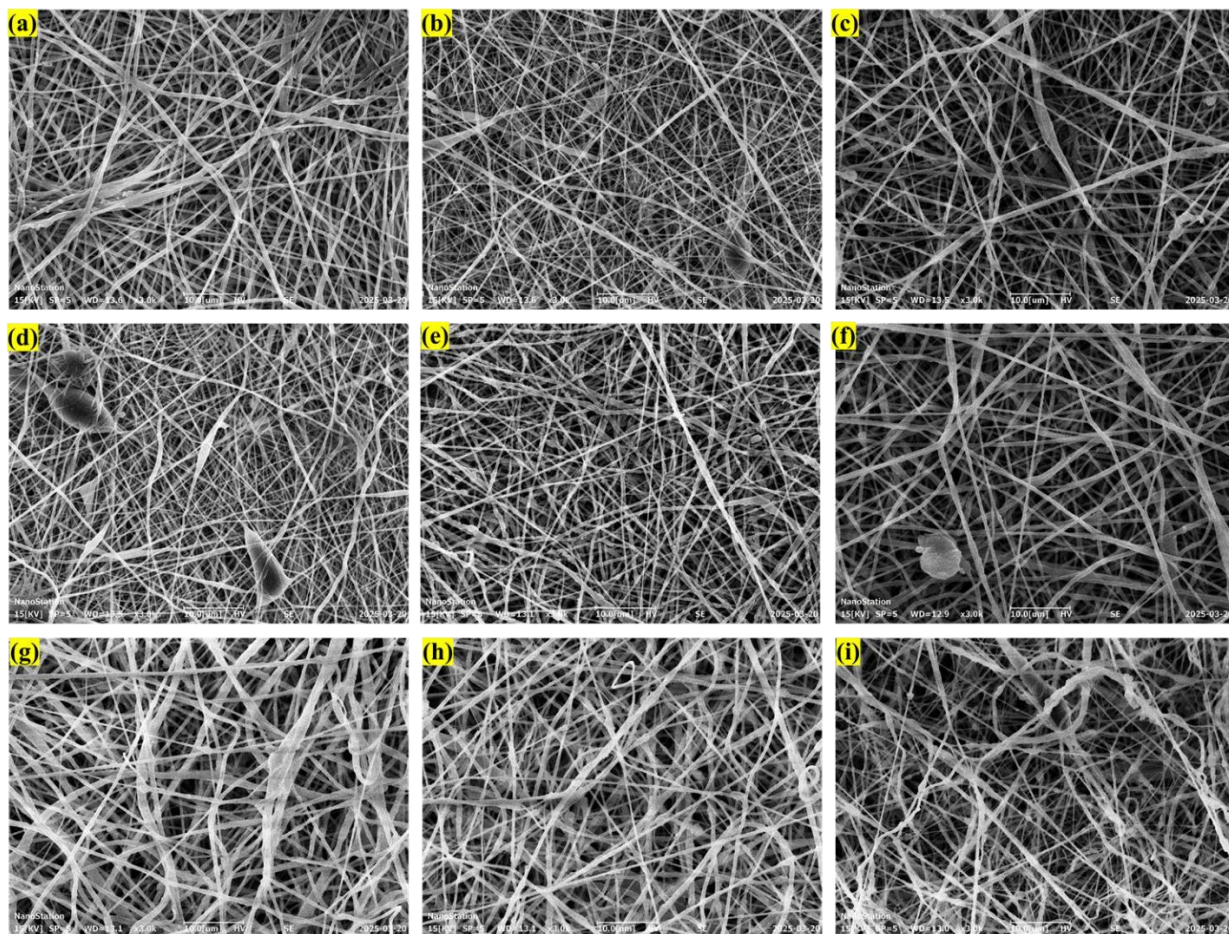


Figure 4.3: SEM images of nanofibrous membranes a) A0 b) A1) A2 d) A3 e) A4 f) B1) B2 h) B3, and i) B4.

4.5.1.2 Fibers size analysis

To further study the effects of the incorporated MOFs additives on both nanofibers, the fibers sizes and distribution were analyzed. This was achieved using the Image J software, with the same SEM image magnifications. As can be seen in **Figure 4.4**, the pristine membrane A0 shows wider size distributions with fiber sizes counts highly concentrated from 0.6 to 0.9 μm . The general trend expected from morphology can be further highlighted by considering the fibers size distributions of membranes A1 to A4. From A1 to A3 membrane, the fibers thicknesses reduce significantly, attributed to an increase in whipping instability and a decrease in fiber thickness. The fiber sizes

in A4 membranes slightly widen which can be attributed to the formation of nano-scale roughness from MOFs on the fibers. In similar ways, the fiber size distribution in B1 to B4 membranes changes significantly with increasing in MOFs concentration, which is attributed to both axisymmetric deformations, whipping instabilities and as well dope solutions' viscosity [124], [126].

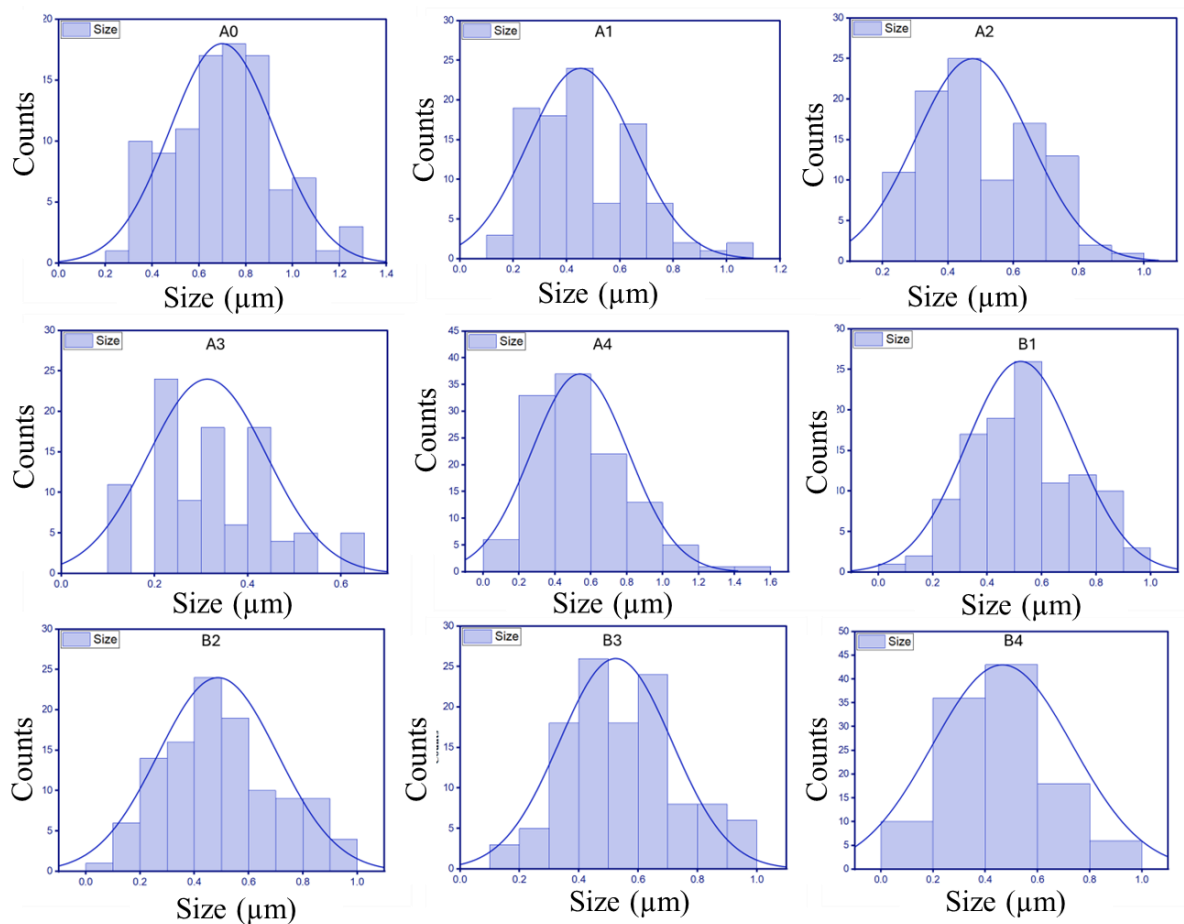


Figure 4.4: Nanofibrous membranes surfaces fiber size analysis of pristine P0, single-layer membranes A1, A2, A3, A4 and Janus membranes B1, B2, B3 and B4.

4.5.1.3 Surface roughness analysis

The observed roughness of the fabricated membranes resulting from MOFs incorporation, especially the hydrophobic surfaces (MOFs-A) was further studied from the tapping mode AFM analysis and highlighted in **Figure 4.5**. As can be seen, the pristine membrane (A0) showed an average roughness of 332.0 nm which might be attributed to highly uniform and interconnected fibers. After the incorporation of 0.25 wt.% of MOFs-A (A1), the average surface roughness increases to 374.9 nm and as well increases significantly to 383.3 nm in A2 membrane which contains 0.5wt% of MOFs-A. As expected, the increase in secondary nano-scale roughness on the fibers increases the physical roughness, reflecting the R_a values obtained in A3 and A4 membrane respectively (410 and 750.88 nm) respectively.

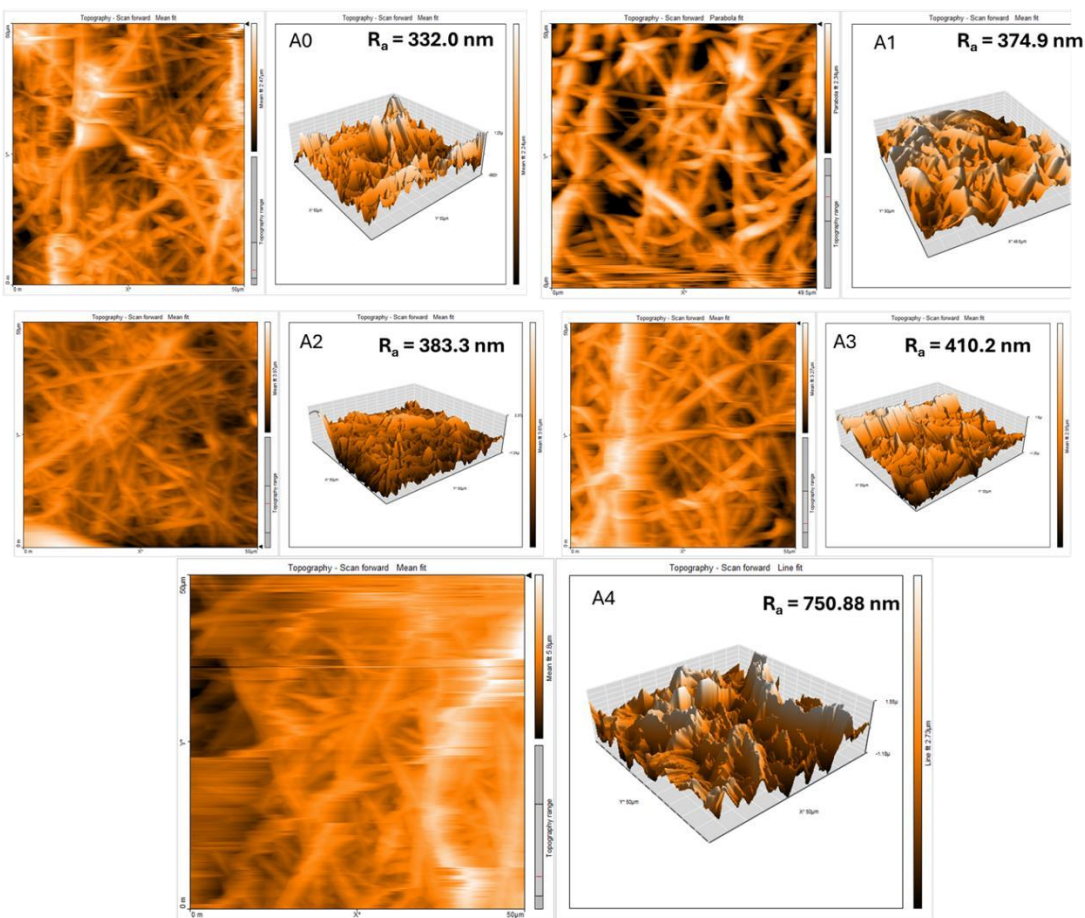


Figure 4.5: Surface roughness analysis of nanofibrous membranes where A0 is the pristine membrane and A1 to A4 are MOFs-A modified membranes respectively.

4.5.1.4 Surface wettability analysis

The sessile water drop analysis for surface wettability analysis was performed and expressed in Water Contact angle (WCA) as highlighted in **Figure 4.6a**. The WCA of the membranes as can be seen increased significantly from 124.3° in A0 membrane to A2 138.2° membrane. A reduction in WCA was observed slightly in A3 to 134.6° membrane which reduces significantly to 128.3° in A4 membrane. Although the roughness of membranes influences the WCA which was mainly because of the increase in air-pockets at the membrane-water droplet interface, the strong interplay between

the surface and the water droplet, however, cannot be underestimated. The likeness of higher contents of MOFs-A to interact with water induced by molecular interactions leads to the observed decrease in WCA. A2, having the highest WCA, was used as an active layer for the Janus membrane fabrication via co-deposition as explained in earlier sections. The bottom layer of the Janus membrane from B1 to B3 showed a remarkable decrease in WCA, with B3 having the lowest WCA of 103.3°. B4 membrane however, showed a slight increase in WCA which might be attributed to both molecular interactions and surface roughness. Overall, B3 membrane demonstrated the lowest WCA. With B3 membrane, the Janus structure shows a difference in WCA of about 35° which might favor higher permeability in membrane distillation.

4.5.1.5 Surface chemistry analysis

Figure 4.6b shows the surface analysis of fabricated nanofibrous membranes achieved from the ATR-mode FT-IR spectra of the fabricated membranes. To begin with the right-side of the spectra, two highly intense peaks were obtained at peaks with wave numbers 840 cm^{-1} and 878 cm^{-1} . The former is usually a common characteristic of mostly all fluorinated compounds and as well, the intensity and the relative positioning of the peak depend on the degree of the fluorination in the molecular formula of the material. As the main polymeric material used in this work is PVDFHFP, this peak corresponds to the β -phase and can be attributed to asymmetric vibration of CF_2 bonds. The latter, however, is attributed to CH vibration present in the polymeric nanofibrous membranes [127], [128]. C-C and C-F stretching bands present in PVDF-HFP nanofibrous membranes are observed at 1072 cm^{-1} and 1173 cm^{-1} respectively [129] [125]. The peaks observed at around 1400 cm^{-1} in both membranes are attributed to the methylene carbon in PVDF-HFP backbone. It's worth noting that the occurrence of the corresponding α -phase is seen by the peak

at 772 cm^{-1} which is present in both membranes and increases with increases in the amount of MOFs-A incorporated into the nanofibrous membranes. The peak at 1578 cm^{-1} is entirely absent in A0 membranes and present in all MOFs-A modified membranes. The intensity of this peak increases with increasing MOFs-A additive in the nanofibrous membranes and can be attributed to C=N stretching vibrations present in MOFs-A. **Figure 4.6c** shows the FT-IR spectra of the bottom layers of the fabricated Janus membranes (B1 to B4) which contain MOFs-B additive in increasing order of the additive concentration. As the main polymeric material used is PVDF-HFP, the same as the nanofibers with incorporated MOFs-A additive, certain peaks describing the chemistry of the fibers are expected to be like those in **Figure 4.6b**. However, a distinction between them can be noticed in the disappearance of the peaks at 1578 cm^{-1} and 772 cm^{-1} and appearances of absorption bands obtained at 745 cm^{-1} and 1619 cm^{-1} . These two peaks are attributed to. Interestingly, the disappearance of the α -phase in the MOFs-B modified hydrophilic nanofibrous membranes means more β -phase is present and these membranes can be applied to nanogenerators and other nano harvesting devices.

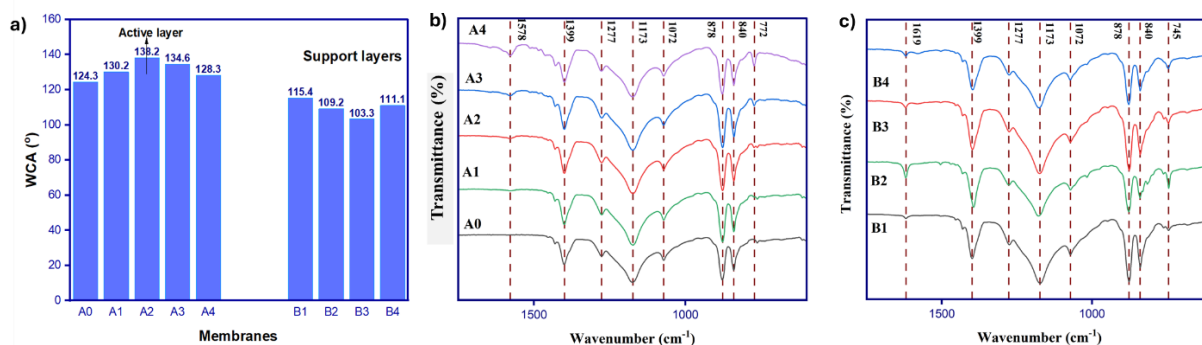


Figure 4.6: a) Wettability analysis of pristine, single-layer and Janus membranes surfaces from the WCA measurements b & c) Surface chemistry analysis of fabricated membranes from the FTIR analysis.

4.5.2 Membranes bulk properties (pore size distribution, liquid entry pressure, thickness)

Table 2 summarizes the intrinsic properties of the fabricated single- and double-layer membranes. For membrane distillation (MD) applications, one of the critical parameters is the LEP, which determines the pressure at which liquid penetrates the membrane pores. As observed, all modified membranes (A1 to B4) exhibited LEP values within the optimum range required for MD processes. The pristine membrane (A0) showed LEP of 0.9 bar. In contrast, the A1 membrane, fabricated with the smallest MOF-A additive (0.25 wt.%), exhibited a significantly higher LEP of 1.5 bar. However, as the concentration of MOF-A increased from A1 to A4, the LEP values progressively decreased. This trend is likely due to the increase in maximum pore sizes induced by the higher MOF-A content, which compromises the membrane's resistance to liquid intrusion. Interestingly, a reverse trend was observed in the double-layer membranes (B1 to B4), where the LEP increased with increasing MOF-B loading. This phenomenon could be attributed to the enhanced membrane thickness arising from the greater concentration of MOF-B in the support layer, as also discussed by [47]. Membrane thickness not only influences LEP but also affects MD performance metrics such as permeate flux and thermal efficiency [130].

Both single- and double-layer membranes showed an increase in thickness upon the incorporation of MOF-based additives. This increment is attributed to the intercalation of MOF particles within the polymeric matrix, leading to a denser and more compact membrane structure. This trend is consistently observed across both single-layer membranes (A0 to A4) and double-layer membranes (B1 to B4), as detailed in Table 2. In addition to LEP and thickness, the incorporation of MOFs influenced the mean pore size and pore distribution. **Figure 4.7a** illustrates the pore size trends. The pristine membrane (A0) exhibited an average and maximum pore sizes of 1.4548 μm and 1.4548 μm respectively, reflecting the lowest LEP value. Upon the addition of 0.25 wt.% MOF-A,

the A1 membrane demonstrated a maximum pore size of 0.8522 μm which corresponds to the highest observed LEP (**Figure 4.7b**) value. As MOF-A content increased, the mean pore size further increased, likely due to the inherent porosity of the MOF structures and their effect on the polymeric network. Conversely, in the double-layer membranes (B1 to B4), a gradual decrease in mean pore size was observed with increasing MOF-B loading. This reduction can be attributed to the increased membrane thickness, which may result in more compact internal structures and lower pore size. Overall, the interplay between these intrinsic membrane properties is critical for evaluating membrane performance in MD applications. The observed trends emphasize the importance of optimizing both material composition and structural configuration to achieve the desired separation efficiency.

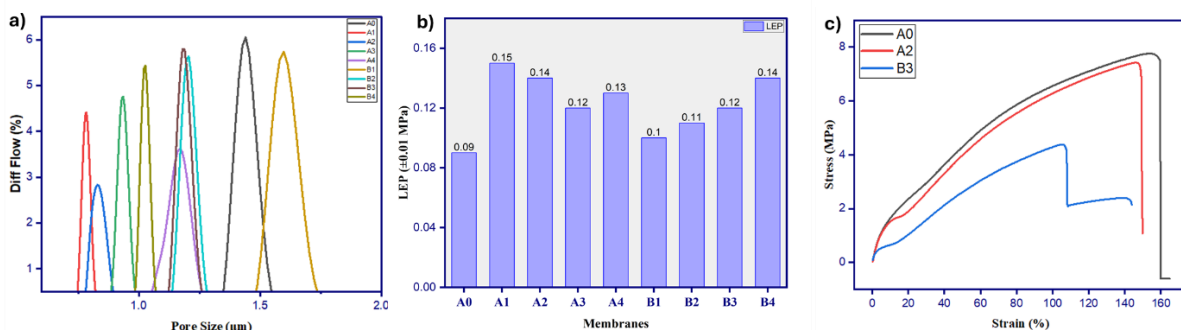


Figure 4.7. a) Pore size distribution analysis of fabricated membranes b) Liquid entry pressure analysis of fabricate membranes c) Mechanical analysis of pristine membrane, A2 single-layer membrane and Janus membrane B3.

Table 4.2: Intrinsic nanofibrous membranes properties.

Membranes	Thickness (μm)	LEP ($\pm 0.01\text{MPa}$)	Mean Pore size (μm)	Max. Pore size (μm)
A0	106.56 $\pm$ 0.3	0.09	1.4270	1.4548
A1	108.97 $\pm$ 0.54	0.15	0.8252	0.8974
A2	112.92 $\pm$ 2.1	0.14	0.9244	0.9712
A3	120.12 $\pm$ 1.5	0.12	0.9964	1.0509
A4	130.65 $\pm$ 0.9	0.14	1.1519	1.2482
B1	115.67 $\pm$ 1.8	0.10	1.5381	1.6458
B2	122.13 $\pm$ 1.6	0.11	1.1961	1.2442
B3	127.12 $\pm$ 2.0	0.12	1.1701	1.2272
B4	136.82 $\pm$ 0.11	0.14	1.0215	1.0427

4.6 Mechanical analysis

The mechanical analysis of the membranes (A0, A2, and B3) as shown in **Figure 4.7c** highlights the influence of MOF incorporation and membrane architecture on their tensile performance. A0, the pristine single-layer PVDF-HFP membrane, demonstrates the highest mechanical strength with a maximum stress of 7.82 MPa, a moderate Young's modulus of 20.38 MPa, and the highest

elongation at break of 155.56%, indicating good ductility and uniform stress distribution. A2, which contains about 1.0 wt.% Al-based MOFs, shows a slight decrease in maximum stress (7.42 MPa) but a notable increase in stiffness, with a higher Young's modulus of 26.77 MPa. This suggests enhanced rigidity due to MOF reinforcement, albeit with a slight reduction in elongation (147.08%) likely due to MOF-induced stress concentration. In contrast, B3, the dual-layer membrane shows a significant drop in mechanical strength (4.35 MPa), similar stiffness to A0 (20.06 MPa), and the lowest elongation at break (106.32%). This decline is likely due to interfacial mismatch or weak adhesion between layers, introducing mechanical discontinuities that compromise strength and flexibility.

4.7 Membrane separation performance

For the membrane distillation (MD) performance evaluation, Water Gap Membrane Distillation (WGMD) was employed. As previously described by Dahiru et al., who reported that WGMD yields higher performance flux than conventional Air Gap Membrane Distillation (AGMD). As explained in earlier sections, the evaluation was conducted using a saline feed concentration of 35,000 ppm at 70 °C, with cycling distilled water as the coolant at 20 °C. All fabricated membranes were tested under the same conditions over a 24-hour period, as shown in **Figure 4.8**. To begin with, the inherently higher thermal conductivity of PVDF-HFP typically results in lower permeate flux due to increased temperature polarization. However, this effect can be mitigated by incorporating metal-organic frameworks (MOFs). In this study, all MOFs-A modified membranes (A1 to A4) were fabricated as single-layer membranes, with thickness increasing as MOFs-A concentration increased in the dope solution. Despite variations in wettability, all MOFs-A membranes exhibited superior permeate flux compared to the pristine A0 membrane, even with

100% saline over 24 hours. The A0 membrane, with a flux of $25.28 \text{ kg m}^{-2} \text{ h}^{-1}$, had the largest pore sizes and thinnest structure. However, the enhanced performance of MOFs-A membranes is attributed not only to structural changes but also to improved thermal conductivity and water contact angle (WCA). Among them, the A2 membrane (0.5 wt.% MOFs-A) achieved the highest performance, with a flux of $34.2 \text{ kg m}^{-2} \text{ h}^{-1}$ and an optimal thickness of approximately $112.92 \text{ }\mu\text{m}$. This membrane also recorded the highest WCA, indicating better hydrophobicity, which contributed to its superior flux. Consequently, the A2 membrane was selected as the top layer for fabricating the Janus membranes (B1 to B4). The increase in MOFs-A concentration in A3 and A4 membrane leads to lower hydrophobicity and as well lower thermal insulation, consequently leading to lower permeate flux as seen in A3 and A4 respectively [125]. For the Janus membranes, similar variations in MOFs concentration were applied to the bottom layer using MOFs-B. As MOFs-B concentration increased, membrane thickness also increased. B1, with the lowest MOFsB concentration, had the highest pore size possibly due to better fiber interconnectivity and recorded a permeate flux of $35.8 \text{ kg m}^{-2} \text{ h}^{-1}$, outperforming all single-layer membranes. However, increasing MOFs-B concentration from B1 to B3 led to a decrease in WCA (from 115.4° in B1 to 103.3° in B3), indicating increased wettability. Despite this, other favorable factors, including reduced thermal conductivity and optimal structure, resulted in B3 achieving the highest permeate flux of $46.58 \text{ kg m}^{-2} \text{ h}^{-1}$. Conversely, B4 with the highest MOFs-B concentration showed a reduced flux of $40.32 \text{ kg m}^{-2} \text{ h}^{-1}$. This decrease is likely due to excessive membrane roughness, increased thickness, and reduced pore size, which negatively affected performance despite the higher MOFsB content.

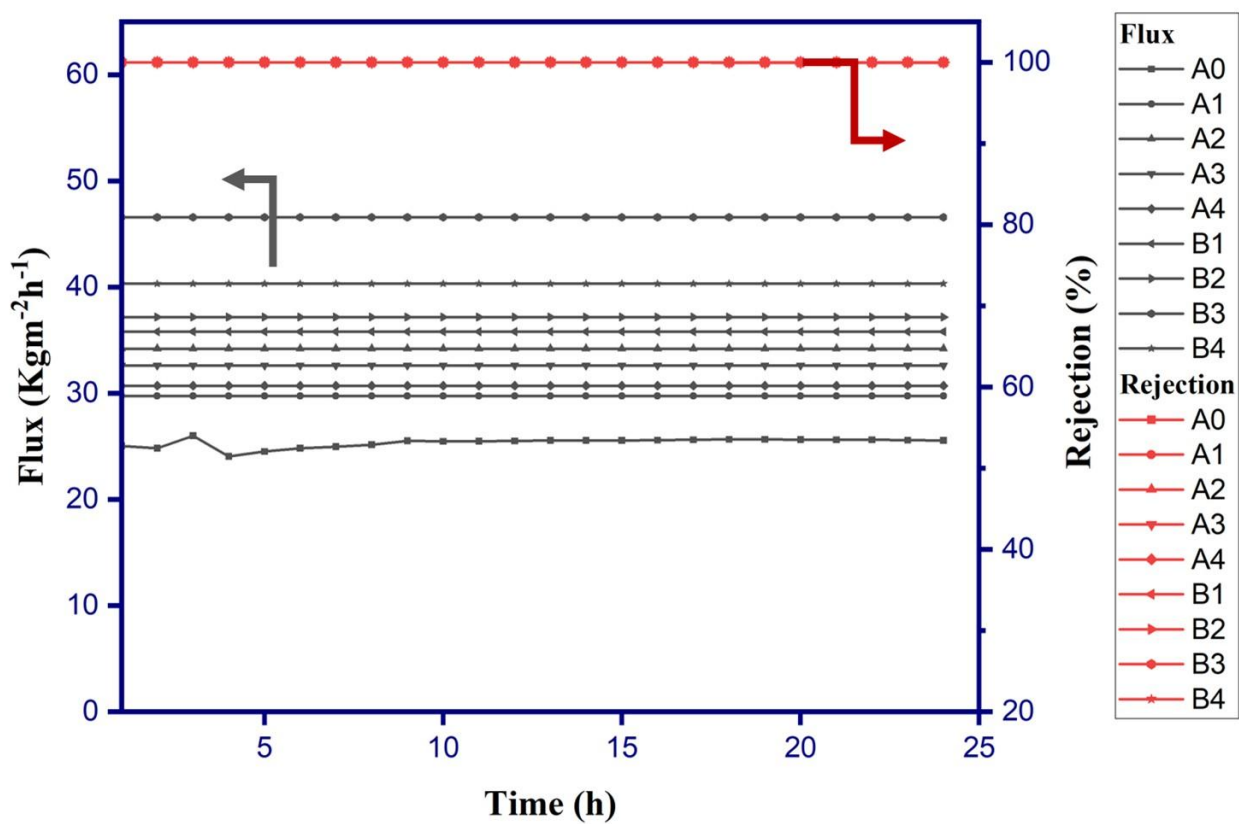


Figure 4.8: WGMD performance evaluation of pristine membrane A0, single-layer membranes (A1 to A4) and Janus membranes (B1 to B4).

Generally, MOF-modified nanofibrous membranes have been reported to exhibit remarkable stability in MD over extended testing periods. In this study, a 60-hour performance evaluation was conducted on a commercial membrane, a pristine nanofibrous membrane (A0), and the Janus membrane (B3), as illustrated in **Figure 4.9**. The B3 membrane maintained a stable permeate flux of approximately $46 \text{ kg m}^{-2} \text{ h}^{-1}$ with a high salt rejection of 99.99%. This superior performance can be attributed to enhanced surface roughness, which influences membrane hydrophobicity and reduces wettability at the membrane-feed interface. At this interface, the increased roughness, combined with turbulence induced by the feed flow rate, helps disrupt the thermal and

concentration boundary layers. This disruption facilitates the establishment of an optimal temperature gradient across the Janus membrane, thereby improving MD performance [131], [132], [133]. Thermal conductivity is a critical parameter in MD. The thermal conductivity of materials incorporated into the membrane significantly influences the overall thermal conductivity of the membrane. Higher thermal conductivity, particularly at the feed-membrane interface can intensify the temperature polarization effect, thereby reducing the effective mass transfer across the membrane [134], [135], [136]. Aluminum-based metal-organic frameworks (Al-based MOFs) have been reported to possess lower thermal conductivity than PVDF-HFP. Therefore, incorporating these MOFs into the membrane tends to reduce the overall thermal conductivity, which mitigates the temperature polarization effect. This, in turn, enhances mass transfer in Janus membranes and leads to higher permeate flux [134].

The high salt rejection (approaching 100%) observed in the B3 membrane is primarily due to its controlled pore size distribution, which permits only vapor transport while effectively blocking NaCl molecules. This performance is not solely due to an increased water contact angle (WCA), but rather the result of a synergistic effect of pore structure and surface characteristics. In comparison, the pristine nanofibrous membrane (A0) exhibited a lower flux of $25.18 \text{ kg m}^{-2} \text{ h}^{-1}$ and a salt rejection of 95.5% after 60 hours, while the commercial membrane recorded a flux of $21.86 \text{ kg m}^{-2} \text{ h}^{-1}$ with a salt rejection of 99.05%.

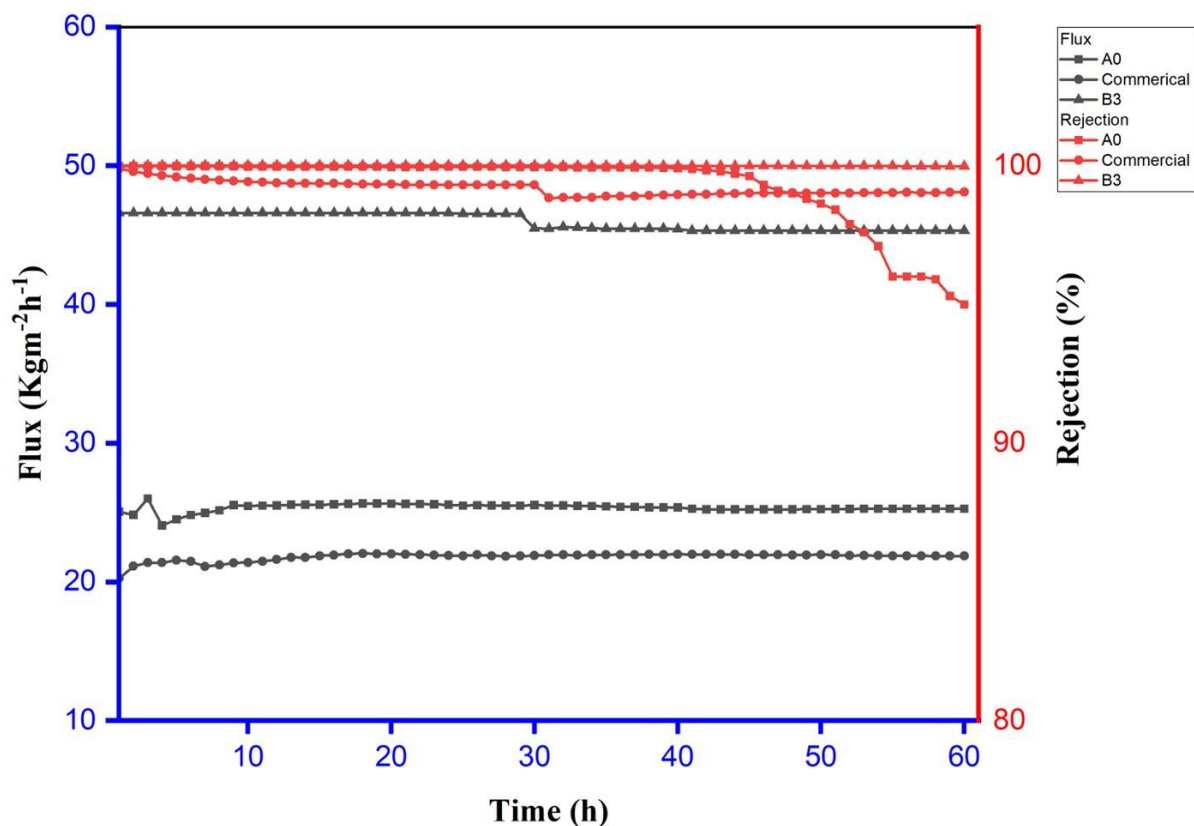


Figure 4.9: Long-term WGMD evaluation of pristine (A0), commercial and Janus membrane (B3).

A comparative summary of the performance of the Janus B3 membrane against previously reported membranes is provided in **Table 4.3**, further demonstrating the effectiveness of the fabricated Janus membranes for MD applications.

Table 4.1: Literature comparisons of Janus membranes fabricated for MD applications.

Hydrophobic/Janus membrane	Fabrication techniques	Flux (kgm ⁻² h ⁻¹)	Saline Rejection (%)	Feed conc. (ppm)	Testing duration	Membrane Distillation type	Reference
CoZn-PVDF-HFP	Electrospinning	20.4	>99.9	35,000	72	DCMD	[125]
AlFu-PVDF-HFP	Electrospinning	15.64	>99.9	35,000	50	DCMD	[134]
MAF-4-PVDF	Electrospinning	27.9	-	35,000	-	DCMD	[137]
PTFE/PVA-AlFu	Coating	45.1	99.9	35,00	48	DCMD	[138]
PTFE/PP-PDA	Coating	>20	-	35,000	-	DCMD	[96]
PVDF/SiO ₂	Electrospinning/ Electrospinning	24.6	99.99	35,000	40	DCMD	[84]
C-PVDF/	Spray-coating	26.55	>99.99	35,000	24	DCMD	[139]
PH-PVA/PAN	Electrospinning/ Electrospinning	15.5	99.99	35,000	20	AGMD	[87]
PVDF/HSiO ₂ -PDA-APTES-TEOS	NIPS/PDA coating	52.6 48.6	99.99	35,000	24 70	DCMD	[70]
PVDF/aPP	Electrospinning/Vacuum filtration	53.1	99.99	35,000	50	DCMD	[140]
PVDF-SiO ₂	NIPS/Spray-coating	7.4	99.99	35,000	10	AGMD	[141]

PVDF-PVA/PAA	Electrospinning/Electrospraying	27	100	35,000	36	DCMD	[73]
PVDF/PDMS- PEI/GA	NIPS/co-deposition	15.7	99.99	35000	36	DCMD	[142]
PVDF/PP/SMMs- PEI/DA/SMMs	Electrospinning/NIPS/ Electrospinning	50-70	99.99	-	95	DCMD	[143]
PVDF-HFP-MOFsA/ PVDF- HFP- MOFs-B	Electrospinning/ Electrospinning	45.6	99.95	38,000	60	WGMD	This work

CHAPTER 5

GECKO-INSPIRED SURFACE ENGINEERED MULTILAYER JANUS MEMBRANE FOR EFFICIENT DESALINATION OF HIGHLY SALINE WATER IN MEMBRANE DISTILLATION

5.1 Experimental sections

5.1.1 Materials

Polyvinylidene fluoride (PVDF) ($M_w \sim 534,000$ by GPC, powder), polyetherimide (PEI), lithium chloride (LiCl) (≥ 99.98 trace metal basis), copper (ii) oxide (CuO) (nanopowder, <50 nm particle size), poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) ($M_w \sim 400,000$), poly(acrylonitrile) (PAN) ($M_w \sim 150,000$), Dimethylformamide (DMF, 99.9%), N-methylpyrrolidone (NMP), and 2-propanol (Isopropanol, 99.9%) were all purchased from Sigma-Aldrich and used without any modifications. De-ionized water from a laboratory-sized Millipore system was used in membrane fabrication and testing.

5.1.2 Single (active) layer membrane fabrication

A predetermined amount of PVDF powder was weighed and oven-treated at 60°C for 1 hour to eliminate any residual moisture. From this treated powder, 3.4 g was measured and added to a 2 wt.% LiCl solution prepared in DMF. The mixture was continuously agitated at 200 rpm for 24 hours to produce a homogeneous dope solution with a final PVDF concentration of 17 wt.%. The resulting dope solution was allowed to degas at room temperature before being cast on a 400-grit sandpaper casting substrate using a doctor blade. To ensure efficient phase separation, the solution was cast at a thickness of $120\ \mu\text{m}$ and immediately immersed in a coagulation bath containing a warm water-isopropanol mixture (80:20 v/v) maintained at a temperature of $35 \pm 0.3^\circ\text{C}$. After

successful phase inversion, the membrane was cleaned in deionized (DI) water for 24 hours while still attached to the substrate to remove residual solvents (**Figure 5.1a**). After drying at room temperature, the resulting membrane, referred to as M1, was subsequently detached from the sandpaper substrate for further processing. This method of using sandpaper casting substrate provided uniform flat sheet unsupported porous membrane as reported in other studies [144], [145].

5.1.3 Multiple layer Janus membrane fabrication

The fabricated single-layer flat-sheet membrane, designated as M1, was placed on a flat plate with the skin facing up. A composite solution, prepared by mixing CuO and PVDF-HFP in a 5:5 wt.% ratio in a DMF solvent, was loaded into a 10 mL syringe for electro-spraying. The solution was sprayed for 15 minutes at a high voltage of 22.0 kV and a flow rate of 1.5 mL⁻¹h. The 15-minute spraying duration was determined as optimal based on the surface morphology and wettability investigation conducted at intervals of 15, 30, and 60 minutes. After spraying, the resulting membrane, labeled M2, was dried in an oven at 60°C. Similarly, another membrane (M3) was fabricated for comparison using the same spraying conditions but with a composite solution of PAN and CuO in the same 5:5 wt.% ratio.

For the support layer deposition, membranes M1, M2, and M3 were subsequently mounted onto a rotating drum covered with aluminum foil in an electrospinning apparatus to create Janus membranes. The membranes obtained after electrospinning were labeled as M4, M5, and M6, respectively. A 20 wt.% PEI solution, prepared by dissolving 2.0 g of PEI polymer in 8.0 g of NMP, was used for fiber spinning. Electrospinning was conducted for 3 hours with the following parameters: a flow rate of 1.0 mL⁻¹h, a voltage of 13.5 kV, and a drum rotation speed of 100 rpm

(Figure 5.1b). To evaluate the role of the interfacial layer, the M6 membrane was fabricated with PVDF active layer and PEI support layer without any electrospun layer in between. A summary of the fabricated membranes and their compositions is provided in Table 5.1.

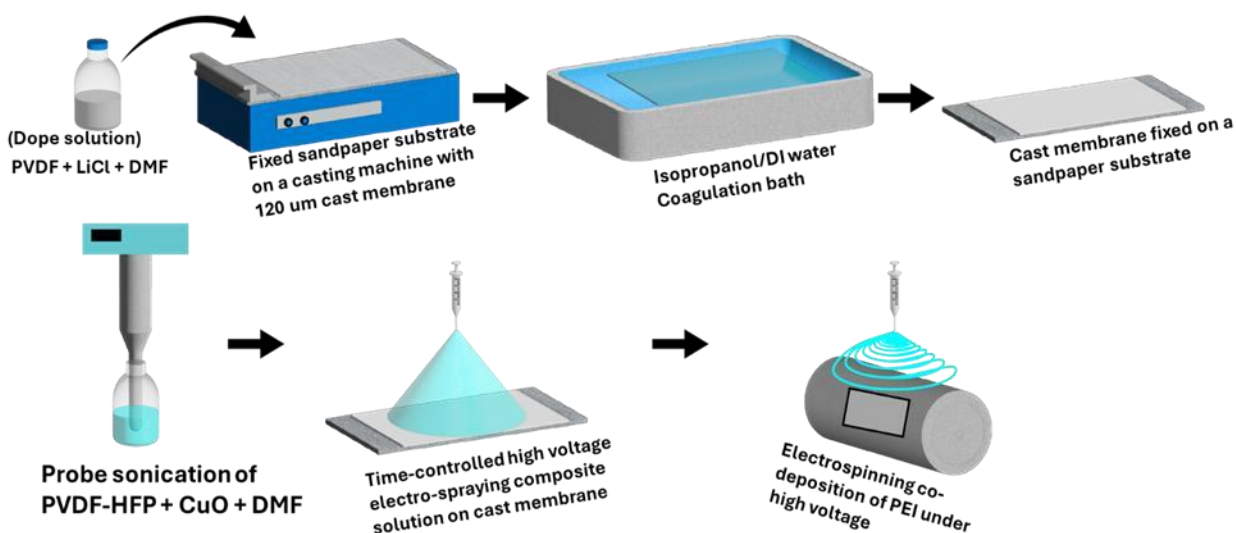


Figure 5.1: a) Schematic of a) single layer and b) multi-layer membrane fabrication.

Table 5.1: Fabricated membranes and compositions.

Membrane	Composition	Hydrophobic layer (wt.%)	Intermediate layer (wt.%)	Hydrophilic layer (wt.%)
M1	Flat sheet PVDF	PVDF		
M2	PVDF-PH/CuO	PVDF	PVDF-HFP+CuO	
M3	PVDF-PAN/CuO	PVDF	PAN+CuO	
M4	PVDF- PH/CuO-PEI	PVDF	PVDF-HFP+CuO	PEI
M5	PVDF-PAN/CuO-PEI	PVDF	PAN+CuO	PEI
M6	PVDF/PEI	PVDF	-	PEI

5.2 Membrane Characterization

5.2.1 Surface characteristics and wettability

The surface morphology of all membrane layers was analyzed using scanning electron microscopy (SEM, JEOL JSM-6610LV). Prior to imaging, the membrane surface was sputter-coated with gold using a DII-29030SCTR smart coater to ensure conductivity. SEM imaging was performed at varying magnifications to capture detailed morphological features. To further investigate the elemental composition of the membrane layers, energy-dispersive spectroscopy (EDS) was conducted in conjunction with SEM. Additionally atomic force microscopy (AFM) (Nanosurf) was also used to evaluate the membrane surface topography and surface roughness.

The wettability of the membrane surfaces was evaluated using water contact angle (WCA) measurements. The WCA was determined using the sessile drop method, where approximately 5 μL of water droplet was dispensed and measurement was performed automatically using Famas software. The average water contact angle was calculated based on measurements taken at several points on the membrane surface.

5.2.2 Membrane bulk properties

The hydrophobicity of fabricated membranes was also assessed through liquid entry pressure (LEP) using a custom laboratory setup designed to measure the penetration pressure of water. The LEP was determined by gradually applying pressure to an enclosed water chamber in contact with the membrane surface, following the methodology described by Smolder and Franklin [45]. The LEP corresponds to the minimum pressure at which water penetrates the membrane pores and

forms visible droplets on the opposite side. The membrane thickness was measured using a LITEMATIC VL-50A precision measurement device (Mitutoyo, Japan) at multiple points to ensure accuracy and consistency. The pore size distribution (PSD) of the membranes was analyzed using a porometer (3Gzh, Quantachrome Instruments, USA). The measurement involved forcing ethanol out of the membrane pores with controlled gas pressure, allowing the PSD to be determined. A discovery hybrid rheometer HR30 from TA instrument with a tensile deformation module was used to assess the mechanical stability of developed membranes. Samples were clamped meticulously and tested at a constant rate of 50 μ /sec. Thermogravimetric analysis (TGA) was carried out with liquid nitrogen heating at a rate of 10°C per minute. The thermal sensitivity fabricated nanofibrous membranes were examined at temperatures ranging from 10°C to 800°C.

5.3 WGMD performance evaluation

The performance of the fabricated membranes was assessed using a laboratory-scale water gap membrane distillation system, as illustrated in **Figure 4.2**. The feed solution, consisting of a 70,000 ppm NaCl was heated to approximately 70°C using a Julabo 601F heater tank connected to the membrane distillation (MD) module. The opposing side of the module, containing deionized water, was connected to a chiller maintained at 20°C to cool a conduction plate. Water vapor permeating through the membrane pores is condensed in the water gap touching the plate. Support with perforations was utilized to rest the membrane and provide the needed gap in the module. Flow meters were installed on both the feed and permeate sides to regulate and monitor flow rates into and out of the system. Detail test conditions of WGMD are provided in **Table 5.2**. The net distillation permeate flux was calculated using **Equation 15**, which incorporates the weight of the collected water, the effective membrane area, and the duration of test. The weight of permeated

water was measured using a high-precision Ohaus PR2200 weighing scale connected to a computer for real-time data acquisition. The salt rejection performance was evaluated using a Hanna HI5321 conductivity/TDS device. The saline rejection percentage was calculated using **Equation 16**, which relates to the feed and permeate conductivity measurements recorded per minute. The permeate flux ‘J’ in (kg/m²h) is calculated as:

$$J = \frac{M}{A \cdot t} \dots 15$$

Where M is the mass of the permeate collected through the membrane in kg, A is the effective membrane area in m², and t is the time taken for the testing in hours.

$$S.R (\%) = \frac{C_f - C_p}{C_f} \times 100 \dots 16$$

Where S.R is the salt rejection (%), C_f and C_p are the concentration of feed and permeate in ppm respectively.

Table 5.2: Detailed WGMD testing conditions.

MD test conditions	Values
Feed temperature	70 ± 0.5 °C
Feed flowrate	0.8 ± 0.1 L min ⁻¹
Coolant temperature	20 ± 0.5 °C
Coolant flow rate	2.0 ± 0.1 L min ⁻¹
Effective membrane area	7.3 × 10 ⁻⁴ m ²

Water gap volume	4 cm x 4 cm x 0.5 cm
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5.4 Results and discussion

5.4.1 Membrane structure analysis, surface morphology, surface chemistry and wettability

5.4.1.1 Membrane architecture

The objective of this study as stated earlier was to integrate an interfacial layer that physically joins a Janus membrane's active hydrophobic layer and hydrophilic support layer. To optimize separation performance, the membrane interface is engineered to reduce mass transfer resistance and increase layer-to-layer adhesion. Although research on interfacial interactions in Janus membranes for MD applications is still in its early stages, most studies have concentrated on adhesion processes inspired by mussels [109]. These investigations, however, frequently fall short in providing thorough explanations of interfacial interactions.

Despite showing promising results for Janus membranes in MD, gecko-inspired adhesion mechanisms are still mostly unexplored because of the difficulty in fabrication, material selection and elucidating adhesion mechanisms. In the past, capillary action was thought to be responsible for Gecko foot adhesion, and the Young-Dupré equation was linked to adhesion energy (W) [146]. According to Young's equation, the water contact angle (WCA) and adhesion energy are inversely related, with higher θ values denoting less adhesion. This theory was later disproved, though, because while diverse surfaces like glass and Gecko feet have different adhesion despite their wettability, identical surfaces show equal wettability. This disparity was explained by additional research, which revealed that Gecko adhesion is unaffected by surface chemistry or WCA. Rather, it relies on surface area and van der Waals interactions. Gecko adhesion strength is determined by

the surface area of interaction rather than surface chemistry or wettability, according to a hydrophobic and hydrophilic polarizable physical surface model [147]. Motivated by these results, this study developed an interfacial layer with “Gecko-state” wettability by simulating the hydrophobic nature and high surface roughness of Gecko feet. A composite solution was electrosprayed onto the PVDF membrane (M1) skin surface to deposit interfacial layer to improve interaction with the hydrophilic PEI support. A net design architecture of the Janus multiple layer membrane is highlighted as shown in **Figure 5.2** below.

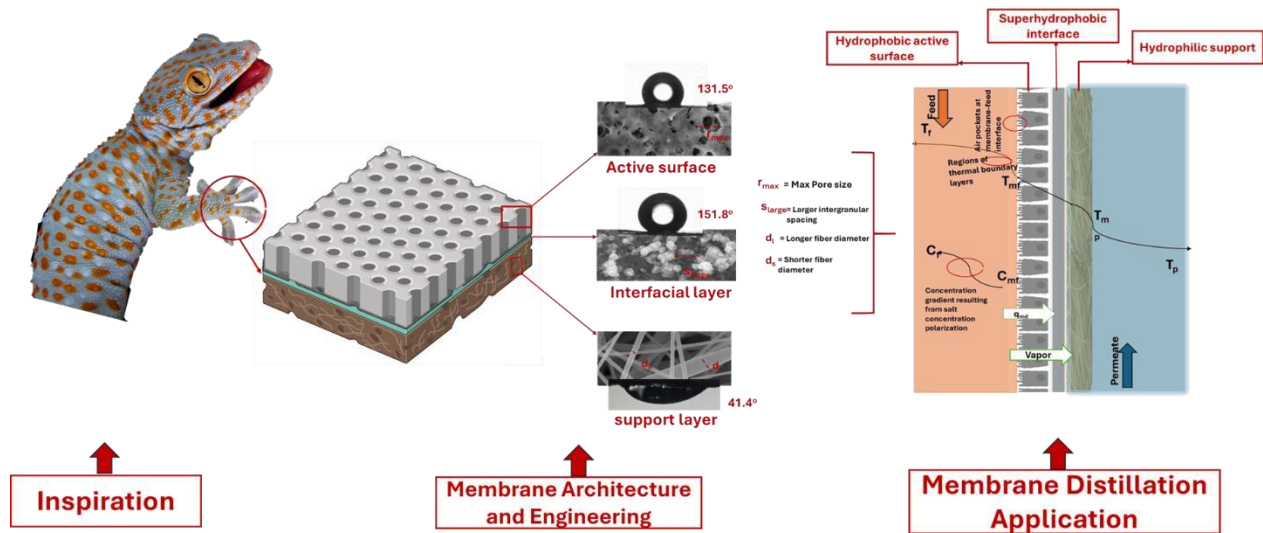


Figure 5.2: Architecture of fabricated Janus membrane.

5.4.1.2 Surface morphology

The morphology of the membrane fabricated via NIPS technique is dependent on several factors, such as the casting substrate, the concentration of the polymer, the mixing thermodynamics, and the precipitation kinetics [148]. The PVDF membrane (M1) developed in this work displayed rough textures (**Figure 5.3a & 5.3b**) due to sandpaper as casting substrate. The substrate's abrasive

effect produced basins, which resulted in a highly porous surface. Phase exchange processes are known to be accelerated by such surface features because they increase the surface area available for solvent-nonsolvent exchange, forming more troughs and locations for water ingress [144][145]. The cross-sectional image of M1 membrane as shown in **Fig. 5.3c** showed thin sheet with dense skin layer and finger-like characteristics from the NIPS process [149]. This structure forms due to thermodynamic instabilities at the solvent-nonsolvent interface near the substrate during immersion in the coagulation bath. Rapid solvent diffusion into the nonsolvent phase initiates pore nucleation, while interactions between the pore-former (LiCl) and the nonsolvent influence pore interconnectivity and the resulting finger-like structure [150]. A uniform thin unsupported PVDF membrane with a rough and porous surface depicting water contact angle of 131.5° (**Figure 5.3d**) was obtained with the help of sandpaper casting substrate, suitable for secondary layer deposition.

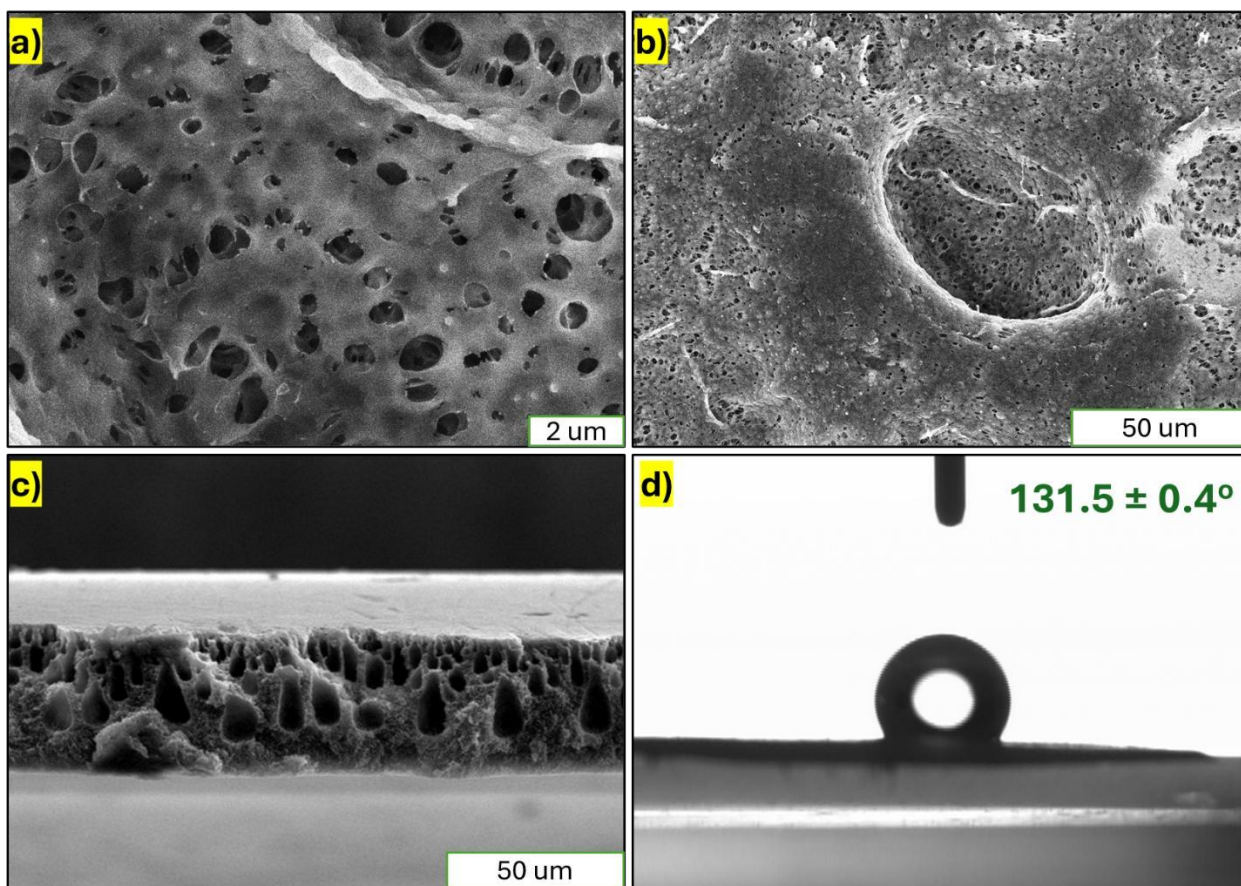


Figure 5.3: (a, b) SEM surface image of membrane M1 at different resolutions, c) cross sectional SEM image of M1 and d) water contact angle measured on textured M1 surface.

As shown earlier in **Figure 5.1**, subsequent electro-spraying and electrospinning techniques were employed to develop the Janus multilayer membranes. As a result, the other side of membrane surface M1 (skin side) has undergone various morphological changes as depicted above in **Figure 5.3**. Typically, after electro-spraying the surface of the flat sheet membrane exhibited pronounced roughness, characterized by granular and spherical features with uniform particle distribution (**Figure 5.4 a1 & 5.4 a2**).

The granular particles also demonstrate uneven height distribution between gaps, a surface characteristic closely mimicking the tiny bristle structure of Gecko feet. The presence of

microscale gaps and rough surface facilitates air trapping and mechanical locking between the membrane surfaces. The superhydrophobic nature of this surface is shown in **Figure 5.4a3**, confirmed through contact angle of water droplet. On the other hand, the intermediate layer involving hydrophilic additive (PAN+CuO) in M3 membrane demonstrated particle distribution in fibrous morphology providing roughness and hydrophilic surface characteristic (**Figure 5.4 b**). Building on these results, the support layer was deposited by electrospinning polyetherimide (PEI) fibers onto the M1, M2 and M3 membrane surfaces. This sequential process produced a Janus multilayer membrane, designated as M6, M4 and M5 respectively. The support layer demonstrated a highly interconnected fibrous structure with uniform size distribution, as shown in **Figure 5.4 c1**. (Size distribution of particles and fibers are shown in **Figure 5.5**). Furthermore, the PEI fibers demonstrated hydrophilic affinity from the water contact measured on the fiber surface (**Figure 5.4 c3**). It's worth stating that the M4, M5 and M6 membranes have the same architecture, only that M4 and M5 contain electrosprayed while M6 don't.

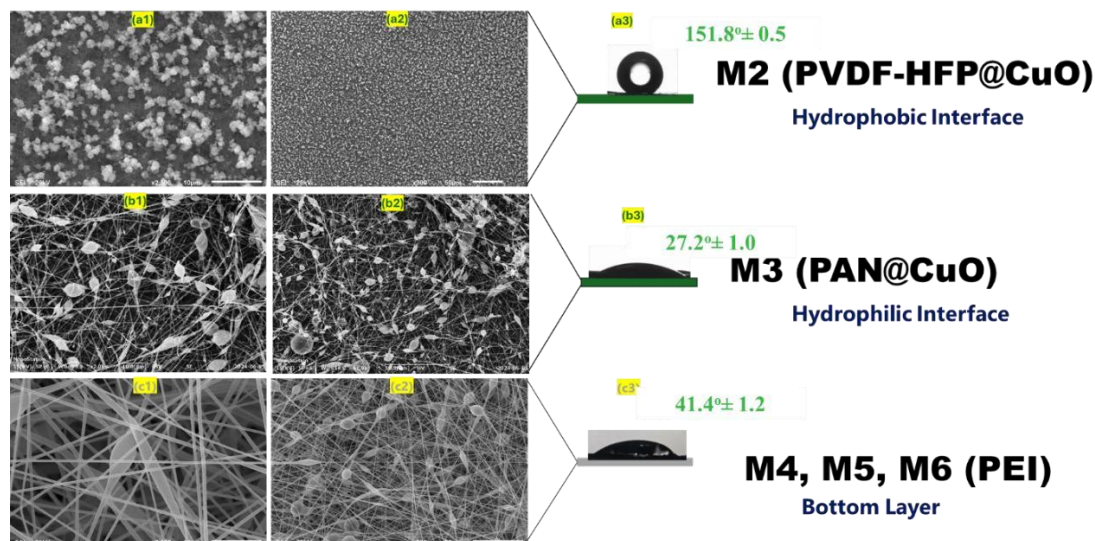


Figure 5.4: (a1, a2) Various resolution SEM surface imaging of M2 membranes (interfacial layer surface, a3) water contact angle value of optimized M2 surface (b1, b2) surface SEM images of M3 membrane at various resolutions, b3) water contact angle value of M3 surface, (c1 and c2)

various resolution SEM surface imaging of support/bottom layer (M4, M5 and M6) membranes, and c3) water contact angle of the bottom layer.

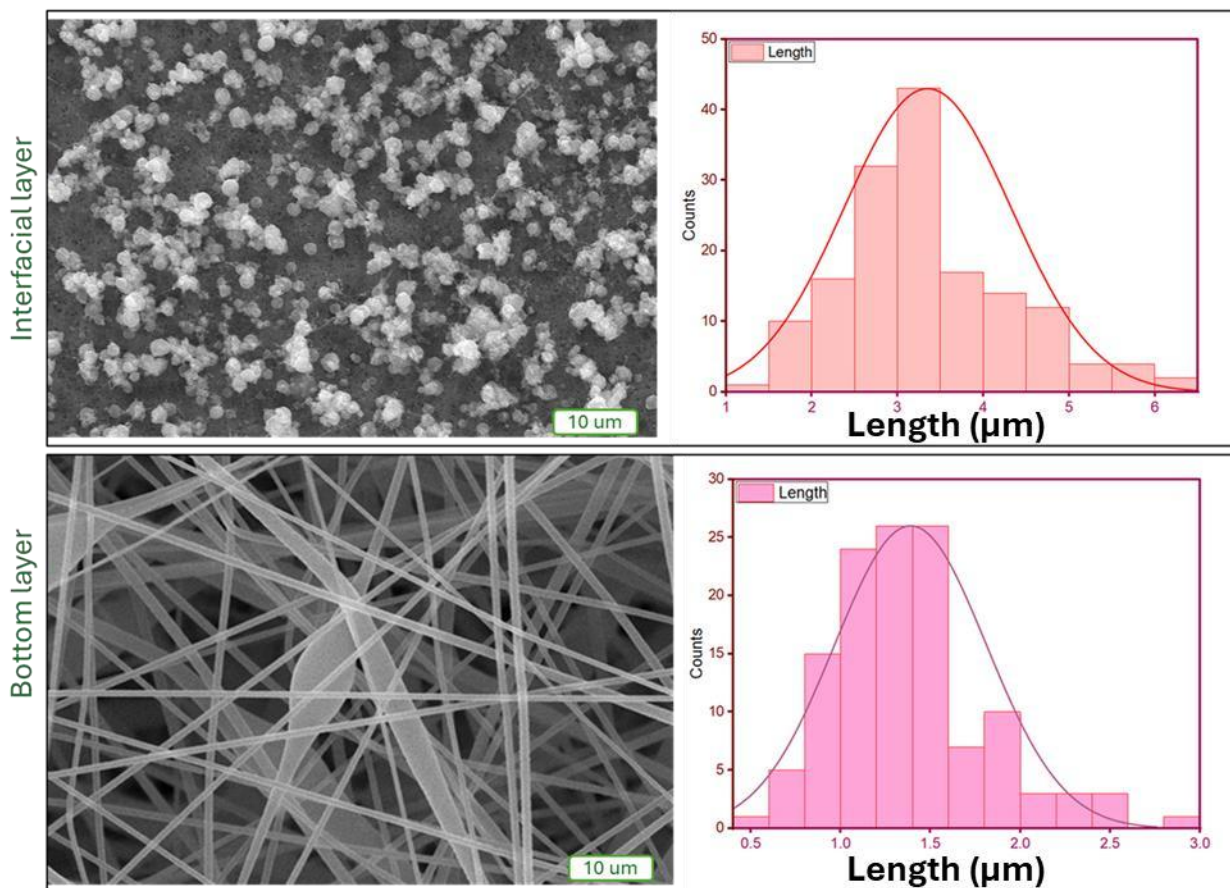


Figure 5.5: Size distributions of the electrosprayed interfacial layer (M2) and the electrospun fibers support layer (M4).

4.5.1.3 Surface wettability

The WCA recorded from membranes surfaces depicted above in **Figures 5.3 and 5.4** depends on several variables, such as the membrane's surface chemistry, topography, roughness, and surface energy [151]. A typical PVDF membrane fabricated through NIPS method in water as the coagulation bath exhibits a WCA value of 77° [152]. A typical glass substrate used to cast PVDF membrane using NIPS conditions in this work showed a WCA of less than 90 degrees (**Figure**

5.6).



Figure 5.6: WCA obtained from glass substrate cast PVDF membrane.

The developed membrane (M1) precipitated using a mixture of non-solvents on a sandpaper substrate displayed a significantly greater WCA of about 131.5° . The increase in hydrophobicity is reasonable considering published research that demonstrated the substantial impact of coagulation media and substrate on membrane surface morphology and, consequently, membrane hydrophobicity [151], [153]. The mimicked rough surface of M2 displayed a superhydrophobic nature with WCA of 151.8° , which gives this surface the ability to “self-clean”, a similar characteristic of a Gecko-feet. The interaction between the water droplet and the membrane surface in this case shows the Cassie-Baxter state. However, various measurements of WCA on the electrosprayed interfacial layer were taken as optimization parameter and displayed in **Figure 5.8**,

the WCA was found to decrease with increase in spraying time. The water contact angle (WCA) of membranes is influenced by surface roughness and molecular interactions. Increased roughness from longer spraying time of the composite solution of PVDF-HFP and CuO, enhances air pockets at the membrane-water interface. However, the hydrophilic nature of the CuO dominates, reducing WCA despite the observed increased roughness. Because of the PAN and CuO particles synergistic influence, the M3 surface displayed a hydrophilic character with a WCA value of 27.2° , whereas the WCA angle of the bottom PEI fiber layer in M4, M5 and M6 showed a value of 41.4° depicting Wenzel state due to the roughness induced by the fibers.

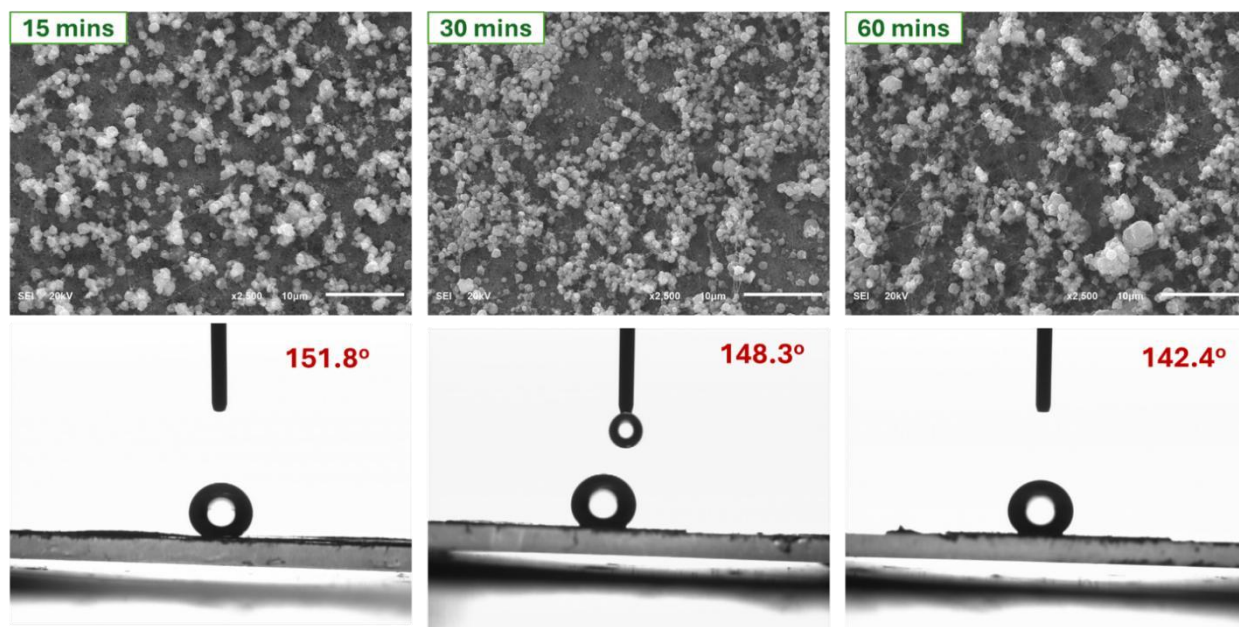


Figure 5.8: Effects of electro-spraying time on surface morphology and interfacial wettability.

5.4.1.4 Surface roughness Analysis

To confirm the surface roughness on critical surfaces of the membranes responsible for hydrophobicity and interfacial adhesion, the average surface roughness (Ra) was obtained from the AFM imaging over a given sampling length. This value was related to the microporous structure

and uniformity on the surface of the membranes [71]. Notably, from **Figure 5.8 a**, M1 was discovered to have a R_a value of 148 nm, indicating the influence of sandpaper on the surface roughness due to observed textures in SEM images of the membrane in **Figure 5.3** above. Although the values of R_a don't fully explain the dependency of surface roughness on WCA values, the higher roughness in PVDF membrane (M1) is a key point in explaining the higher WCA [154]. However, it's worth mentioning that the texture and surface porosity on M1 membrane introduced water enclosed air pockets, producing an air-water droplet interface, essential for increasing the WCA of the surface [144], [155].

The rough morphology of M2 membrane surface was quantitatively supported by the AFM data displayed in **Figure 5.8 b**, which shows an average surface roughness (R_a) of approximately 665 nm. The potential interfacial area for fiber interlocking is maximized by the textured landscape depicted in the 3d topographic image. As can be observed, critical surface characteristics are represented by the peaks and valleys in the AFM picture, where fibers can mechanically engage and embed themselves into the granule-formed crevices.

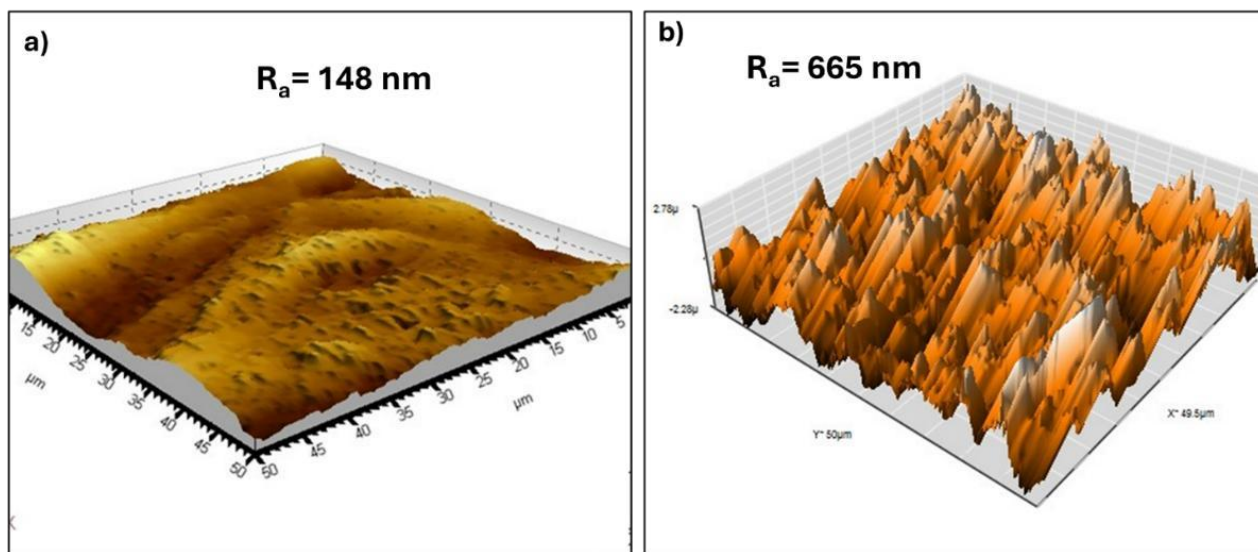


Figure 5.8: AFM surface topography of M1 membranes b) AFM surface topography of interfacial layer (M2 membrane surface).

It is noteworthy that surfaces with more sprayed duration produced higher surface roughness (**Figure 5.9**). However, the main reason for selecting 15-minute spraying period was the uniform distribution of particles and hydrophilic effects of CuO at higher spraying duration.

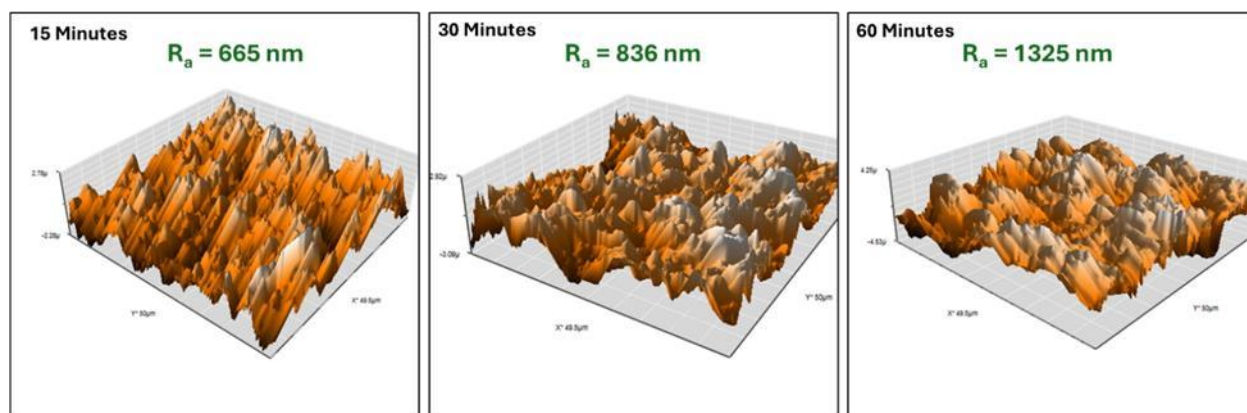


Figure 5.9: Influence of electro spraying time on the roughness of interfacial layers in M2.

4.5.1.4 Surface chemistry analysis

The FT-IR spectra obtained from various layers of the proposed membrane samples is shown in **Figure 5.10**. The sandpaper cast PVDF membrane represented M1 and made the top layer and similar at the top for all other membranes. PEI fibers made up the bottom layers in membranes M4, M5 and M6, and the intermediate layers comprising the M2 and M3 membranes with composites of PVDF-HFP+CuO and PAN+CuO layers respectively. In M1 membrane, the peaks formed at around 1072 cm^{-1} and 1278 cm^{-1} were attributed to the α - and β - phases which are mostly found in PVDF membrane surface fabricated through NIPS method. The highly intense peaks occurring at around 1171 cm^{-1} correspond to the C-F bonds which are highly distributed within the polymer chain and the peaks just below 880 cm^{-1} indicate the presence of C-C bonds [156] [157].

In M2 membrane surface, the peak attributed to -CF_2 stretching modes appeared at 1175 cm^{-1} [158]. For PVDF-HFP, this peak was observed at 1168 cm^{-1} (**Figure 5.11**). A susceptible reason for this is attributed to the interaction between the polymeric matrix and the dispersed CuO [159]. This is like the findings explained elsewhere in the literature where additives in a polymeric PVDFHFP matrix interact with the bonds and correspondingly results in peaks shift [119]. The peak present in at around 2243 cm^{-1} in M3 corresponds to $\text{-C}\equiv\text{N}$ of PAN polymer while the vibrations noticed at 2984 cm^{-1} and 1666 cm^{-1} are attributed to $\text{sp}^3\text{ C-H}$ and amide group bonds respectively [160], [161]. However, considering the surfaces of M4, M5 and M6 which are spectra of PEI fibers, stretching and bending motions of -C-N bonds are shown by the peaks at 1359 cm^{-1} and 746 cm^{-1} . Finally, the different etheric functional groups in polyetherimide are confirmed by the peaks formed at 1273 cm^{-1} and 1235 cm^{-1} [162].

It is worth nothing that certain similarities were observed in M1, M2 and M3 membranes as can be seen in Fig 5. M1 membrane, which was PVDF membrane, predominately contains C-F as the only free fluorinated carbon bond. In M2 membrane, various fluorinated carbon bonds are present such as the CF_2 and CF_3 . This is reflected in the intensity of the bond stretching observed above 1170 cm^{-1} in both membranes. Furthermore, the spectra of M1 and M3 exhibit notable similarities. Given the short electrospraying duration, full surface coverage of PAN + CuO is unlikely (in M3). Consequently, ATR-mode FT-IR analysis of M3 may predominantly reflect the spectra of M1, with additional peaks corresponding to the presence of PAN on the surface.

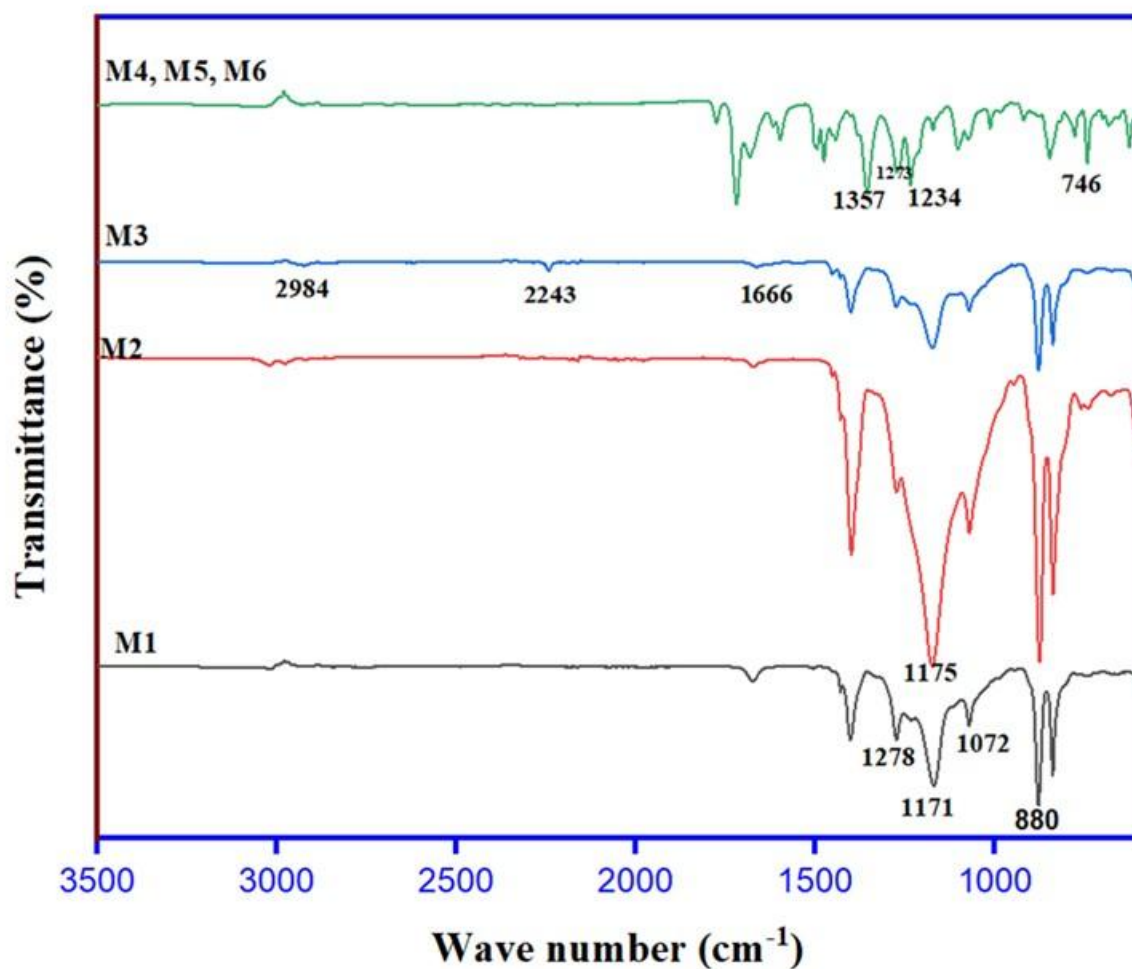


Figure 5.10: Surface analysis from FT-IR spectra of fabricated membranes (M1 is the sandpaper casted membrane before modification, M2 and M3 are modified membrane with electrospun PVDF-HFP@CuO and PAN@CuO respectively, M4, M5 and M6 are Janus membranes with electrospun PEI).

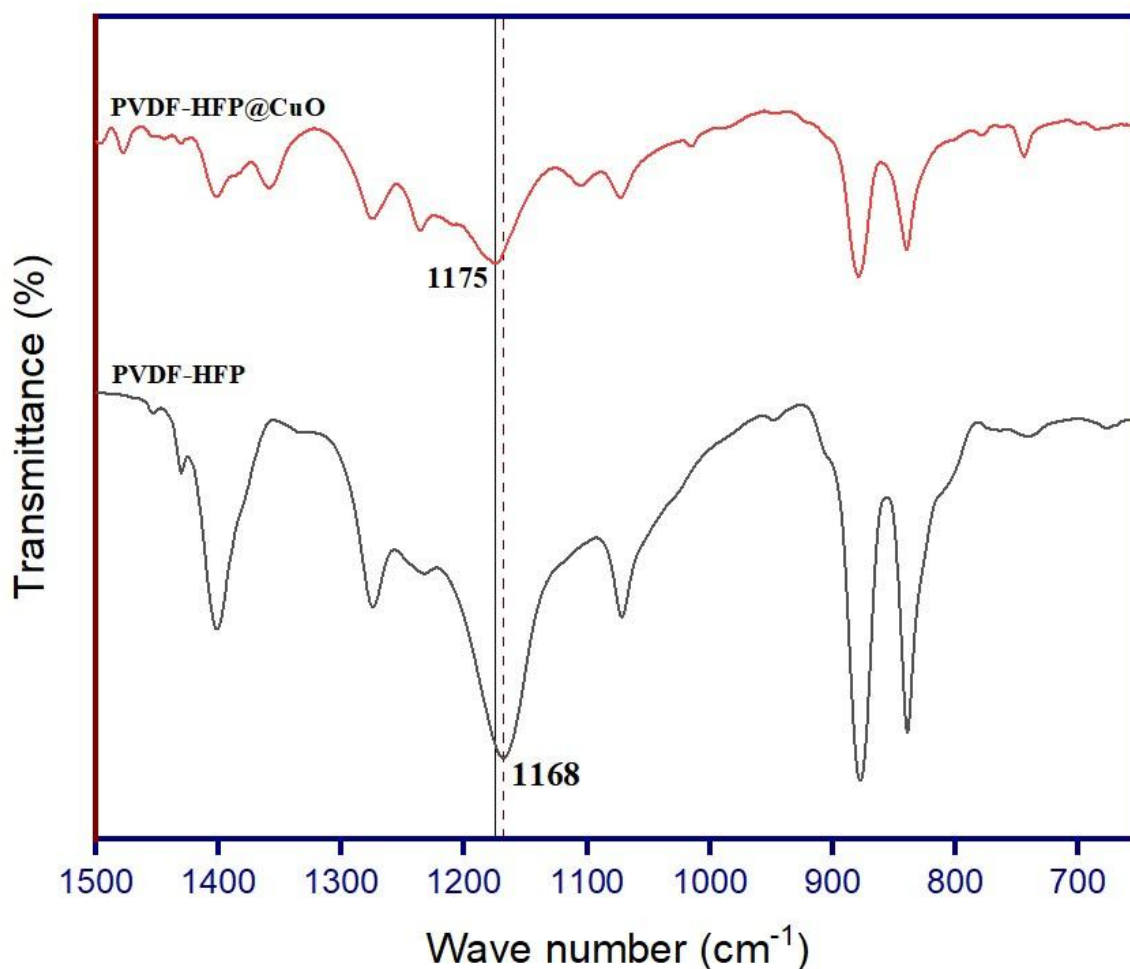


Figure 5.11: $(-\text{CF}_2)$ stretching modes up-field shift from 1168 cm^{-1} denoted by the dash brown line to 1175 cm^{-1} denoted by solid black line.

5.4.2 Janus membrane interface analysis (interlocking mechanism)

This study investigated the interaction between the active hydrophobic surface and the support hydrophilic layer of a multi-layer Janus membrane. The weak interaction between the NIPS-cast membrane and the electro-spun PEI layer often results in delamination, compromising the membrane's performance in hypersaline treatment. To address this, a gecko-inspired adhesion

mechanism was developed to engineer a robust interface between these layers. To achieve the desired interface properties, a highly porous, thin active PVDF surface was developed using substrate-induced NIPS. The interface was further engineered using PVDF-HFP and CuO, leveraging their highly hydrophobic and polarizable nature. Measurements from SEM images (**Figure 5.5**) using ImageJ software revealed that the average spacing on the electro-sprayed particles surface was approximately 3.47 μm , while the average diameter of the electrospun PEI fibers was 1.30 μm . This size ratio allowed the M2 surface to effectively accommodate, penetrate, and anchor the nanofibrous layers. The penetration and anchoring of fibers were further facilitated by the strength of the electrospinning potential, which ensures sufficient ejection and deposition force. To validate the importance of surface engineering, the hydrophilic, polarizable membrane (M3) composed of PAN and CuO particles demonstrate possible weak interaction due to the formation of beaded thin fabric structure with high packing irregularities typically due to low concentration and higher operational voltage [163], [164]. The resulting low wettability of this layer also contradicted the gecko-type adhesion behavior, further highlighting the significance of surface modifications introduced in M2.

The adhesion behavior of the M4 multilayer Janus membrane was evaluated using a peeling test. Physical force was applied to peel the PEI layer deposited on the rough M2 surface, and the peeledup surface was analyzed via SEM to understand the proposed adhesion mechanism (**Figure 5.12 a1 & 5.12 a2**). The results revealed that the fibrous PEI network was intermingled with the rough, granular surface of the M2 membrane. Several factors contributed to the observed adhesion mechanism including mechanical action, surface roughness enhancement and frictional forces (**Figure 5.12 b**). To begin with, multiple contact points could be observed from PEI nanofibers anchored and held fixed within the textured sprayed surface which can improve the mechanical

strength of this physical interaction. Also, the granular structure of the electro-sprayed particles fixed on the M1 surface provided a high surface area that can enhance the penetration of the deposited fibers leading to stronger physical adhesion. Another reinforcement worthy of explanation is the frictional force that enhances the resistance of fibers shearing, sliding or detaching from the interlocked points, a feature like the gecko-type adhesion. The FTIR analysis of peeled interface of the Janus membrane indicated a plethora of peaks belonging to both PVDFHFP in electrospayed layer and PEI fibers from the support (**Figure 5.13**). Furthermore, the interaction of fibers and particles in the interfacial zone was also confirmed from the WCA shown in **Figure 5.12 a3** which drops to 112.2° from 151.8° due to the anchored hydrophilic PEI fibers.

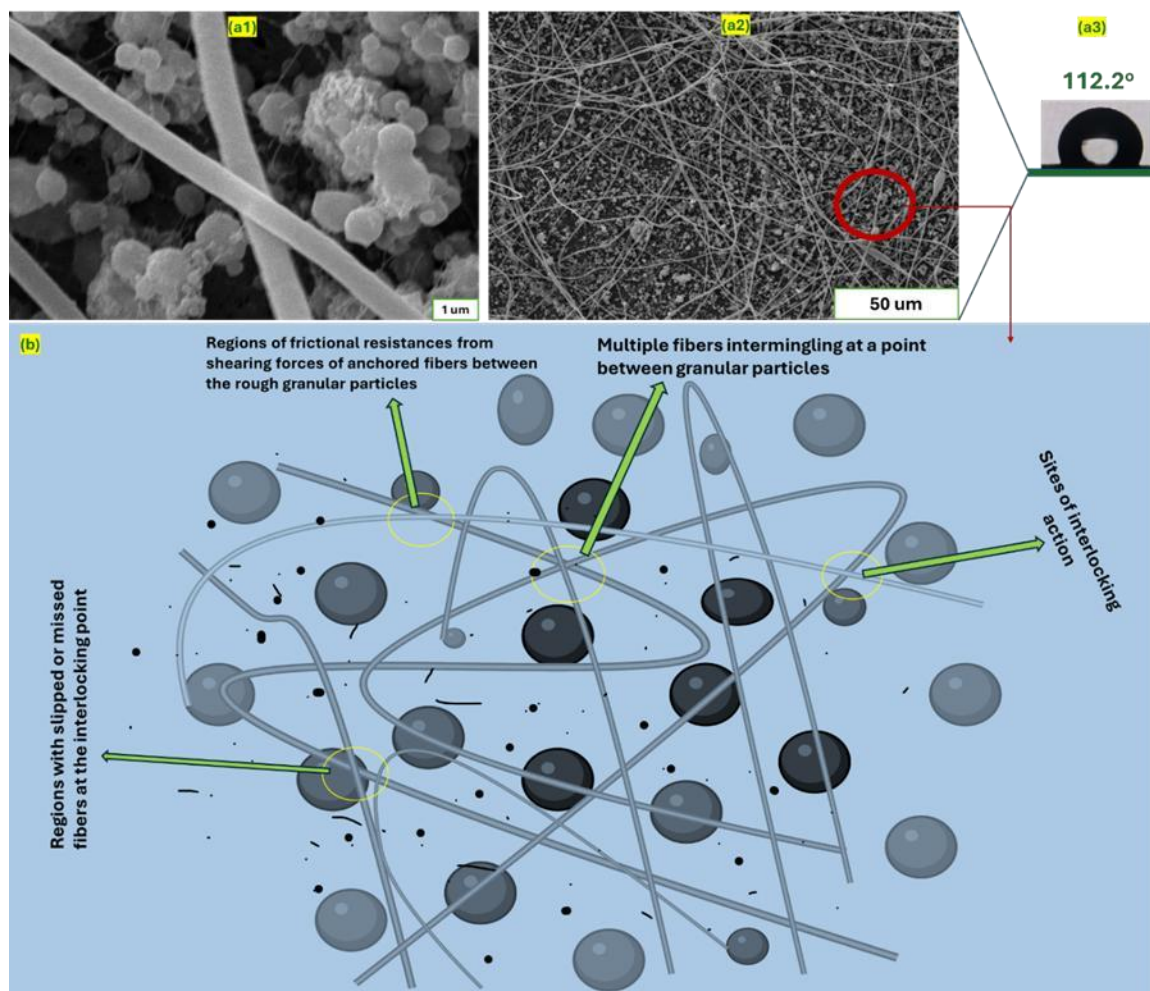


Figure 5.12: (a1, a2) SEM images of peeled Janus membrane highlighting interlocked fibers in the highly rough interface a3) water contact angle of the peeled surface c) schematic explanation of various interactions at the Janus membrane interface.

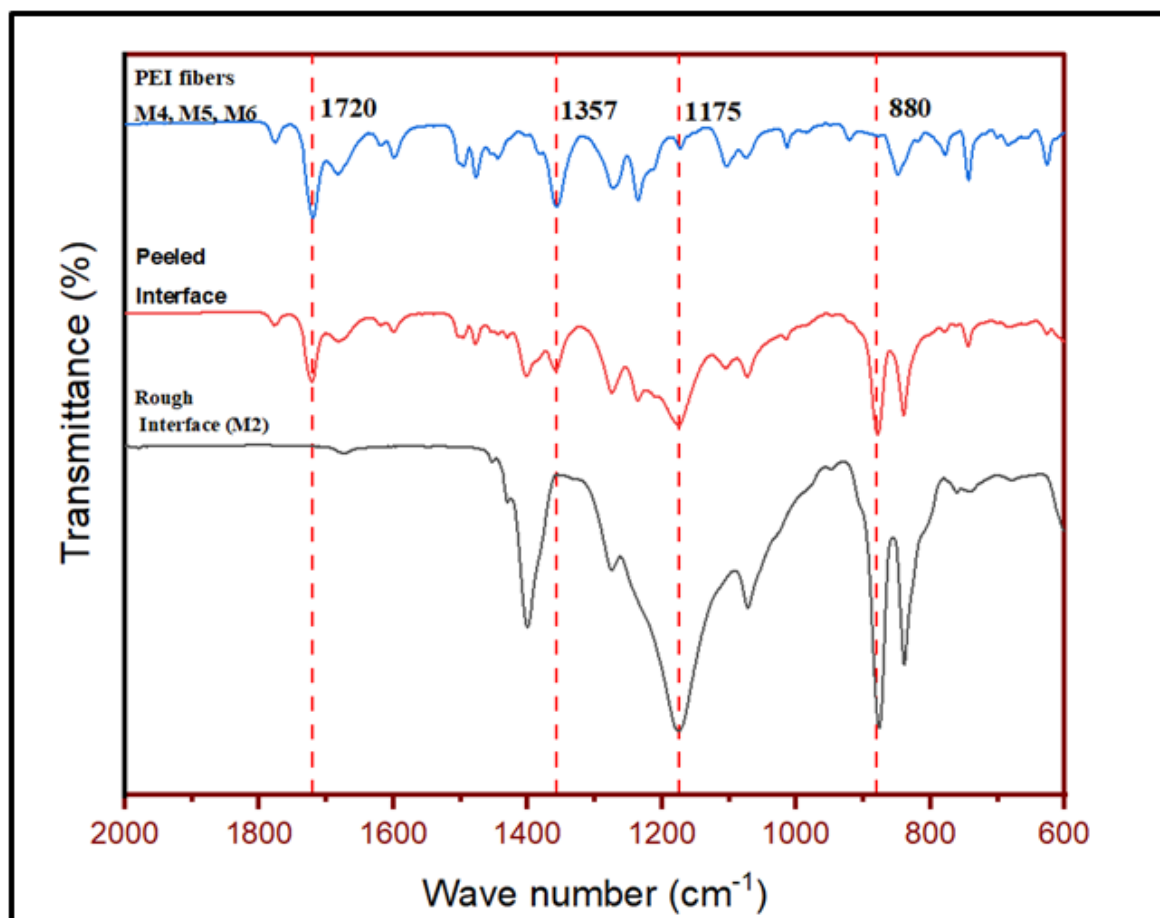


Figure 5.13: FT-IR analysis of the peeled interface of Janus membrane showing plethora of peaks belonging to both PVDF-HFP and PEI fibers which further supports the claims of fibers interlocking action at the interface.

For comparison and provision of supplementary evidence to support the claims on the interlocking mechanism as seen from the peeled surface of M4 membrane, the surfaces of M5 and M6 membranes were peeled and studied. As can be seen from the surface imaging in **Figure 5.14**, none of either M5 or M6 showed this interlocking action.

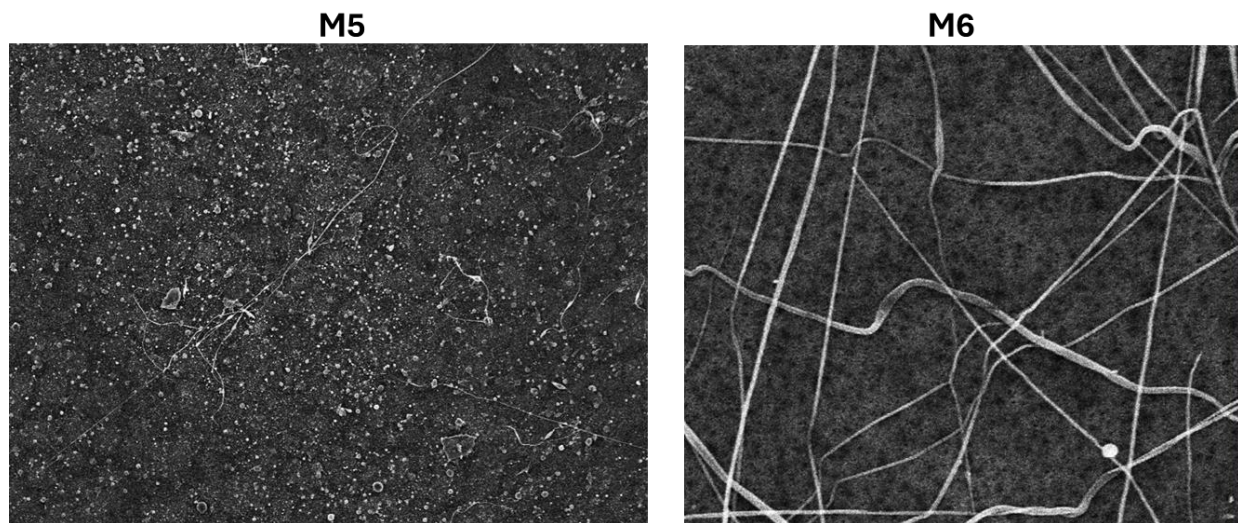


Figure 5:14: Peeled surfaces of M5 and M6 Janus membranes showing poor interactions between the fibers and the bare membrane surfaces.

The Janus multilayer membrane (M4) cross-sectional image is shown in **Figure 5.15** which shows distinct morphologies between the layers and interlocking structures. EDS elemental composition and mapping of the interface between hydrophobic and hydrophilic layer shows distribution of the main components of the PVDF (C, F) and PEI (C, N) polymer and presence of CuO particles at the interface. Furthermore, the EDS mapped images show a sharp change in the elemental distribution (especially F) which verifies the interfacial region in the Janus membrane.

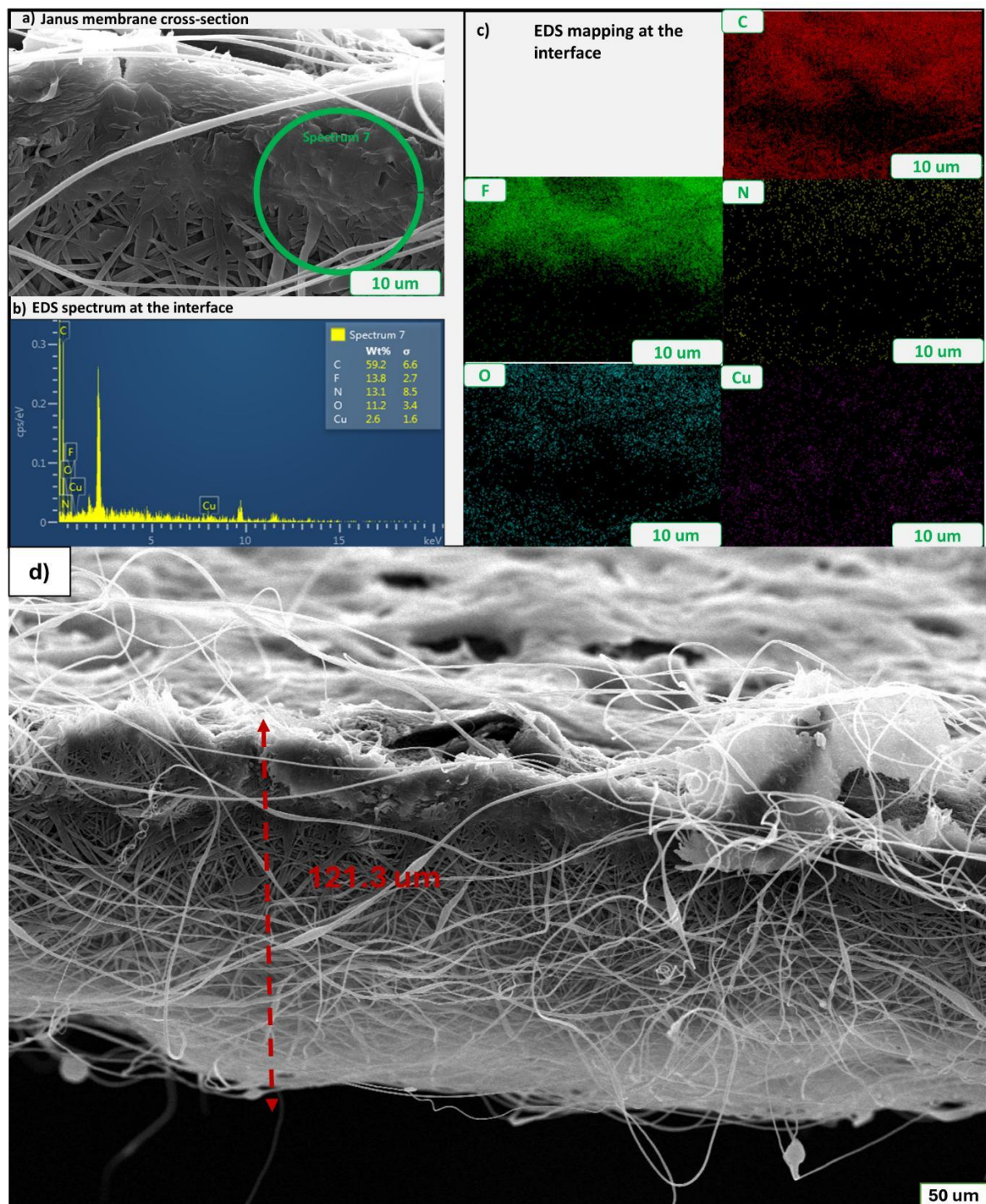


Figure 5.15: a) Janus membrane interface cross sectional SEM image b) EDS spectra obtained from a region around the Janus membrane interface highlighting the elemental composition c) EDS mapping highlighting the distribution of elements at the interface of Janus membranes d) Janus membrane cross-section SEM image.

5.4.3 Janus membrane interfacial polymerization

5.4.3.1 Zeta potential

The zeta potential data for the Janus membrane surfaces near the interfacial layer at different Ph values is displayed in **Figure 5.16**. It was found that under both basic and acidic conditions, the M1 membrane skin surface maintains a negative zeta potential value. At neutral conditions, the zeta potential value was nearly -17 mV, indicating a stronger negative potential. Over a broad Ph range, the electrosprayed PVDF-HFP+CuO membrane (M2) retains positive zeta potential, though it does change only at higher Ph levels to neutral or slightly negative values [165]. The interaction of CuO nanoparticles with the PVDF-HFP matrix is likely the cause of this phenomenon, which points to a surface rich in polarizable functional groups. On the other hand, CuO was recognized as a polar substance that can contribute to surface polarization due to its localized surface charges [166]. In contrast, dipole formations were shown to be supported by PVDF-HFP, which forms the rough matrix, when it encountered charged species. Therefore, this polarizability can help make rough surfaces more dynamically sensitive to interactions.

In line with these results, it is anticipated that polyetherimide, which was described as having a significantly negative potential, will interact more favorably with M2 surface than with M1 [167]. Strong adhesion is promoted by an electrostatic interaction between the negatively charged PEI fibers and the positive zeta potential of M2 at lower Ph values. Van der Waals forces and polar contacts can still promote advantageous interfacial interactions at higher pH levels, when M2 is closer to a neutral zeta potential. M1, on the other hand, would mostly encounter repulsive electrostatic forces due to its continuously negative zeta potential over the pH range, which would limit its ability to interact with PEI.

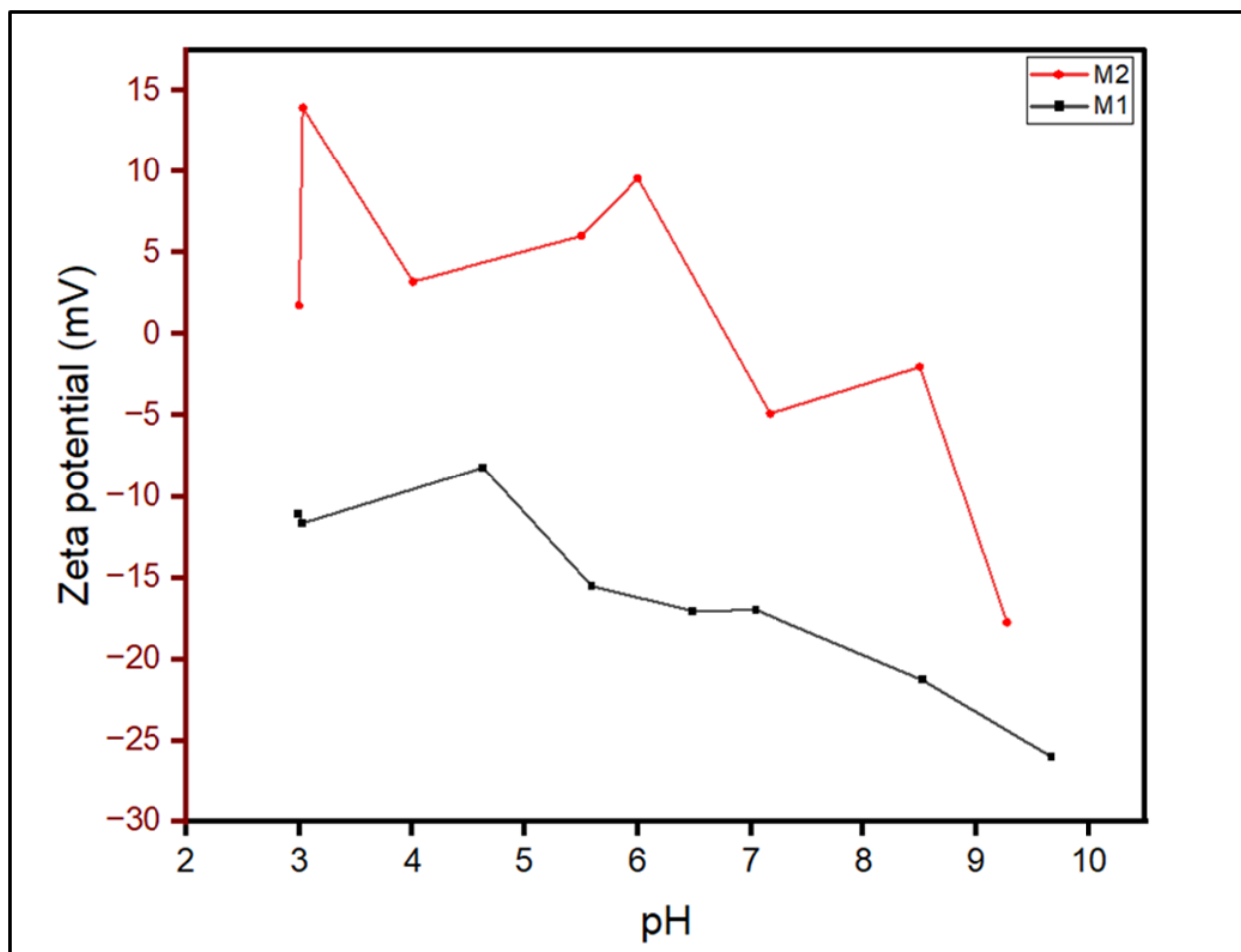


Figure 5.16: Zeta potential analysis of the interfacial layer M2 in comparison with M1.

5.4.3.2 Polarizability

Moreover, the polarizability of the interfacial layer could be explained relative to the PVDF phases present at the interface. Out of many phases known for PVDF-HFP, the β -phase appeared to be highly electro-active which is attributed to the alignment of dipoles in its configuration [168]. This configuration which is referred to as TTTT state was reported in the literature to have the maximum dipole moment and hence could increase the interactions between dipoles [169]. As can be seen in **Figure 5.17**, the FT-IR spectra of the M2 membrane surface shows distinctive peaks at 1400 cm^{-1} ,

1276 cm^{-1} and 840 cm^{-1} which corresponds to the β -phase and other peaks at 762 cm^{-1} and 975 cm^{-1} correspond to the α -phase. Noticeably, the peaks of the β -phase were found to be highly intense while the α -peaks are hardly seen. To confirm the availability of the β -phase and the disappearance of α -phase in M2 membrane surface, XRD analysis was conducted, and the result was displayed in **Figure 5.18**. As can be observed, the peak at 20.02° was broad and clear and corresponds to the β -phase crystal planes while that just above 18° corresponds to the α -phase crystal planes [168]. These findings suggest that the proposed interface in this work is highly polarized and electroactive which opens to various physical dipolar interactions. Hence the CuO and PVDF-HFP layer deposited through electro-spraying process provided a polarizable and superhydrophobic surface. The ionic character of CuO and PVDF-HFP's dipolar nature are the causes of the polarizability, respectively [170], [171].

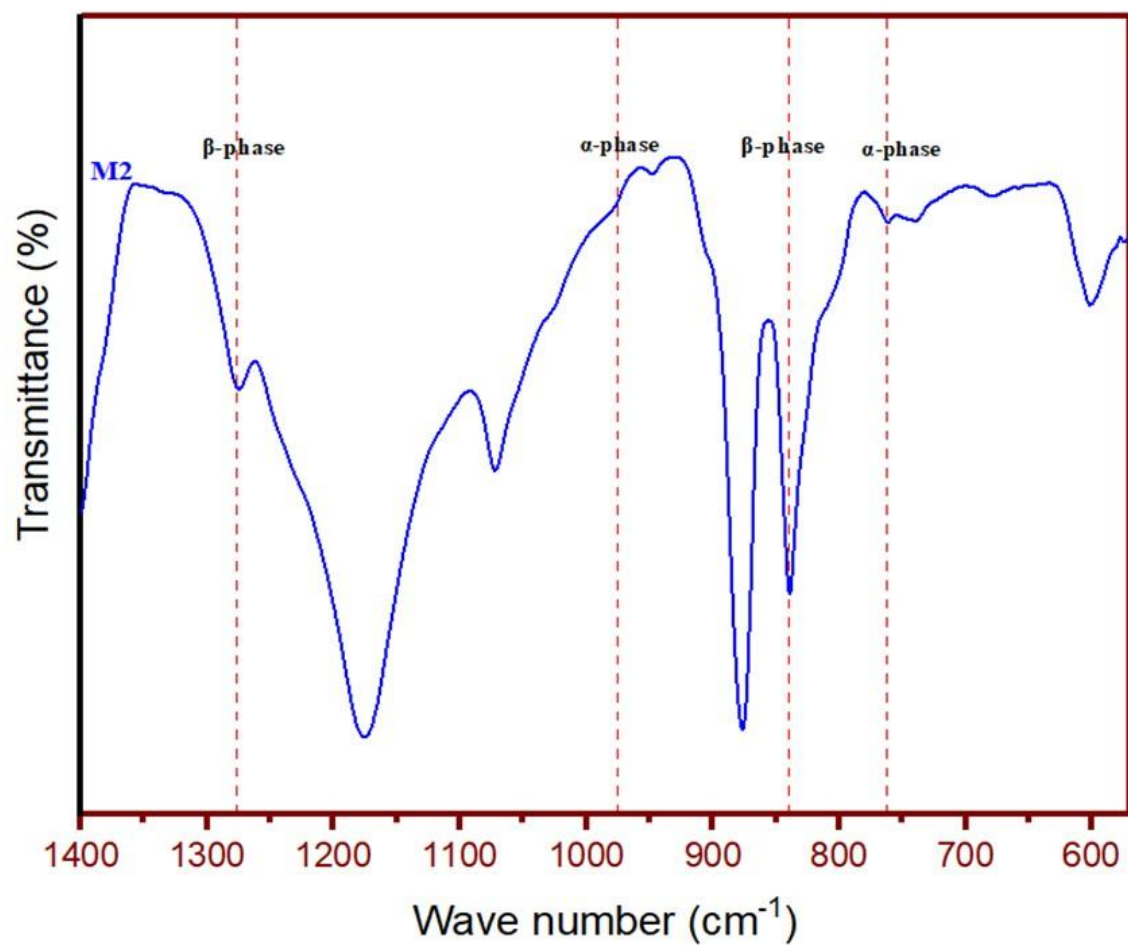


Figure 5.17: FT-IR analysis of the interfacial layer of Janus multiple layer membranes highlighting the polarizability of the surface contributed by plethora of β -phase.

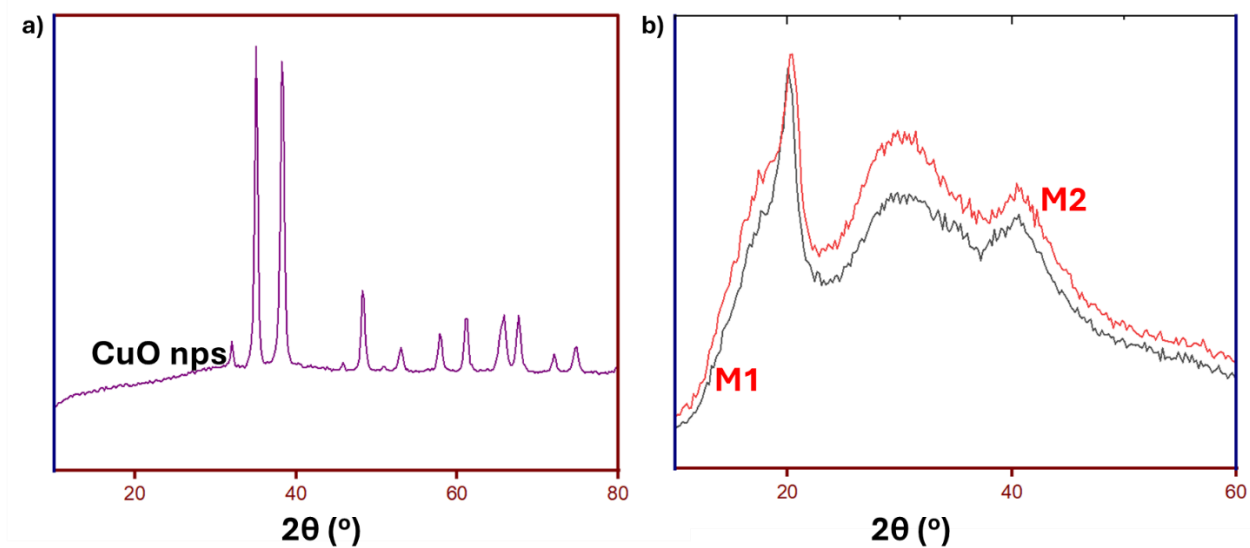


Figure 5.18: a) XRD analysis of commercial CuO nps b) XRD analysis of the interfacial layer of Janus multiple layer membranes highlighting the polarizability of the surface contributed by the presence of β -phase.

5.4.4 Membrane bulk properties

5.4.4.1 Liquid entry pressure

One of the crucial factors in determining membrane performance in MD is liquid entry pressure, which also assesses membrane's pore wetting resistance. From **Table 5.3**, the LEP of M1 membrane, which was only roughened surface (single layer), showed a value of 1.6 bar. This value agrees with Franken's equation related to the maximum pore size and the water contact angle of the active surface as well as with the desired reported LEP values in the literature for long-term operation of membranes [172][173]. The concentration of the host active polymer and the higher WCA produced, as explained in the preceding sections, resulted in the higher LEP. As a result, the deposition of interfacial layer in M2 and M3 membranes resulted in a slight increase in LEP to 1.7 bar. This can be attributed to the electro-sprayed particles which could obstruct a portion of the membrane's surface porosity. Furthermore, it was observed that the LEP values further increased with the co-deposition of the electro-spun PEI fibers in multi-layer membranes due to the decrease in pore size and increase in membrane thickness consequently increasing the density of the membranes and LEP (**Table 5.3**). The modest rise suggests that membrane linked pores are not significantly affected by the hydrophilic PEI layer. The net membrane thickness affects the mean pore sizes of the membranes due to the addition of layers. M4 and M5 Janus membranes with multiple layers exhibit higher thickness and smaller pore sizes which results in higher LEP. The

thickness of the support hydrophilic layer falls within the range of 60–70 μm and was evaluated by comparing the thickness of the active layer before and after co-deposition.

Table 5.3: Intrinsic membrane properties.

Membranes	Thickness (μm)	LEP (bar)	Mean Pore size (μm)
M1	54.2 ± 5.5	1.6 ± 0.1	0.581
M2	65.2 ± 4.3	1.7 ± 0.05	0.551
M3	67.0 ± 5.3	1.7 ± 0.12	0.530
M4	121.3 ± 8.2	1.9 ± 0.2	0.477
M5	137.2 ± 7.1	1.9 ± 0.2	0.472
M6	117.4 ± 2.4	1.8 ± 0.0	0.498

5.4.4.2 Pore size distribution

The pore size distribution data for all developed membranes is illustrated in **Fig 5.19** which depicts narrow PSD in all membranes and relatively large pores in the initial membrane layer M1 attributed to the effects of casting substrate, NIPS process and membrane thickness [144], [145], [174]. However, as can be seen in **Table 5.3**, the net membrane thickness affects the mean pore sizes of

the membranes due to the addition of layers. M4 and M5 Janus membranes with multiple layers exhibit higher thickness and smaller pore sizes which results in higher LEP.

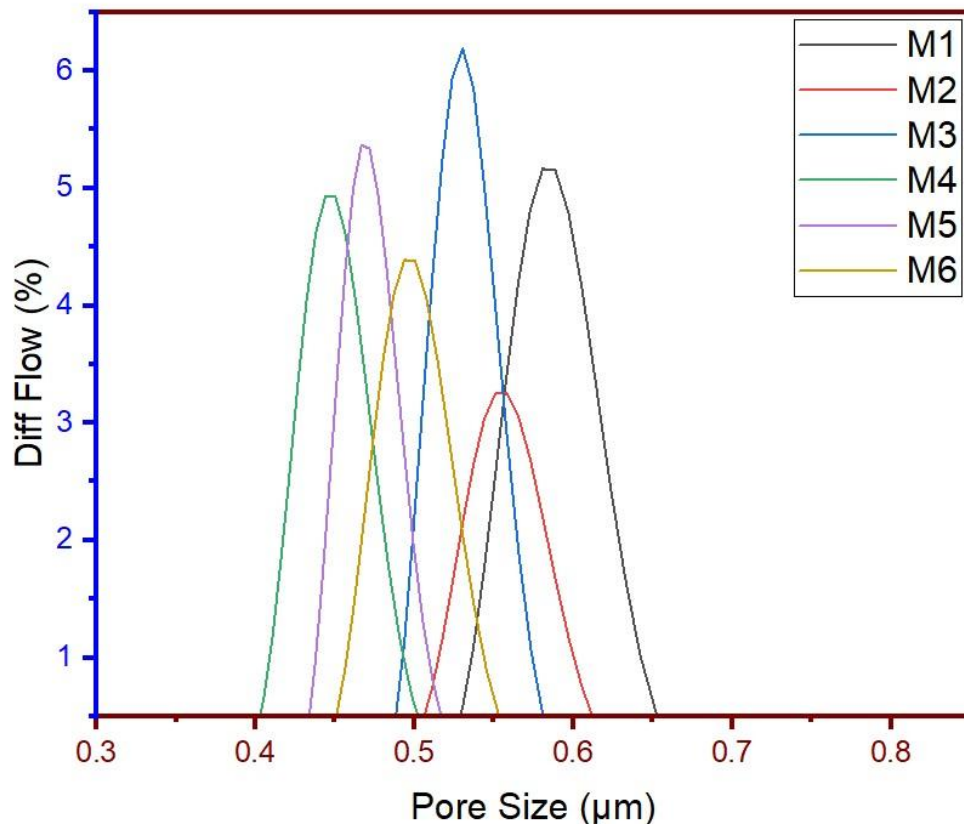


Figure 5.19: Pore size distribution analysis of fabricated membranes.

5.4.4.3 Mechanical analysis

The stress-strain relationship of fabricated membranes with different layers (M1, M4, and M6) was examined to develop a better understanding of the interfacial influence on the mechanical stability of the developed Janus membrane. Table 3 gives a summarized detail of Young's modulus, maximum stress, and elongation at break of the examined membranes. The single layer M1 membrane achieved a maximum stress of approximately 3.4 MPa and an elongation strain of approximately 28.34 % as shown in **Figure 5.20**. Typically, PVDF flat sheet membranes through

NIPS process leads to a consistent composition and structure with effective stress distribution, responsible for the observed uniform deformation and smoothness in the curve [144], [175]. The mechanical behavior of M4, a multiple-layer membrane with an interlocking interface, was distinct. Over a strain range of around 15–25%, the stress-strain curve showed a plateau region at approximately 3.10 MPa. After this point, M4 showed a progressive rise in strain, peaking at about 45.04 % before failing. The interlocking interface appears to be essential for improving adhesion and promoting stress transmission between layers, allowing the membrane to withstand greater elongation. Nevertheless, the stress plateau indicates the existence of shear and interfacial friction forces resistance, which would have counterbalanced the advantages of improved adhesion by adding resistance to deformation. Because of these characteristics, the triple layer M4 membrane has demonstrated superior mechanical stability. Conversely, M6 dual layer membrane without interfacial layer showed the least effective mechanical performance revealing a sudden stress reduction, indicating premature failure, after reaching a maximum stress of about 2.3 MPa at a strain of about 23%. Under tensile stress, delamination resulted from ineffective load transfer between layers caused by a lack of interfacial connection. To study the overall stiffness of M1, M4 and M6 membranes, the Youngs' modulus is evaluated from the stress-strain parameters and highlighted in **Table 5.4**. As can be seen, M4 exhibited the highest stiffness (107.32 ± 0.827 MPa), indicating superior resistance to deformation under stress, while M6 showed moderate stiffness (80.42 ± 0.68 MPa), and M1 demonstrated the lowest stiffness (62.72 ± 1.38 MPa). The relative error bars observed in Youngs modulus.

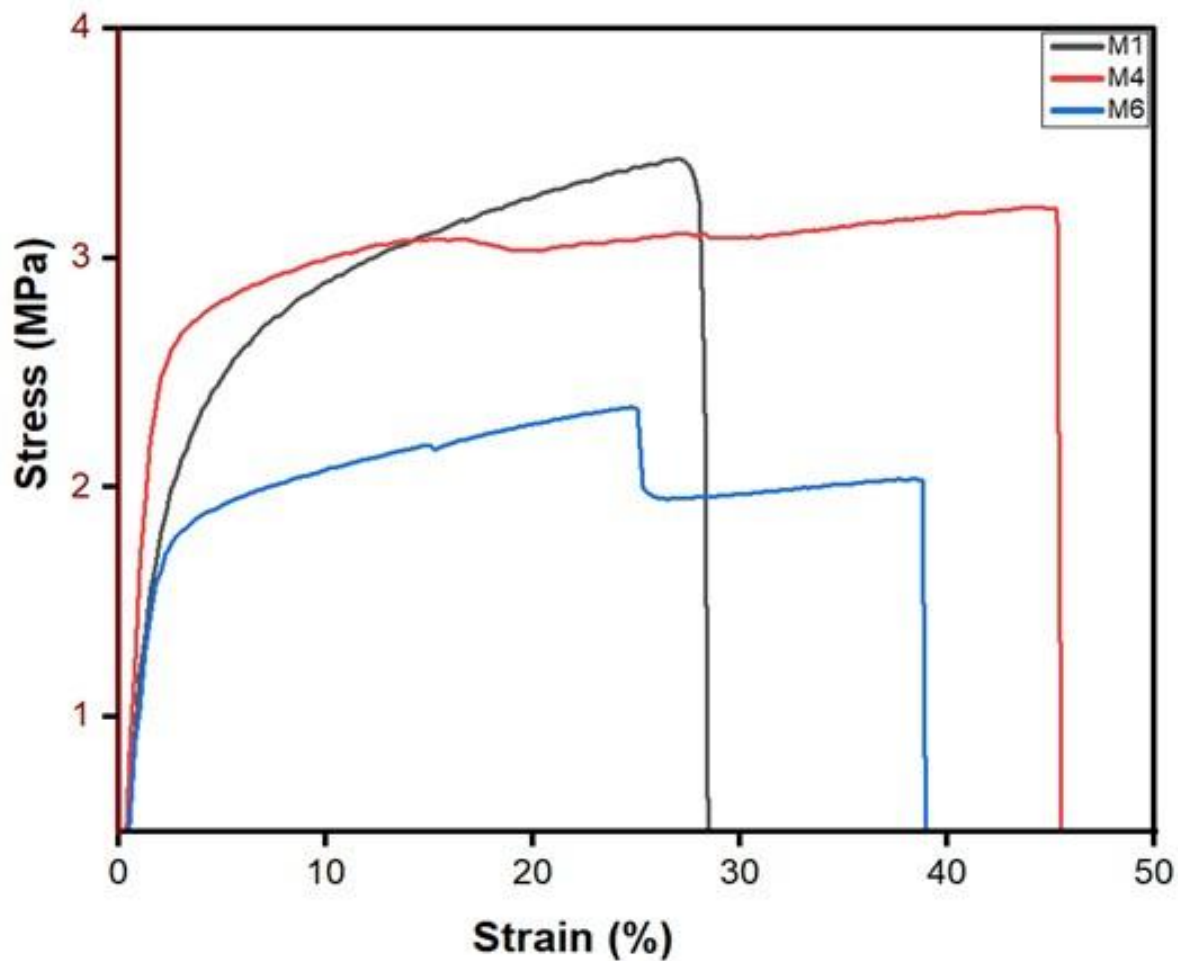


Figure 5.20: Mechanical analysis of fabricated membranes M1, M4 and M6.

Table 5.2: Mechanical analysis parameters of fabricated membranes M1, M2 and M3.

Membrane	Youngs modulus (MPa)	Maximum stress (MPa)	Elongation at break (%)
M1	55.7 ± 7	3.4 ± 0.1	28.34 ± 2
M4	105.32 ± 6	3.10 ± 0.2	45.04 ± 4
M6	80.42 ± 4	2.34 ± 0.2	38.55 ± 4

5.4.4.4 Thermal analysis

Figure 5.21 displays a comparison between the thermal behaviors of single layer membrane M1 and Janus multiple layer membrane M4. As can be seen, both membranes exhibit thermal stability up to approximately 400 °C, with no significant loss in weight, indicating the stability of the components in the Janus membrane within this range. However, a significant loss in weight was observed between 400 °C and 500 °C which is usually common in PVDF membranes, and which corresponds to decomposition of the polymer. Although the decomposition of M4 membrane occurred earlier, it shows higher residual weight in comparison to M1 above 700°C which might be attributed to the presence of CuO in the interfacial layer. The findings show that the presence of interfacial layers might contribute to enhancing the thermal stability of the Janus multiple layer membranes at higher temperatures.

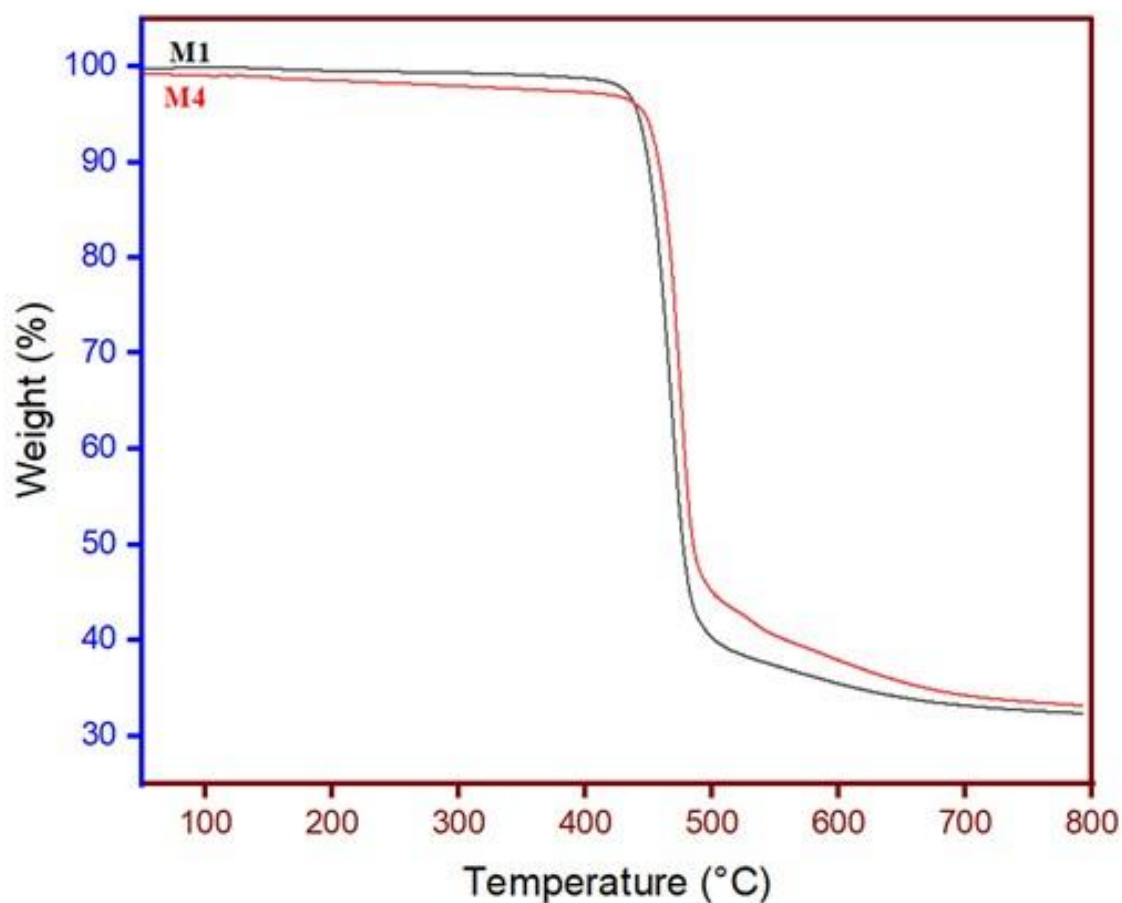


Figure 5.22: Thermal analysis of Janus multiple layer membrane.

5.5 Comparison of the Janus membrane interface with Gecko adhesion

The naturally occurring microscopic adhesion system of geckos and the adhesion mechanism displayed by M2 surface and M4 multilayer membrane's interfacial surface are quite comparable. Setae, which branch into even finer structures (spatulae) at their tips, are micro- and nanoscale structures used by geckos. By maximizing contact area, these hierarchical structures allow van der Waals forces to produce strong adhesion without the need for adhesives. Likewise, the roughened surface through electrospraying found in M2 membrane imitates this hierarchical structure. The

granules function as a microscale counterpart of gecko setae, and the interconnecting fibers mimic the spatulae that embed themselves in the rough surface. For both systems to generate robust adhesion, a mixture of secondary interactions, contact area maximization, and rough surface is required. The high value of water contact angle of M2 membrane surface emphasizes even more how similar the superhydrophobic qualities of geckos are to their ability to self-clean and retain adhesion in a variety of environments. Additionally, gecko adhesion is flexible and adaptable, enabling robust attachment on a variety of surfaces. Similar versatility is provided by the variable zeta potential in M2 surface, which can encourage contact in a variety of pH ranges and replicate the Gecko-type adaptable adhesive behavior [146], [147].

5.6 Membrane distillation evaluation

Using a bi-functional interfacial layer and successive layer-by-layer co-deposition, a delaminationfree Janus membrane was developed in this research. To increase permeate flux during WGMD treatment of high-salinity water (up to 70,000 ppm), the main objectives were to improve water uptake and retain adhesion between the hydrophobic and hydrophilic layers during MD test. The membrane's performance was assessed using MD experiments, such as treating high-salinity feed for 24 hours, long term test operating for 60 hours, and evaluating antifouling and anti-wetting properties. Following MD tests, other characterization methods were used to examine surface characteristics, including WCA measurements, SEM imaging, and EDS analysis. Firstly, the WGMD results with flux and salt rejection for all developed membranes are displayed in **Figure 5.22**. After 24 hours of testing, the single layer M1 membrane showed a permeate flux of 21.70

$\text{kgm}^{-2}\text{h}^{-1}$ and salt rejection of 99.97%. Because of the concomitant increase in the interfacial surface area of the membrane facing the feed side, surface roughness has been reported to improve membrane performance in MD [176]. According to earlier research, it is easier to induce roughness using a textured surface like sandpaper in the NIPS process than it is to use surface chemical modification, which raises the net cost of membrane fabrication and results in a less sustainable and environmentally friendly product [145]. On the other hand, dual layer membranes involving CuO particles with hydrophobic (M2) and hydrophilic (M3) polymer additive demonstrated a flux of $26.61 \text{ kgm}^{-2}\text{h}^{-1}$ with 99.99% and $27.3 \text{ kgm}^{-2}\text{h}^{-1}$ with 99.92% salt rejection respectively. Due to its higher thermal conductivity, the presence of CuO on the permeate side of the membrane was responsible for the abatement of temperature polarization and consequently increased in flux relative to the single layer membrane (M1). CuO nanoparticles also improved selectivity through hierarchical architectures, improved adhesion and membrane stability under ideal spraying circumstances and composite ratios used in this work. According to previous research, nanoparticles enhance the fabrication of multilayer Janus membranes for MD applications by encouraging faster water absorption and reduced mass transfer resistance [56]. Zhang et al. demonstrated the use of ferrous oxide nanoparticles as adhesion materials, which enhanced performance through improved interfacial bonding [177]. Sarwar et al., explained the excellent interactions of CuO particles with nanofibers matrix, which resulted in excellent mechanical property [178].

Furthermore, the permeate flux of triple layer membranes M4 and M5 increased to $37.2 \text{ kgm}^{-2}\text{h}^{-1}$ and $28.62 \text{ kgm}^{-2}\text{h}^{-1}$ respectively, compared to their predecessors (M2 and M3). This improvement is attributed to the hydrophilic layer's (PEI fibers) ability to draw vapor closer to the permeate side for condensation. With controlled membrane layer thicknesses and interfacial surfaces, the

multilayer Janus membrane provided low heat and mass transfer resistance due to the intrinsic properties of CuO and PEI fibers. However, the performance difference between M4 and M5 was linked to the interaction between the hydrophilic fibers and the composite adhesion layer. While both membranes had identical PEI thicknesses, M5 exhibited a gradual decline in flux after 10 hours due to early delamination of the PEI fibers. This delamination likely arose from weak physical interactions and interfacial stress caused by water retention in the membrane. In contrast, M4 maintained steady flux and strong salt rejection, demonstrating superior MD performance.

On the other hand, the M6 Janus membrane without interfacial layer exhibited significantly lower performance showing gradual decrease in flux, underscoring the importance of the interfacial composite layer in enhancing adhesion and vapor flux. Hence material selection played a critical role, as layer adhesion and effective heat transfer across the membrane surface diffused thermal gradients, ensuring uniform temperature distribution and enhancement in membrane performance in MD. The performance of M4 was benchmarked against previously reported Janus membranes in **Table 5.5**, confirming its suitability for treating highly saline water with optimal water permeation and rejection.

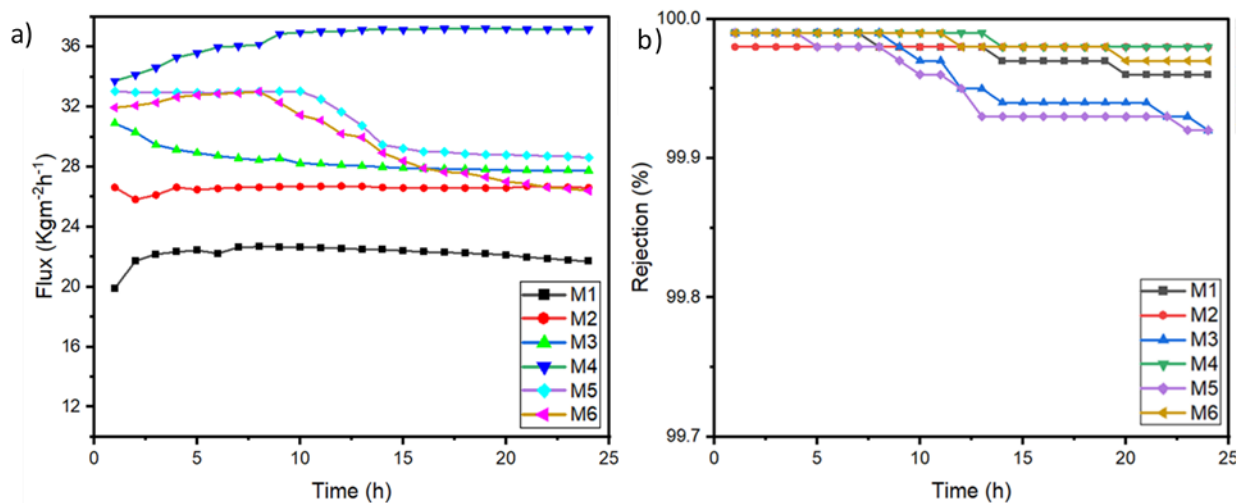


Figure 5.22: WGMD performance of fabricated membranes.

The increase in interfacial surface area on the feed side of the membrane has been shown to enhance membrane performance due to surface roughness. Greater membrane roughness can induce turbulence at the feed-membrane interface, disrupting both the thermal and concentration polarization layers. This disruption raises the temperature at the membrane-feed interface, thereby reducing the temperature gradient between the feed bulk and this interface, ultimately improving net thermal efficiency (**Figure 5.23**). Consequently, this effect increases the temperature gradient between the membrane's feed-side surface and the permeate bulk [131], [132], [133]. Considering various optimization parameters, including thermodynamic properties and mechanical stability, a Janus membrane was designed with a rough hydrophobic PVDF active layer, a thin interlayer of CuO and PVDF-HFP, and a hydrophilic PEI layer. The hydrophobic PVDF, with its higher thermal conductivity, enhances vapor transport and thermal transfer, while the hydrophilic PEI, with lower thermal conductivity, helps maintain a strong heat gradient across the membrane, further improving thermal efficiency. More so, Janus membranes in WGMD are susceptible to improved flux due to the presence of Wet hydrophilic layer which favors and facilitate faster condensation of vapor and as such reducing the mass transfer distance resulting in a net performance”.

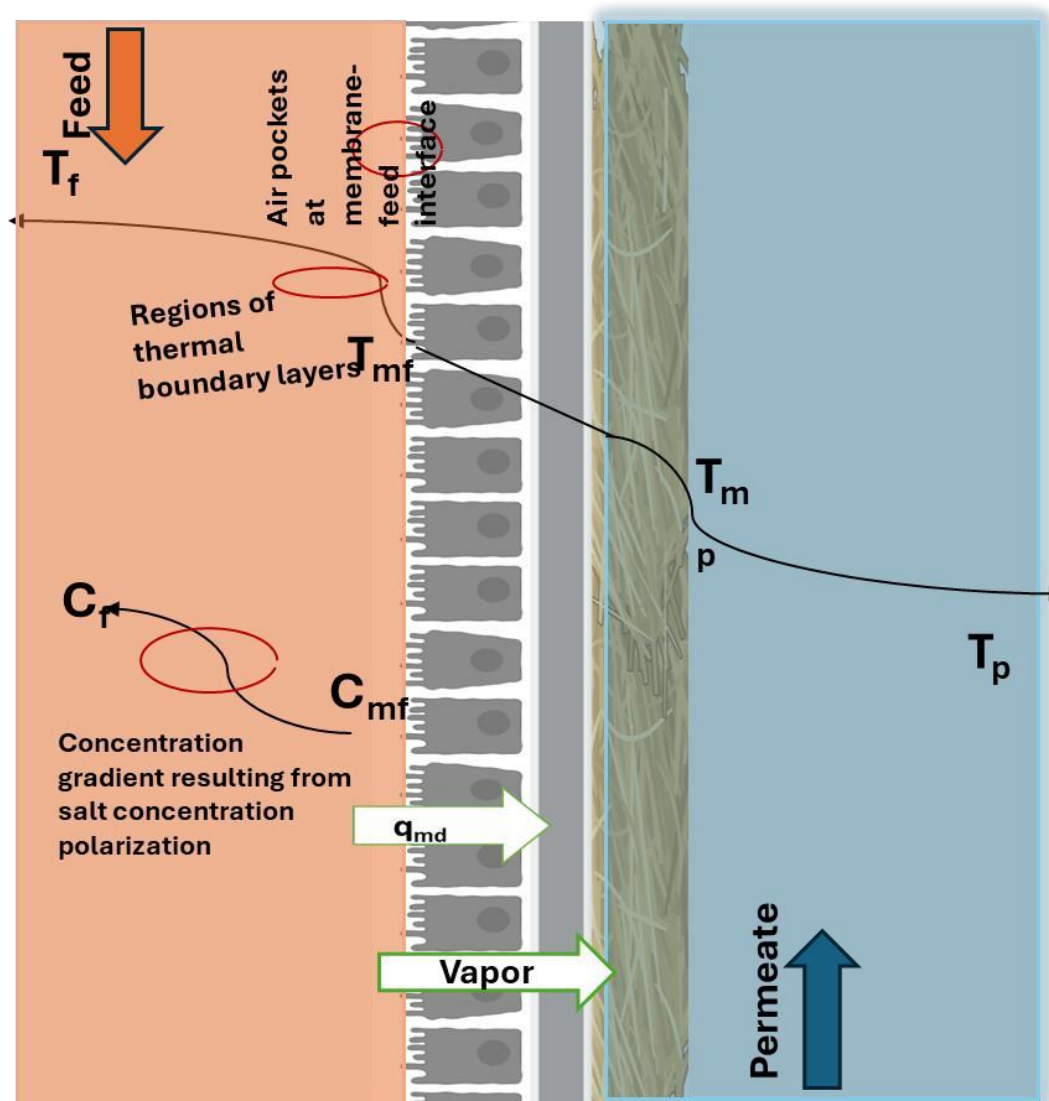


Figure 5.23: Thermodynamics explanation of Janus membrane performance in WGMD.

Table 5.3: Literature comparisons between previously reported Janus membranes.

Hydrophobic/ Janus membrane	Fabrication techniques	Flux (kgm ⁻² h ⁻¹)	Saline Rejection (%)	Feed conc. (ppm)	Testing duration	Membrane Distillation type	Reference
PVDF-Psf	Electrospinning/ Electrospinning	53.6	99.99	30,000	-	DCMD	[83]
PVDF-SiO ₂	Electrospinning/ Electrospinning	24.6	99.99	35,000	40	DCMD	[84]
PH	Electrospinning	22	99.99	10,000	24	DCMD	[86]
PH-PVA/PAN	Electrospinning/ Electrospinning	15.5	99.99	35,000	20	AGMD	[87]
PVDF/HsiO ₂ -PDA- APTES-TEOS	NIPS/PDA coating	52.6 48.6	99.99	35,000	24 70	DCMD	[70]
PPSU/SiNP	NIPS	42.64	94.9	35,000	5	DCMD	[179]
PVDF-SiO ₂	NIPS/Spray-coating	7.4	99.99	35,000	10	AGMD	[141]
PVDF-PVA/PAA	Electrospinning/Electrospraying	27	100	35,000	36	DCMD	[73]
PVDF/PDMS- PEI/GA	NIPS/co-deposition	15.7	99.99	35000	36	DCMD	[142]

PVDF/PP/SMMs- PEI/DA/SMMs	Electrospinning/NIPS/ Electrospinning	50-70	99.99	-	95	DCMD	[143]
PVDF-CuO-PEI	NIPS/Electrospraying/Electro- spinning	36.23	99.97	70,000	60	WGMD	This work

5.7 Membrane wetting resistance evaluation (Long term MD test)

The fabricated Janus membranes with interfacial layers (M4 and M5) were assessed under prolonged WGMD test. After 48 hours of operation, the M5 membrane showed a flux of $27.15 \text{ kg} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ and 99.90% salt rejection (**Figure 5.24a & 5.24figureb**). A sharp decline in flux was noted in M5 membrane after 10 hours indicating delamination of hydrophilic layer due to poor adhesion provided by the interfacial layer composite involving PAN and CuO. However, over 60 hours of WGMD testing, the M4 Janus membrane maintained a flux of $36.23 \text{ kg} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ and a salt rejection of 99.97%, indicating long-term stability. Since the interfacial/composite layer in Janus membrane (M4) is superhydrophobic with hierarchical granular structures as explained earlier, the long-term stability of the membrane is due to the robust hydrophobic layer of Janus membrane induced with self-cleaning effect from the synergistic impact of CuO particles as well as the strength of the electric field in the electrospraying process binding the particles in the matrix of the PVDF membrane. Consequently, the higher LEP and nominal pore size of the membrane (M4) provided stable rejection performance in MD. The observed drop in flux for M4 membrane during prolonged operation was minimal and could be attributed to the combined effects of membrane surface wetting and the aggressive chloride ions (Cl^-) present in the high-salinity feed.

These factors likely induced minor surface modifications that marginally impacted flux over time. Notably, the M4 membrane exhibited no delaminated layers after long-term testing, with the layer attachment and thickness remaining nearly identical to their initial states before testing. This result highlights the superior adhesion and structural integrity provided by the interfacial layer of PVDFHFP and CuO in M4 membrane, which enabled it to outperform M5 in maintaining stable flux and salt rejection over an extended operational period. A schematic representation of M4 and M5 Janus membrane's performance before and after MD is depicted in **Figure 5.25**.

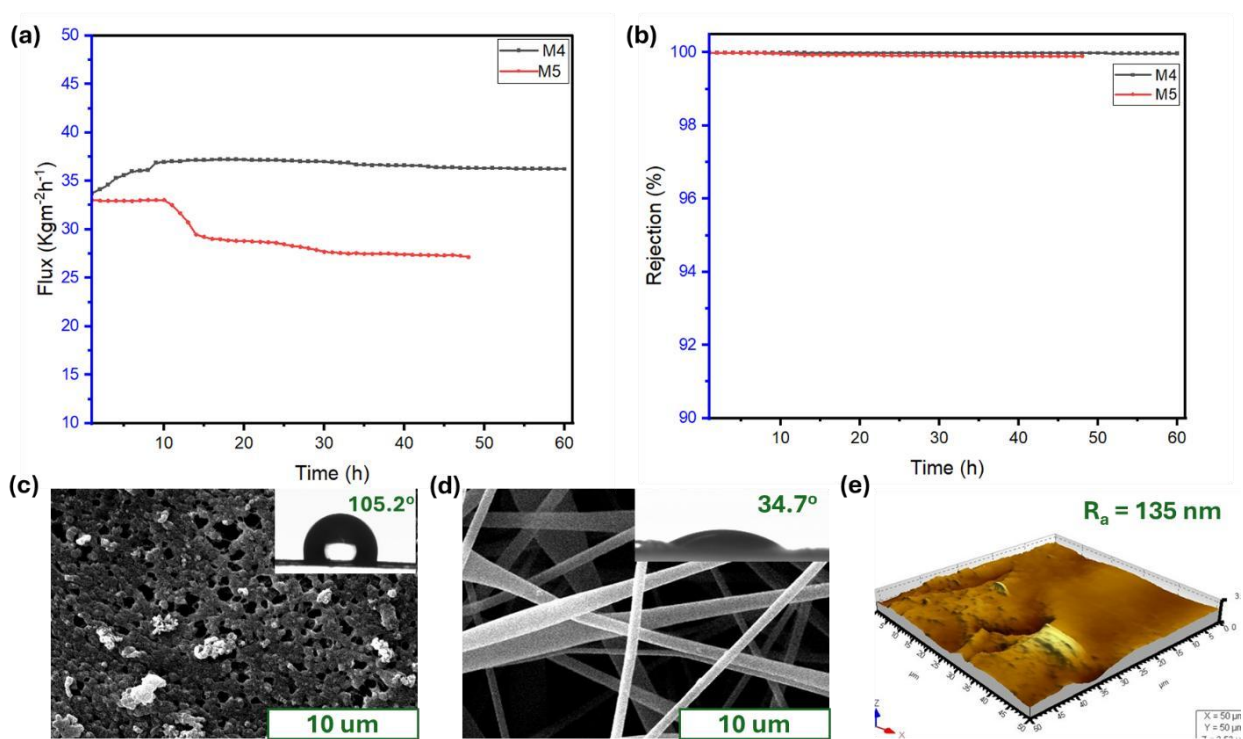


Figure 5.24: (a, b) Long term WGMD performance of fabricated Janus membranes in terms of flux and rejection respectively. SEM surface morphology and WCA (inset) of c) active layer of Janus membranes and b) PEI support after 60 hours MD testing and d) AFM imaging of the active layer of Janus membrane after long term testing.

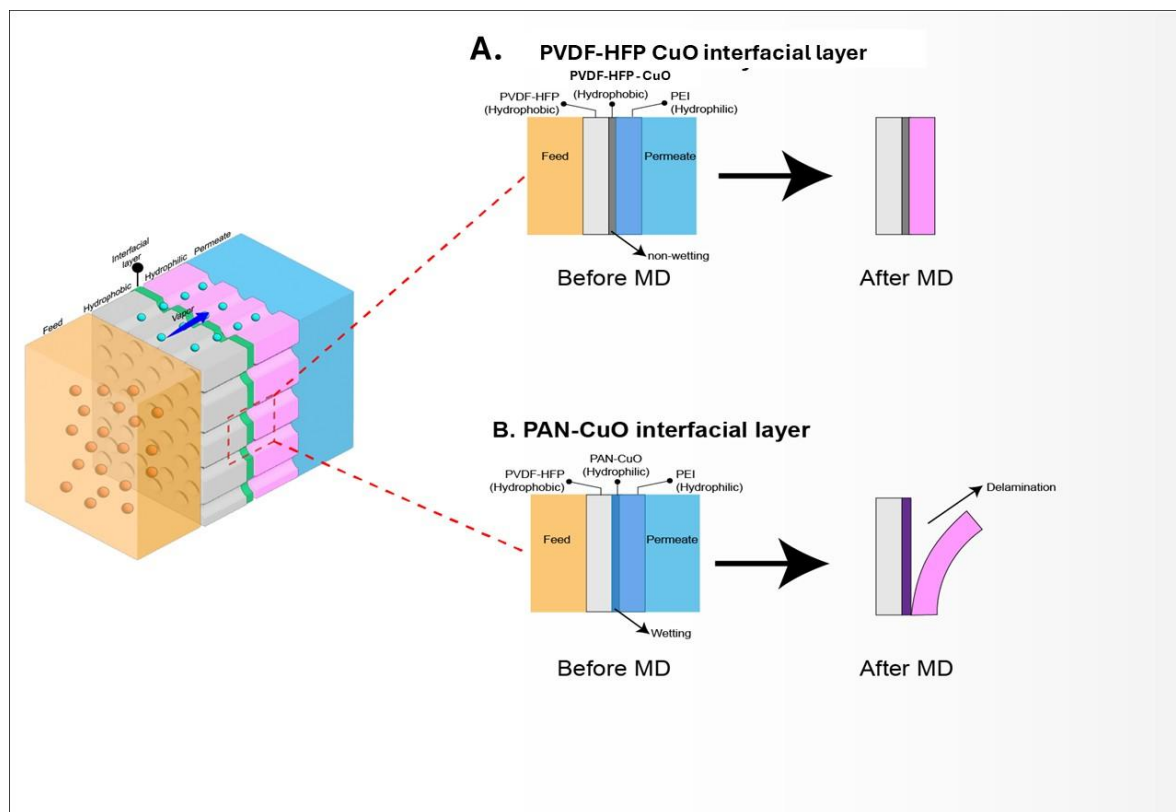


Figure 5.25: A schematic representation of M4 and M5 Janus membrane's performance before and after MD.

As can be in **Figure 5.26a**, certain regions around M5 membrane show detachments or poor attachment between the layers of the Janus membrane. However, the results from MD suggested that the layers detached completely as the performance drops. To support this claim, an image of the detached layers was taken and shown in **Figure 5.26b**. As can be seen, these layers detached separately in the module which renders the SEM difficult to obtain. One more important reason worthy of mentioning here is the hydrophilicity of the interfacial layer. As PAN and CuO both possesses inherent wettability, the accumulation of water at this region might favor the permeate flux and can exert stress and pressure on the support layer, leading to an ultimate washing and detachment as observed.

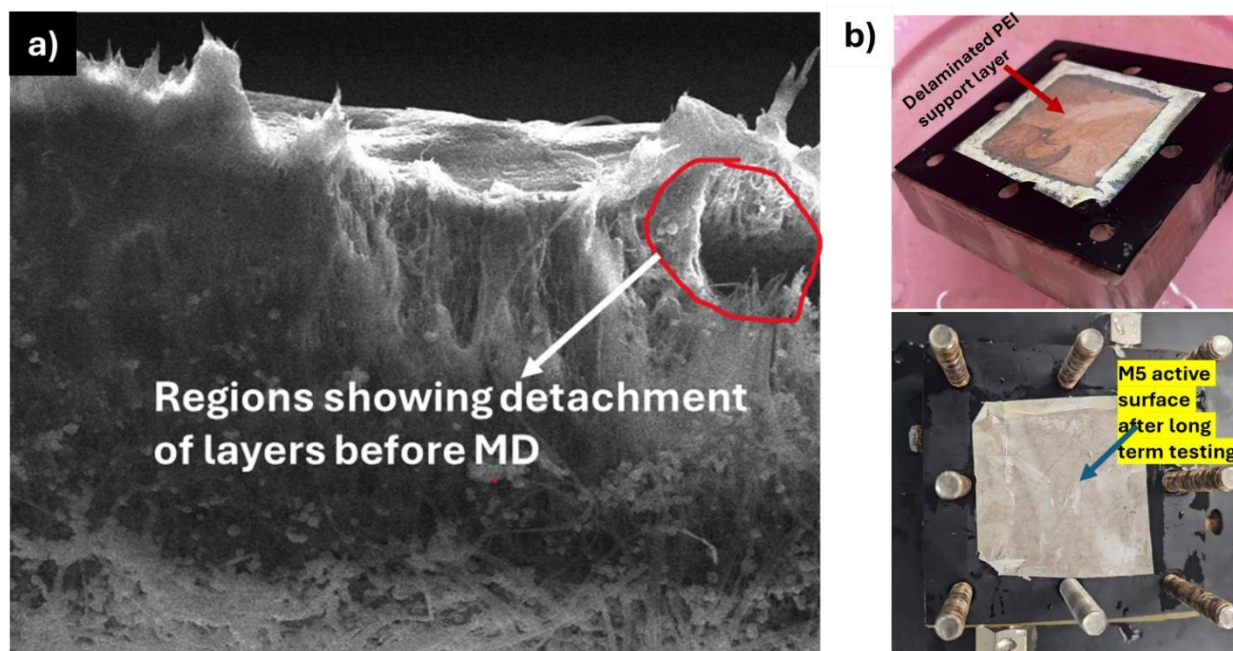


Figure 5.26: a) Regions of layers detachment in M5 membrane prior to MD analysis b) a complete detachment of PEI layer after long term MD analysis.

It is worth mentioning that the hydrophobic active layer in M4 Janus membrane was stable after 60 hours with minimal change in the surface porosity (from the SEM image) and WCA (105.2°) as seen in **Figure 5.24c**. The membrane stability is also established from the roughness of the active hydrophobic layer after long term test, observed from the AFM image (**Figure 5.24e**), where the R_a value of the active surface was measured as 135 nm. In a similar scenario, surface analysis was performed on the hydrophilic PEI layer; the interconnected fibers remained stable, and the morphology remained like that observed prior to the WGMD (**Figure 5.24d**). A literature comparison is given in **Table 5.6**, highlighting the stability of the Janus membrane M4 in hypersaline treatment. In a similar vein, M4 membrane performance in desalination was compared with commercial PVDF membrane. Even though M4 membrane has comparable pore size to the commercial membrane used for comparison ($\sim 0.44 \mu\text{m}$), the outstanding performance displayed

by M4 was confirmed in terms of both flux and salt rejection (**Figure 5.27 a and b**), highlighting the importance of developed Janus membrane in improving efficiency of MD process for desalination of highly saline water.

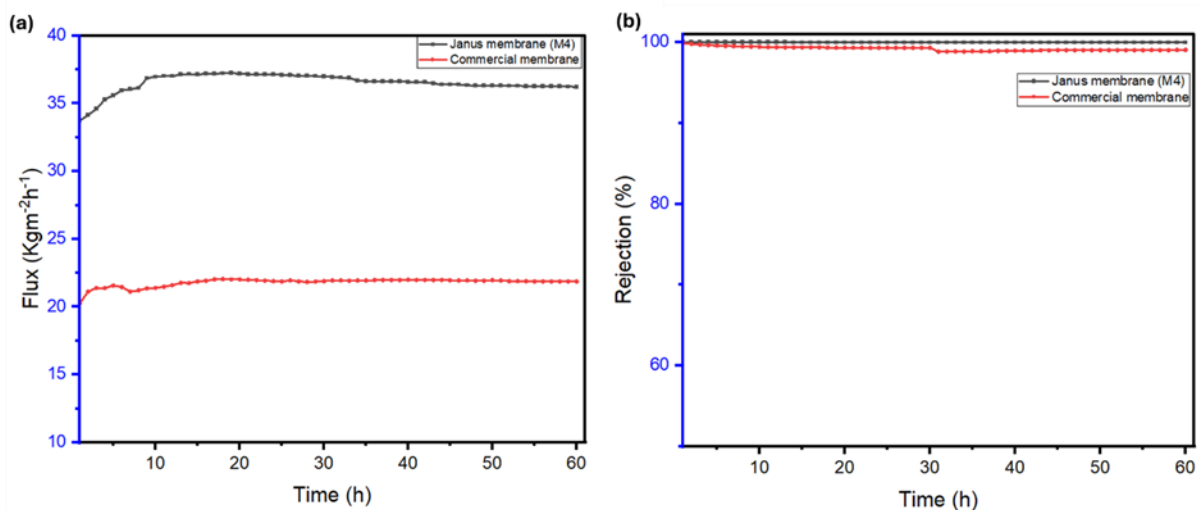


Figure 5.27: Comparative WGMD performance of fabricated Janus membrane (M4) and commercial membrane a) permeate flux b) salt rejection.

Table 5.4: Literature comparisons between previously reported Janus membranes.

Hydrophobic/ Janus membrane	Fabrication techniques	Flux ($\text{kgm}^{-2}\text{h}^{-1}$)	Saline Rejection (%)	Feed conc. (ppm)	Testing duration	Membrane Distillation type	Reference
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PH	Electrospinning	22	99.99	10,000	24	DCMD	[86]
PH-PVA/PAN	Electrospinning/ Electrospinning	15.5	99.99	35,000	20	AGMD	[87]
PVDF/HsiO ₂ -PDA- APTES-TEOS	NIPS/PDA coating	52.6 48.6	99.99	35,000	24 70	DCMD	[70]
PPSU/SiNP	NIPS	42.64	94.9	35,000	5	DCMD	[179]
PVDF-SiO ₂	NIPS/Spray-coating	7.4	99.99	35,000	10	AGMD	[141]
PVDF-PVA/PAA	Electrospinning/Electrospraying	27	100	35,000	36	DCMD	[73]
PVDF/PDMS- PEI/GA	NIPS/co-deposition	15.7	99.99	35000	36	DCMD	[142]
PVDF/PP/SMMs- PEI/DA/SMMs	Electrospinning/NIPS/ Electrospinning	50-70	99.99	-	95	DCMD	[143]
PVDF-CuO-PEI	NIPS/Electrospraying/Electro- spinning	36.23	99.97	70,000	60	WGMD	This work

5.8 Membrane fouling and scaling evaluation

Two obstacles that have also hampered the integration of MD applications are membrane fouling and scaling, both of which have an impact on the permeate flux or rejection during MD evaluation. The anti-wetting characteristics of the membrane are frequently compromised, and its porous structure is destroyed when foulants are present in the feed stream. To assess the fouling and scaling properties of the membrane, MD operation was set up for the Janus membrane (M4) in a 70,000-ppm saline feed that was combined with 20 Mm solution each of SDS, MgCl_2 , CaCl_2 and Na_2CO_3 . **Figure 5.28a illustrates** how, for various foulant combinations, the membrane's flow stays nearly constant throughout the course of the 24-hour testing period, with saline rejection of >99%. After the MD test, the membrane was removed from the module, dried, and imaged under SEM (**Figure 5.28 b**). The measurements of the water contact angle, and EDS were made and reported inclusive. The initial WCA of the active layer reduced to 115° , demonstrating slight decrease in hydrophobicity due to the foulants' synergistic action. Although the porous nature of the membrane was not greatly affected, the decrease in the WCA of the active skin can be attributed to the interfacial energy increase which is primarily contributed by the interaction of the ionic species with aggressive Cl^- driven by the thermal effect from the hot feed. As shown on the EDS spectrum in **Figure 5.28 c**, almost no traces of elements on the membrane surface that originates from the foulants except few traces of S from SDS and Mg which might be attributed to the small ionic size and high ionic charge of Mg ions. The Janus membrane reported in this work was compared with a brief description of prior fouling results from the literature in **Table 5.7** below. The superior interaction between the layers, as well as the wettability of the active membrane

surface in the created Janus membrane provided stable flux and consistent rejection under combination of foulants in MD test.

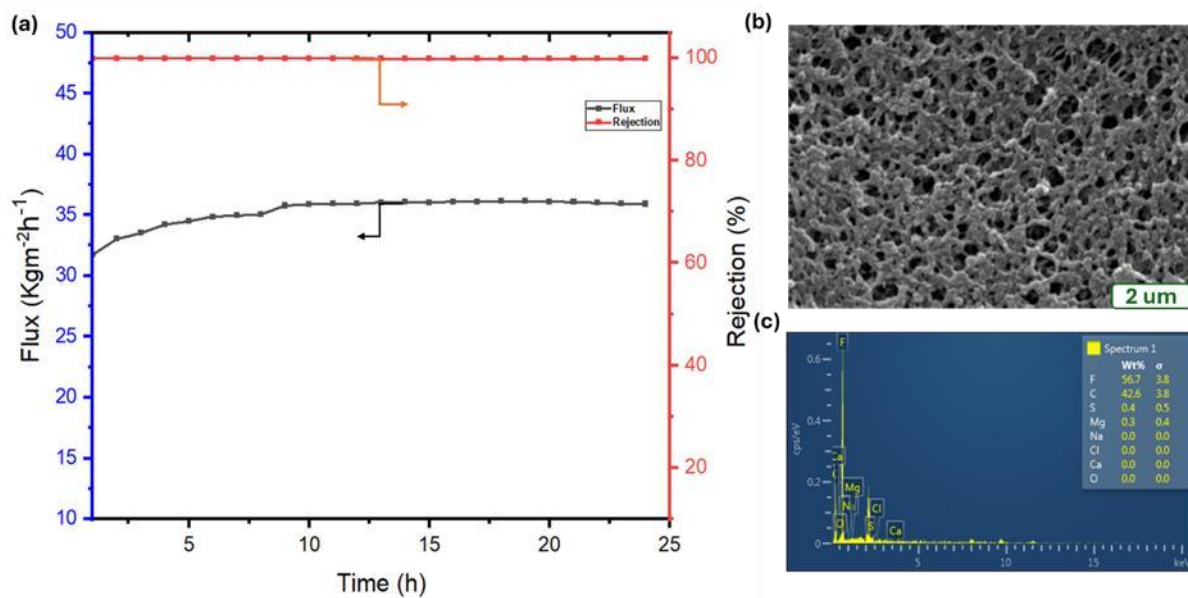


Figure 5.28: MD test results with foulant feed b) SEM morphology of active layer and c) EDS spectra of the active layer of Janus membrane after fouling testing.

Table 5.5: Literature comparison of Janus membranes fouling and scaling tests in MD.

Janus membrane	Foulants/scalants	Stability	Saline condition	Reference
PVDF-PDA/PEI	0.5M NaCl, 1g/L mineral oil, 0.1Mm NaCl	Stable for 8 hours	35 g/L	[180]
PVDF-PDA/TEOS/APTES	0.1Mm SDS, 0.5g gasoline	Stable for 10 hours	35 g/L	[70]
PVDF/POTS/SiO ₂ -PVAM	0.1 Mm SDS	Stable for 32 hours	35 g/L	[106]
PVDF-PVA/Cu-BTC	CaCl ₂ , crude oil	Stable for 20 hours	35 g/L	[92]
PVDF-PVA/PAA	0.05 Mm, 2g/L mineral oil 20 Mm CaCl ₂ , 20 Mm Na ₂ SO ₄	Stable for 8 hours	35 g/L	[139]
PVDF-PDA	4 g/L of mineral oil,	Stable for 24 hours	0.6M NaCl	[181]
PVDF-OH	Canola oil	Stable for 6.6 hours	0.6M NaCl	[182]
PVDF-SiO ₂	1 g/L crude oil, 0.1 Mm SDS	Stable for 10 hours	35 g/L NaCl	[72]
PVDF-PVDF-HFP/CuO-PEI	0.2 mM each SDS, and 20 mM MgCl ₂ , CaCl ₂ and Na ₂ CO ₃	Stable for 24 hours	70 g/L NaCl	This work

CHAPTER 6

6.1 Conclusion

The scarcity of water resources and the limitations of existing membrane technologies have necessitated the continuous exploration of more resilient, efficient, and sustainable membrane systems. In this study, we proposed the development of Janus-type engineered surface multilayer membranes for membrane distillation (MD) applications, aiming to overcome issues of wetting, low stability, and delamination typically associated with conventional and first-generation Janus membranes. Initially, one-sided modified nanofibrous Janus membranes were fabricated through the electrospinning of PVDF-HFP, incorporating silica nanoparticles to create a hydrophilicity gradient. These membranes exhibited good initial flux and high salt rejection performance during MD operations. However, stability tests indicated a lifespan of approximately 36 hours, after which membrane failure and reduced performance were observed. This limitation motivated further research into enhancing membrane stability through material modification.

To address the short operational lifespan, MOFs were incorporated into the membranes. Aluminum-based MOFs were embedded on the hydrophobic layer while Nickel-based MOFs were incorporated into the hydrophilic side. The resultant MOF-modified Janus membranes demonstrated improved vapor flux, enhanced hydrophilicity, and a prolonged operational stability of up to 60 hours under MD conditions. Despite these improvements, long-term testing revealed delamination issues between the hydrophobic and hydrophilic layers, especially under prolonged exposure to saline feed solutions and temperature gradients.

Recognizing that weak interfacial adhesion was the primary cause of membrane failure, a new strategy was introduced: engineering the interface with a PVDF-HFP/CuO nanocomposite layer

inspired by gecko-type adhesion. Here, a robust interfacial layer was fabricated between the NIPScasted hydrophobic PVDF active layer and the electrospun PEI hydrophilic layer. This innovative design effectively enhanced adhesion at the interface, significantly improving the membrane's mechanical robustness and preventing delamination during extended MD operations. The geckoinspired interfacial design facilitated better stress distribution and mechanical interlocking, enabling the membrane to withstand operational challenges for a longer duration. The final engineered Janus membranes showed high permeate flux, excellent salt rejection (>99.98%), and outstanding stability during extended membrane distillation operation.

In conclusion, this study successfully addressed key limitations in Janus membrane development for MD applications by systematically progressing through one-sided modification, MOF-based material enhancement, and finally, interface engineering for long-term durability. The findings provide a strong foundation for the design of next-generation Janus membranes that are not only high-performing but also stable and durable under harsh operational conditions.

6.2 Recommendation

Based on the findings of this work, several recommendations can be made for future research and practical applications:

6.2.1 Future Research Directions

- **Optimization of Interfacial Materials:** Although PVDF-HFP/CuO composites demonstrated enhanced adhesion, further exploration of other nanocomposite materials, such as graphene oxide or MXene-based composites, may offer even better mechanical and chemical stability.

- **Advanced Durability Testing:** Long-term operational studies exceeding 100 hours should be conducted to further validate the membranes' industrial viability and to understand degradation mechanisms under different MD configurations such as AGMD and VMD.
- **Scale-up Studies:** Investigate the scalability of the membrane fabrication processes, particularly the combination of NIPS casting and electrospinning with nanocomposite interfacial engineering, to facilitate transition toward pilot and industrial scale applications.
- **Energy Efficiency Analysis:** Detailed energy balance and economic analysis studies should be undertaken to better quantify the practical benefits of these membranes compared to commercially available MD membranes.
- **Hybrid Membrane Designs:** Integration of photocatalytic, antibacterial, or anti-scaling functionalities into the Janus membrane system could be explored to further enhance longterm performance.

6.2.2 Practical Implications

The findings from this research suggest that a systematic design approach combining surface engineering, material innovation, and interface modification can significantly improve the performance and operational life of membranes for high-salinity water treatment. The gecko-type adhesion approach developed herein offers a promising strategy that could be adapted not only for MD membranes but also for membranes used in oil-water separation, gas separation, and energy harvesting applications. Future membrane distillation systems aiming for sustainable, long-term

operation under challenging environmental conditions can greatly benefit from the advances introduced in this study.

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