

**SURFACE ENGINEERED JANUS MEMBRANES: DUAL
APPROACHES FOR HIGH PERFORMANCE WATER
DESALINATION**

BY
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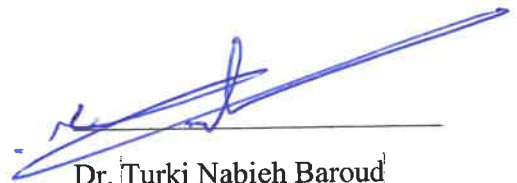


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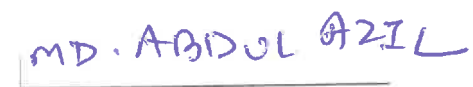
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Dedication

This work is dedicated to my parents, wife, kids, siblings, and friends. |

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In the name of Allah, the Most Merciful, the Most Compassionate. I offer all praise for bestowing upon me the strength and opportunity to successfully complete my master's degree at KFUPM.

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LIST OF ABBREVIATIONS

AGMD = Air gap membrane distillation

CAPEX = capital expense

CDI = Capacitive Deionization

CNF = Carbon nanofibers

CNT = Carbon nanotube

DCMD = Direct contact membrane distillation

DI = Deionized water

DMF = N, N-dimethylformamide

ED/EDR = electrodialysis

FO = Forward osmosis

FTIR = Fourier transform infrared

GO = Graphene oxide

JC = Jute carbon

LEP = Liquid entry pressure

LMH = Liter per square meter per hour

MD = Membrane distillation

MED = multi-effect distillation

MPS = Mean pore size

MSF = multi-stage flash evaporation

MVC = Mechanical vapor compression

NF = Nanofiltration

OPEX = Operating expense

PAN= polyacrylonitrile

PBI = Polybenzimidazole

PDMS = polydimethylsiloxane

PE = polyethylene

PEG = Polyethylene glycol

PEI = polyetherimide

PEO = Polyethylene oxide

PP = Polypropylene

PSD = Pore size distribution

PSU = Polysulfone

PTFE = Polytetrafluoroethylene

PU = Polyurethane

PVC = Polyvinyl Chloride

PVDF = polyvinylidene fluoride

PVDF-co-HFP = Poly Vinylidene Fluoride-co-Hexafluoropropylene

PVP = Polyvinyl Phenol

RO = Reverse osmosis

SEM = Scanning electron microscope

SGMD = Sweeping gas membrane distillation

SP = Sandpaper

SR = Salt rejection

TGA = Thermogravimetry analysis

VMD = Vacuum membrane distillation

VP = Vapor compression

WCA = Water contact angle

WGMD = Water gap membrane distillation |

ABSTRACT

Full Name : [MD EMDAD HOSSAIN]
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Membrane distillation is an emerging thermally driven desalination process that utilizes low-grade heat to recover fresh water from hypersaline and contaminated sources. However, enhancing vapor transport through the membrane surface while minimizing heat loss remains a critical challenge. In this study, we strategically developed two types of high-performance Janus membranes—electrospun dual-layer nanofibrous membranes and ZnO-sputtered phase inversion PVDF membranes—each demonstrating asymmetric wettability to enable directional vapor transport throughout the membrane's pore. The electrospun membranes were fabricated with a hydrophobic carbon nanofiber integrated top layer and a hydrophilic biomass-derived carbon incorporated bottom layer, demonstrating superior water flux—more than twice that of pristine PVDF-co-HFP membranes—while maintaining nearly 100% salt rejection. The developed membranes demonstrated long-term operational stability in real seawater, exhibiting superior flux in harsh conditions under scaling and fouling conditions. Similarly, phase inversion membranes were modified by sputtering a thin ZnO layer onto the skin layer of PVDF membranes, creating a robust Janus interface without the risk of delamination. The ZnO-sputtered membranes exhibited significant improvement in flux compared to unmodified PVDF membranes and showed excellent durability and anti-wetting behavior under high

salinity and prolonged operation. The combined strategies of distinct carbonaceous materials integration, surface energy tuning, and structural alignment highlights a scalable route for fabricating next-generation Janus membranes with strong potential for advanced desalination and hypersaline brine management.

Keywords: Biomass carbon, Carbon Nanofibers, Sputtering, Electrospinning, Janus membranes, Anti-delamination strategies, WGMD

ملخص الرسالة

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تُعد عملية التقطير الغشائي تقنية ناشئة لتحلية المياه تعتمد على الطاقة الحرارية، وتستغل فروق درجات الحرارة لاستخلاص المياه العذبة من مصادر المياه شديدة الملوحة والمياه الملوثة. ومع ذلك، يظل تحسين انتقال البخار عبر سطح الغشاء مع تقليل الفقد الحراري تحديًا بالغ الأهمية. في هذه الدراسة، قمنا بتطوير وتصنيع نوعين من أغشية جانوس عالية الأداء ذات طبيعتين مختلفتين للسطح: أغشية نانوية ليفية ثنائية الطبقة مُحضّرة بتقنية الغزل الكهربائي، وأغشية PVDF مُحضّرة بتقنية قلب الطور ومُرَسَّعة بأكسيد الزنك باستخدام الترسيب بالرش الكاثودي. يتميز كلا النوعين بخاصية ترطيب متباينة وعالية، مما يُمكن من انتقال بخار الماء بشكل مُوجّه عبر المسام النانوية للغشاء. صُنعت الأغشية المغزولة كهربائياً بطبقة علوية مُدمجة من ألياف الكربون النانوية الكارهة للماء والمقاومة للبلل، وطبقة سفلية مُدمجة بالكربون الحيوي المحب للماء. أظهر هذا النوع من الأغشية تدفقاً مائياً فائقاً، يتجاوز ضعف تدفق أغشية PVDF-co-HFP النقية، مع الحفاظ على معدل رفض للأملاح يقارب 100%. كما أظهرت هذه الأغشية استقراراً تشغيلياً طويل الأمد عند اختبارها في معالجة مياه البحر، حيث أظهرت تدفقاً فائقاً في الظروف القاسية التي تتسم بوجود مكونات التلوث والترسبات الكلسية. وبالمثل، تم تعديل أغشية قلب الطور عن طريق ترسيب طبقة رقيقة من أكسيد الزنك على الطبقة السطحية لأغشية PVDF باستخدام تقنية الرش الكاثودي، مما أدى إلى تكوين واجهة جانوس قوية وغير قابلة للانفصال. أظهرت الأغشية المُرَسَّعة بأكسيد الزنك تحسناً ملحوظاً في التدفق مقارنة بأغشية PVDF غير المعدلة، وأبدت متانة ممتازة وسلوكاً مقاوماً للبلل واستقراراً أثناء التشغيل لفترات طويلة. تسلط الاستراتيجيات المشتركة لدمج مواد كربونية متباينة، والتحكم في طاقة السطح، والمحاذاة الهيكلية للأغشية الضوء على مسار جديد وقابل للتطوير لتصنيع أغشية جانوس من الجيل التالي ذات إمكانات قوية لتحلية المياه وإدارة المحاليل الملحية عالية التركيز.

CHAPTER 1

INTRODUCTION

1.1 Background Study

Urbanization has caused people to face several challenges in the modern world, with water scarcity being one of the significant issues, and producing potable water is a pressing concern [1], [2]. The world's population has increased from 700 million to over seven billion since the Industrial Revolution, and it is predicted to reach at least 10 billion by the 22nd century, with Asia and Africa seeing the fastest growth due to rising water demands [3], [4], [5]. Since ecosystems and human health depend on clean water, water purification technologies are critical to sustainable development [9]. Physico-chemical techniques like chemical precipitation, coagulation, ion exchange, and adsorption are among the most popular treatment methods because of their effectiveness, affordability, and simplicity of use [6], [7], [8], [9], [10]. The high surface area, numerous adsorption sites, and regeneration capability of advanced nanocomposites have demonstrated significant promise in wastewater decontamination [11], [12], [13]. However, freshwater resources are scarce, and despite the possible environmental consequences, desalination is being utilized more and more to alleviate water scarcity [11], [12], [13], [14], [15]. Seawater is one source of water that can be utilized and transformed into a solution to this problem because it makes up 97.5% of all the water on Earth [16].’ **Fig. 1.1** shows the regional desalinated water consumption including the desalination capacity globally.

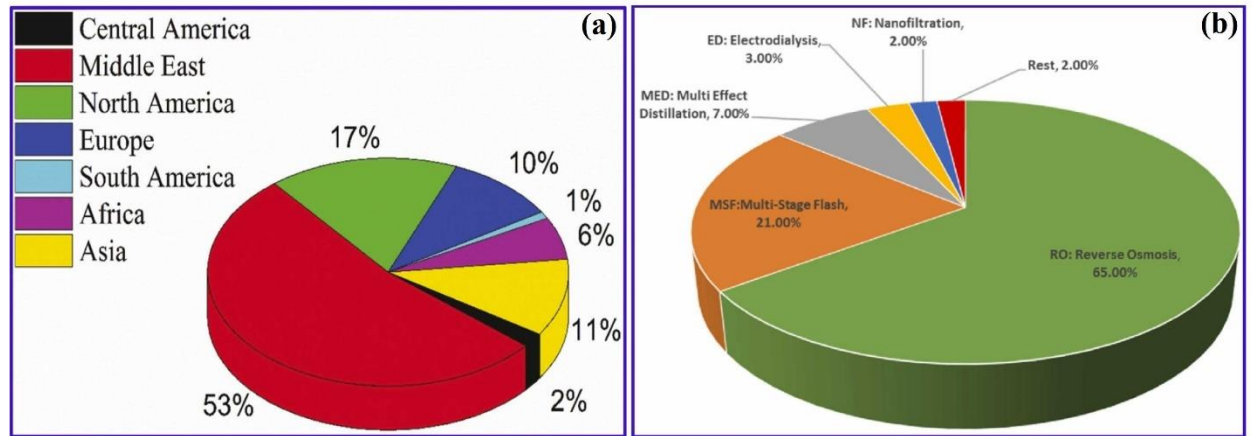


Figure 1. 1 (a) Regional consumption of desalinated water; (b) Global desalination capacity [17].

A viable solution for freshwater scarcity is seawater desalination, which makes use of technologies such as electrodialysis (ED/EDR), reverse osmosis (RO), forward osmosis (FO), vapor compression (VP), multi-stage flash evaporation (MSF), and multi-effect distillation (MED) as shown in **Fig. 1.2**. However, there are several challenges, including its high energy consumption, environmental problems, and expensive pricing. For end consumers, desalinated water is costly due to the high capital (CAPEX) and operating expenses (OPEX) involved. Depending on energy prices, desalination employs either thermal or electrical energy, resulting in large-scale systems. Unfortunately, especially in areas experiencing economic water scarcity, the socioeconomic realities of regions that require desalination are frequently disregarded. Because of this, research on small-scale, affordable desalination systems is crucial for areas with insufficient municipal water infrastructure [17]. Membrane-based desalination technologies is a promising approach which currently accounts for about 68% of total desalination capacity due to its simplicity and environmental benefits [18]. However, pressure-driven membranes require high

energy with the increased concentration of brine. MD offers a promising technique by enhancing water desalination efficiency while ensuring cost-effectiveness, high-quality water, and environmental sustainability [18], [19]. Beyond desalination, MD stands out for its potential to use renewable energy sources, demonstrated by its integration with solar energy [20], harness waste heat from industry [21], and its ability to pre-concentrate the highly saline solution for resource recovery [22],[23]. Additionally, MD efficiently removes organic substances and heavy metals from various brine solutions, making it a versatile separation technique [24], [25]. Furthermore, MD's versatility allows it to handle complex waste streams, such as radioactive waste that ensures the environmentally safe discharge of effluents [26].

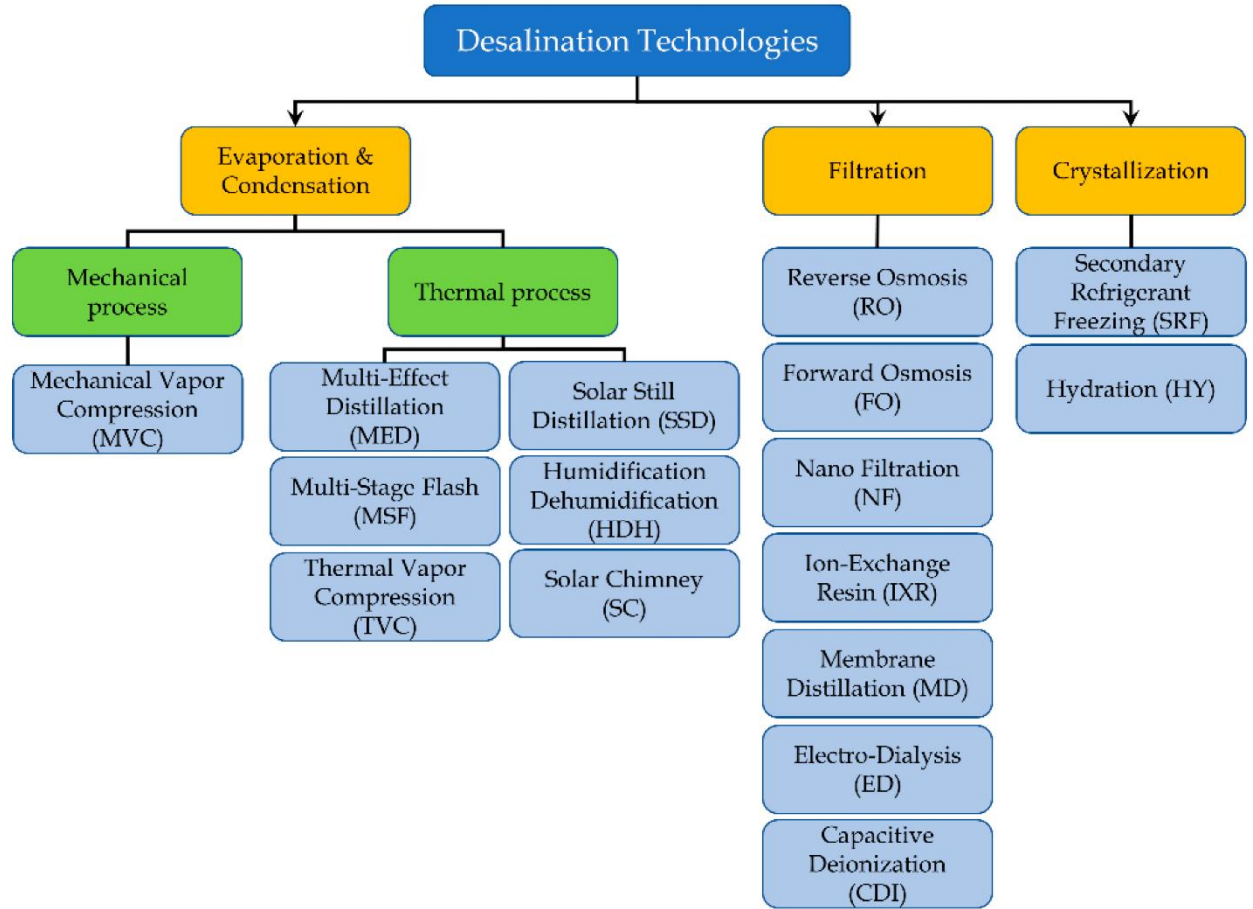


Figure 1. 2 Desalination technologies based on their working principles [27]

1.2 Membrane Distillation (MD)

MD is a thermally driven separation process that uses a hydrophobic porous membrane to transfer vapor molecules while restricting liquids and other dissolved solids [28]. Depending on the vapor transfer process, MD configurations can usually be divided into four categories which include Direct contact (DCMD), Air Gap (AGMD), Sweeping Gas (SGMD), and Vacuum MD (VMD) [29], [30] as described in **Fig. 1.3**. The AGMD process is thermally efficient due to the gap between the membrane surface and condensation plate, which effectively minimizes heat loss through conduction. However, AGMD possesses a lower permeate flux compared to the DCMD process, while the latter suffers from lower

thermal efficiency due to significant heat loss through conduction [31]. Recently, researchers have been interested in a new modified MD module named Water Gap MD (WGMD) [32], [33], [34]. The WGMD combines the features of AGMD and DCMD, improving the weakness of these designs, and exhibiting promising results [35], [36]. In AGMD, the feed solution is directed over the surface of the membrane, where hot water evaporates on the membrane's interface [37]. WGMD has a similar design to AGMD but with stagnant clean water filling the gap between the membrane and condensation plate [38]. The Vapor transfers through the membrane and condenses quickly into the gap of the water-filled area, resulting in a higher flux compared to AGMD [39]. WGMD consists of a thin layer of water between the membrane and the condensing surface, serving as a thermal buffer that lowers heat loss and improves energy efficiency in contrast to DCMD, where the feed solution and permeate are in direct contact across the membrane [33], [40]. The main advantage of WGMD over DCMD lies in its superior thermal efficiency. The water gap in WGMD reduces the amount of heat loss that is usually seen in DCMD and increases overall energy efficiency by minimizing conductive heat transfer over the membrane. Additionally, especially in high-salinity situations, the water gap improves flux performance by creating a more consistent temperature gradient across the membrane [40], [41], [42], [43]. This makes WGMD a more effective choice for water desalination nowadays compared to conventional DCMD.

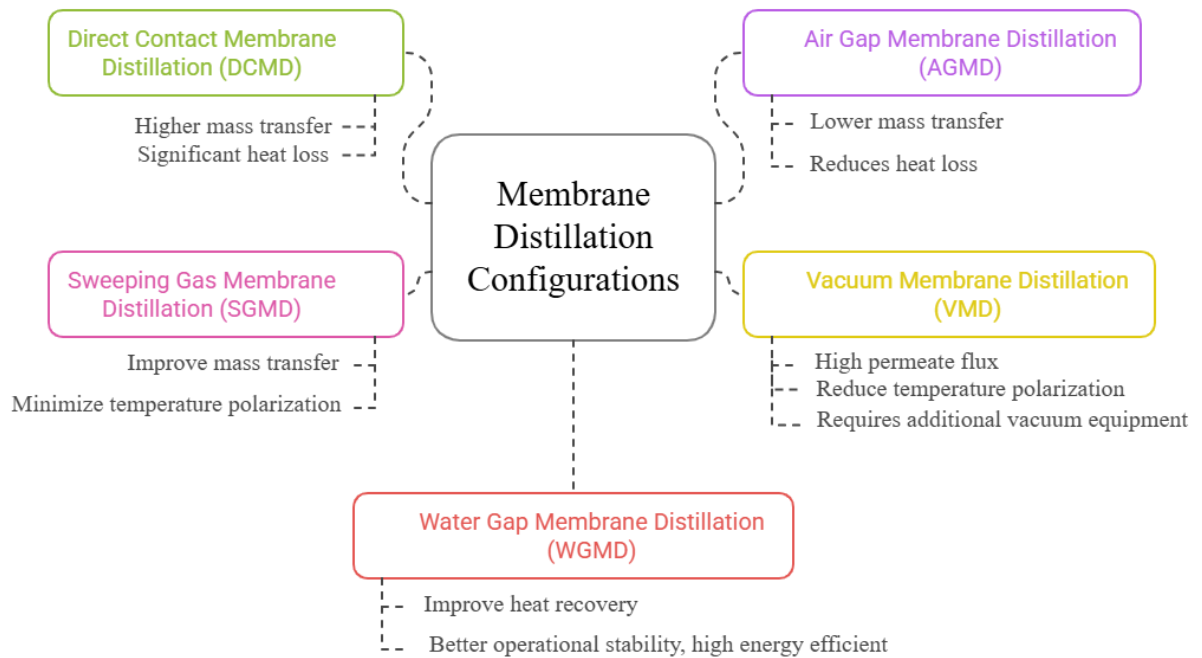


Figure 1. 3 Different configurations of MD

Despite its many advantages, MD encounters several challenges associated with membrane performance as described in **Fig. 1.4**. The MD membrane can experience various challenges including pore wetting, limited permeate flux, and the gradual deterioration of mechanical properties over extended use. These challenges stem from the membrane's inherent characteristics, including pore size, porosity, thickness, and hydrophobicity. As a result, optimizing MD membranes often involve balancing permeate flux, material selection, and their fundamental properties [44], [45]. In MD, water vapor from the feed side diffuses through hydrophobic membrane and condenses on the permeate side as

distillate. This process is driven by the transmembrane vapor pressure difference, which arises due to the temperature gradient between the two sides of the membrane [46]. However, hydrophobic membranes typically experience limited mass transfer, which lowers permeate flux and reduces overall water recovery. To address these challenges Janus membrane structures have gained significant attention recently, leading to different fabrication techniques that can be divided into asymmetric fabrication and asymmetric surface engineering approaches for enhancing the MD performance. Asymmetric fabrication techniques involve the direct formation of dual-layered membranes, often achieved through processes like sequential filtration of functional nanomaterials [47], [48], spray coating of polymers and nanoparticles [49], and casting solutions containing surface-migrating additives [50]. These fabrication techniques enable the development of distinct surface properties of the membranes, enhancing their separation performance. On the other hand, asymmetric surface engineering approaches modify only one surface of an existing porous membrane through physical or chemical treatments. This method involves introducing a new phase interface at one of the membrane surfaces, restricting the other side. For instance, mussel-inspired polydopamine coatings can be selectively deposited at a liquid-gas interface while the membrane floats in a fluid [51]. Alternatively, a solid-gas interface can be used as a polymer barrier that protects part of the membrane from surface modification which can be removed via dissolution, peeling or etching [52], [53]. Another technique uses photosensitive coating, in which selective activation is controlled by light attenuation inside the membrane. The degree of photochemical alteration can be carefully controlled by researchers by varying exposure time and light intensity [54], [55].

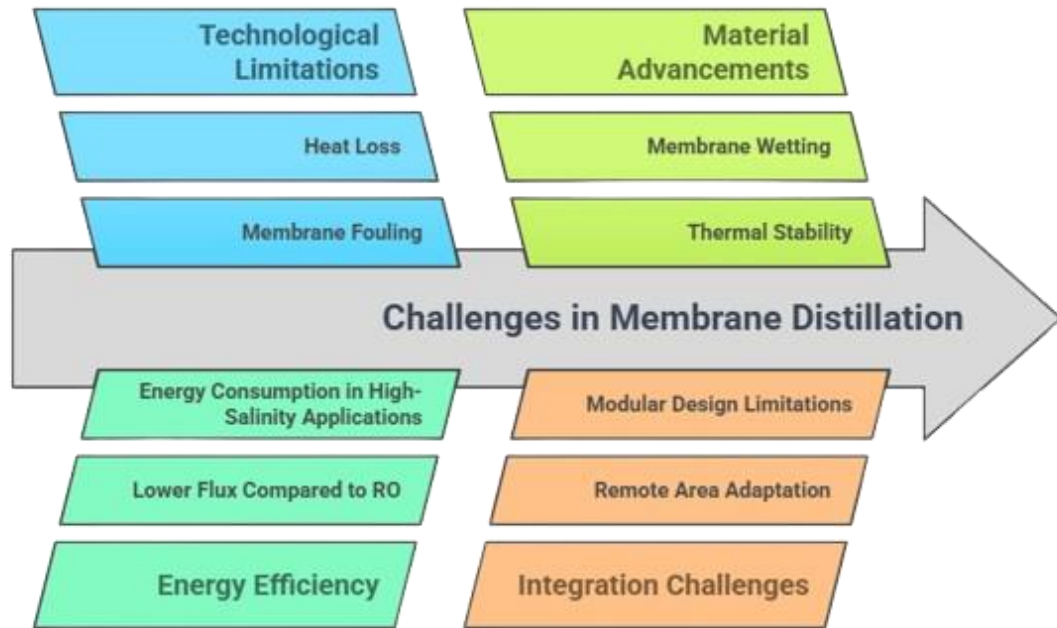


Figure 1. 4 Challenges associated with MD

1.3 Materials Used for MD

MD uses porous, hydrophobic membranes that allow water vapor to flow through but keep liquid water out. Commercially available microfiltration membranes are frequently used in MD experiments, yet despite their hydrophobic nature, these membranes have problems with limited permeability and long-term wetting. The widespread application of these membranes emphasizes the necessity of specifically engineered membranes meeting the particular design for MD. Therefore, there is a demand for the development and manufacturing of new membranes optimized for MD applications [56], [57]. Membrane characteristics determine the performance in MD applications which should have some

properties like high hydrophobicity, higher permeability, higher LEP value, lower fouling rate, and longer durability [19], [58]. Hundreds of polymers both natural and synthetic can be electrospun into nanofibers if the molecular weight of the polymer is considerably high enough and the solvent used in electrospinning can quickly evaporate during the jet transition period in the distance between the spinneret and drum collector. Many standard polymers are mostly used and successfully electrospun, Poly Vinylidene Fluoride-co-Hexafluoropropylene (PVDF-co-HFP), polyvinylidene fluoride (PVDF), polyethylene (PE), Polystyrene (PS), Polysulfone, and Polytetrafluoroethylene (PTFE), Polyethylene terephthalate (PET), Polyvinyl Chloride (PVC), Polypropylene (PP), Polyurethanes (Pus), Polyvinyl Phenol (PVP), Polybenzimidazole (PBI), Polyethylene Oxide (PEO), etc [59], [60]. The incorporation of nanoparticles or clay materials into the membranes can enhance their hydrophobicity greatly via surface modification or deformation and it is used in various industries and academics [61]. For instance, TiO₂ nanoparticles can improve the antifouling property of the membrane [62], SiO₂ nanoparticles can create excellent dynamic adsorption capacity [63], carbon nanotubes (CNTs) to enhance the membranes' mechanical properties [64], [65], the composition of clay particles can improve the gas separation process [66], [67], [68], [69] as well as provide better performance in MD process [70], [71], clay modified ceramic membrane has shown a promising performance in MD [72]. Additionally, polymer composite with clay materials resulted in significant improvement in the membrane characteristics including mechanical properties [73], [74], [75], barrier properties [76], optical properties [77], [78], flame retardant properties [79], [80] etc. Researchers found that the composition of clay particles with polymeric membranes increases thermal, chemical, and surface properties [81], [82] due to their

strong interactions between themselves. Further, these composite membranes can be synthesized easily, economically, and effectively for water filtration.

1.4 Scope of This Study

This thesis study explores the fabrication and optimization of advanced high performance Janus membranes with asymmetric wettability for the enhancement of membrane distillation. This work is divided into two different approaches to fabricate the Janus membranes: (i) integration of distinct carbonaceous materials with PVDF-co-HFP polymers to construct electrospun nanofibrous membranes that have an asymmetric wettability on both layers, and (ii) sputtering with ZnO on PVDF phase inversion membrane's skin layer to make hydrophobic/hydrophilic interfaces on both surfaces of PVDF membranes.

In the first part of this work, the scope involves the integration of biomass-derived carbon nanoparticles that were synthesized in low temperature from jute stick, containing lots of functional oxygen groups that impart hydrophilicity on one side of the polymeric nanofibrous membrane surface. On the other side of the membrane surface, commercial hydrophobic carbon nanofibers were incorporated into the polymer matrix that were sequentially electrospun as a top layer of the Janus membrane. A layer-by-layer electrospinning strategies were employed to create mechanically stable Janus nanofibrous membranes by optimizing surface roughness, porosity, membrane pores, and microstructure. Various types of characterization techniques were carried out including water contact angle, porosity, pore size, SEM, XRD, FTIR, and mechanical and thermal properties, to correlate the membrane morphology, structural integrity with membrane

performance during WGMD operation. The developed membranes demonstrated outstanding performance under highly saline feed solution, real seawater to evaluate the long-term stability, anti-fouling and anti-wetting resistance.

In the second part of this thesis, the scope expands to a solvent-free DC magnetron sputtering approach to deposit Zinc nanoparticles in an oxygen atmosphere, forming a thin ZnO nanolayer on the PVDF membrane surface. This modification makes a wettability gradient within the membrane structure that prevents the risk of delamination issues often observed in conventional Janus membranes. The PVDF membranes were cast on two different substrates including glass and sandpaper to evaluate the substrate effect on the membrane surface morphology. Systematic studies were carried out to assess the impact of sputtering time on the overall WGMD performance under highly saline conditions, with real seawater for long term stability testing.

In a nutshell, this comprehensive work aims to provide a comparative understanding of two different fabrication approaches to develop Janus membranes that are risk free of delamination, achieve stable WGMD performance under various conditions, highlighting their potential for next-generation desalination technologies.

1.5 Objectives

1. To develop delamination free Janus-type membranes by incorporating biomass-derived carbon materials and carbon nanofibers into PVDF-co-HFP polymer via electrospinning and through magnetron sputtering of Zinc nanoparticles onto PVDF phase inversion membranes for MD applications.

2. To optimize the concentration of carbon materials and sputtering duration to make asymmetric wettability of the membranes.
3. To attain an appropriate balance between hydrophobicity and hydrophilicity of the membrane surfaces for enhanced water vapor transport in WGMD operation.
4. To study the wetting properties, chemical and physical structural changes, mechanical and thermal stabilities of the modified Janus membranes to ensure structural stability for long term MD operation.
5. To investigate the performance under harsh conditions like in highly saline brine solution, foulant and scaling components.
6. To evaluate the suitability of the modified Janus membranes for real seawater desalination for longer duration by analyzing their flux and salt rejection.

1.6 Thesis Structure

This thesis is organized into six chapters for easy comprehension that is presented below.

Chapter 1: This chapter presents the background study of water desalination technologies, the principles of MD, the challenges associated with conventional distillation systems, different types of materials that are used in MD system, the scope of the study, and objectives.

Chapter 2: This chapter provides a brief literature review of MD focusing on the Janus membrane, the challenges associated with Janus membrane fabrication, MD performance comparison of Janus membranes that are previously reported.

Chapter 3: This chapter describes the detailed experimental section of fabrication of the Janus membrane with different approaches, characterization techniques used to assess the morphology, structural integrity of the developed membranes, and the experimental setup of water gap membrane distillation (WGMD).

Chapter 4: This chapter presents electrospun Janus nanofibrous membranes fabrication including their characteristics in terms of wettability, intrinsic nature, structural and morphological analysis, also it demonstrates the WGMD performance in various types of saline conditions for a long-run operation.

Chapter 5: This chapter explains another approach of fabricating PVDF Janus membranes by sputtering ZnO on its skin layer, describing the membrane's characteristics in different aspects of structural and morphological analysis, the membrane's wettability analysis, the surface roughness, their intrinsic properties analysis including porosity, tortuosity, pore size, and the thermal analysis. Finally, the WGMD performance of the developed membranes with highly saline feed solution and with real seawater.

Chapter 6: This chapter gives an overview of this thesis with concluding remarks, and future recommendations to synthesize different types of nanomaterials that may have distinct characteristics to incorporate into the polymer matrix to develop Janus membranes, coupled with membrane crystallization for valuable resource recovery, and developing multilayer Janus membranes for an efficient vapor transport and salt rejection.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

In MD, water vapor from the feed side passes through the hydrophobic membrane and condenses into distillate, driven by the trans-membrane pressure difference created by the temperature gradient between the two sides of the membrane [46]. However, hydrophobic membranes often suffer from low mass transfer, reducing permeate flux and water recovery. To address this challenge, hydrophobic/hydrophilic composite Janus membranes have gained increased research interest and offer unique advantages over traditional membranes due to their asymmetric wettability [83], [84]. Because of their asymmetric surface, water or solutes can be transported in a specific direction, increasing separation effectiveness and lowering fouling concerns. This unique design improves flux and selectivity by enabling controlled water flow over the membrane. Furthermore, Janus membranes' contrasting surfaces improve wettability control, making them highly suitable for applications requiring efficient water purification and pollutant rejection [85]. This design combines the anti-wetting properties of the hydrophobic layer with enhanced mass transfer and a hydrophilic layer which reduces the vapor transfer path.

The asymmetric wettability of Janus membranes, which are hydrophilic on one side and hydrophobic on the other, has drawn a lot of interest in MD because of their capacity to improve vapor flux, lessen wetting problems, and minimize fouling, making them more effective than traditional hydrophobic membranes. High salt rejection and thermal efficiency are ensured by the hydrophobic bottom layer, which stops liquid entry, and the hydrophilic top layer, which encourages quick water vapor transfer. Janus membranes have been created using a variety of methods, such as electrospinning, phase separation, dip coating, layer-by-layer assembly, and surface modification via chemical grafting or plasma treatment. These methods allow for fine-grained control of the membrane's surface characteristics, which maximizes performance in MD applications. To increase surface energy and improve antifouling properties, hydrophilic layers are usually introduced using polyethylene glycol (PEG), polydopamine (PDA), zwitterionic polymers, or nanoparticles like silica (SiO_2), graphene oxide (GO), and titanium dioxide (TiO_2). Hydrophobic components are typically made of a variety of polymeric materials, PVDF, PTFE, PES, and PSU [86]. According to recent research, adding nanoparticles to Janus membranes greatly improves their temperature stability and wetting resistance, both of which are essential for long-term MD applications. Because of their high surface area and distinct physicochemical characteristics, carbon-based nanomaterials—such as carbon nanotubes (CNTs) and graphene derivatives—have been used to increase mechanical strength and improve water vapor movement. Furthermore, metal oxide nanoparticles, such as ZnO and AlO_3 , have been employed to reduce biofouling and scaling on the membrane surface by introducing photocatalytic and antibacterial capabilities [87]. Even with their benefits, there are still a number of obstacles to overcome, such as the difficulty of large-scale

manufacturing, stability over time in demanding working environments, and possible environmental issues with the application of chemical surface changes. Research is being done to address these issues by creating economical and environmentally friendly production techniques, such as bio-inspired coatings and green chemistry techniques. For MD applications, good permeability and selectivity also depend on optimizing membrane thickness and porosity while preserving the Janus effect [88]. Future studies should concentrate on creating scalable production methods, improving membrane durability using sophisticated material engineering, and carrying out thorough life-cycle analyses to gauge their environmental impact. Additionally, hybrid membrane systems that combine Janus membranes with cutting-edge desalination techniques like electrodialysis and pervaporation may present fresh possibilities for environmentally friendly water treatment options, especially in areas with extreme water scarcity and high salinity.

2.2 Challenges associated with Janus membrane

Two major obstacles stand in the way of Janus membranes' performance and commercialization potential, regardless of the manufacturing technique used. Because of their different chemical compositions, the hydrophobic and hydrophilic layers have poor contact, which presents the first challenge. This incompatibility can eventually cause delamination while the membrane is in use, lowering its structural integrity and rendering it unfit for long-term use. Strong interfacial adhesion between the two layers is essential to Janus membrane endurance in industrial applications [89], [90]. Fouling is the second problem, especially from hydrophobic materials and low-surface tension substances like surfactants. These hydrophobic foulants can be somewhat repelled by the hydrophilic layer, but if they manage to get past it, they can reach the underlying hydrophobic layer and wet

the membrane. Wetting impairs the membrane's capacity to efficiently distinguish water from impurities, which could result in membrane breakdown or diminished performance. Improving the longevity and dependability of Janus membranes for commercial applications requires addressing problems with delamination and wetting [91], [92].

2.2.1 Delamination

Delamination is a major challenge that limits the Janus membranes' being widely used and long-term stability in practical applications. Two different layers with opposing wettability normally make up a Janus membrane; the hydrophilic layer is intended to attract and transport water, while the hydrophobic layer provides water-repellent qualities that prevent membrane wetting. Because of the design, these layers must be made of various materials, which, if left unmodified, frequently results in poor interlayer adhesion and increase the possibility of delamination over time. A re-entrant structure is often created on the surface of the hydrophobic layer, which acts as the substrate, during the overall manufacturing of a Janus membrane. After that, low-surface-energy materials are applied to this structure to create an omniphobic membrane. The hydrophilic layer is put on top of the omniphobic substrate to create the Janus structure. However, the hydrophobic base and the hydrophilic coating tend to interact less when low-surface-energy coatings are applied to the omniphobic membrane, which results in weak adhesion between the two layers. The membrane's stability and strength are compromised by this poor adherence, particularly in long-term applications where structural integrity is crucial. The delamination issue becomes more severe during water treatment when the hydrophilic layer absorbs water and

gets hydrated. Owing to the hydrophilic and hydrophobic layers' intrinsic differences in wettability, the hydrophilic layer's expansion may exacerbate the mechanical stress and incompatibility at the interface. The two layers gradually separate or delaminate as a result of increased interfacial tension and adhesion conflicts between them. Over time, the mechanical stability and separation performance of the membrane is reduced due to the weakening of the membrane structure caused by delamination [88],[93]. A significant focus needs to be placed on enhancing interlayer adhesion while preserving Janus membrane separation performance to address this problem. Finding a balance between layer compatibility and performance is essential to increasing Janus membranes' operational lifetime and improving their dependability in practical applications. **Fig. 2.1** shows how the delamination process contributes to membrane failure during operation by showing how weak adhesion and swelling of the hydrophilic layer occurs.

Even though multi-layer polymer membrane production has advanced significantly, delamination is still a problem. It is challenging to balance the attachment and detachment pressures because of the variations in the layers' physical and chemical characteristics. In certain instances, layer-by-layer application of the hydrophilic layer is used to enhance the accuracy and quality of the top layer. Nevertheless, this process evenly disperses stress throughout the coating, which may cause successive separation in certain operational scenarios. The best strategy is to use dope solutions made from similar solvents or polymers in the same family to reduce the likelihood of delamination. More cohesive coating is produced by promoting adhesion and using the same solvent for both layers. For instance, Liu et al. [94] used a water-soluble ϵ -Caprolactam solvent for both the hydrophobic PVDF layer and the hydrophilic PVDF-PVA layer. The same solvent and PVDF polymer helped

to create an integrated membrane, resulting in delamination-free Janus membranes for DCMD.

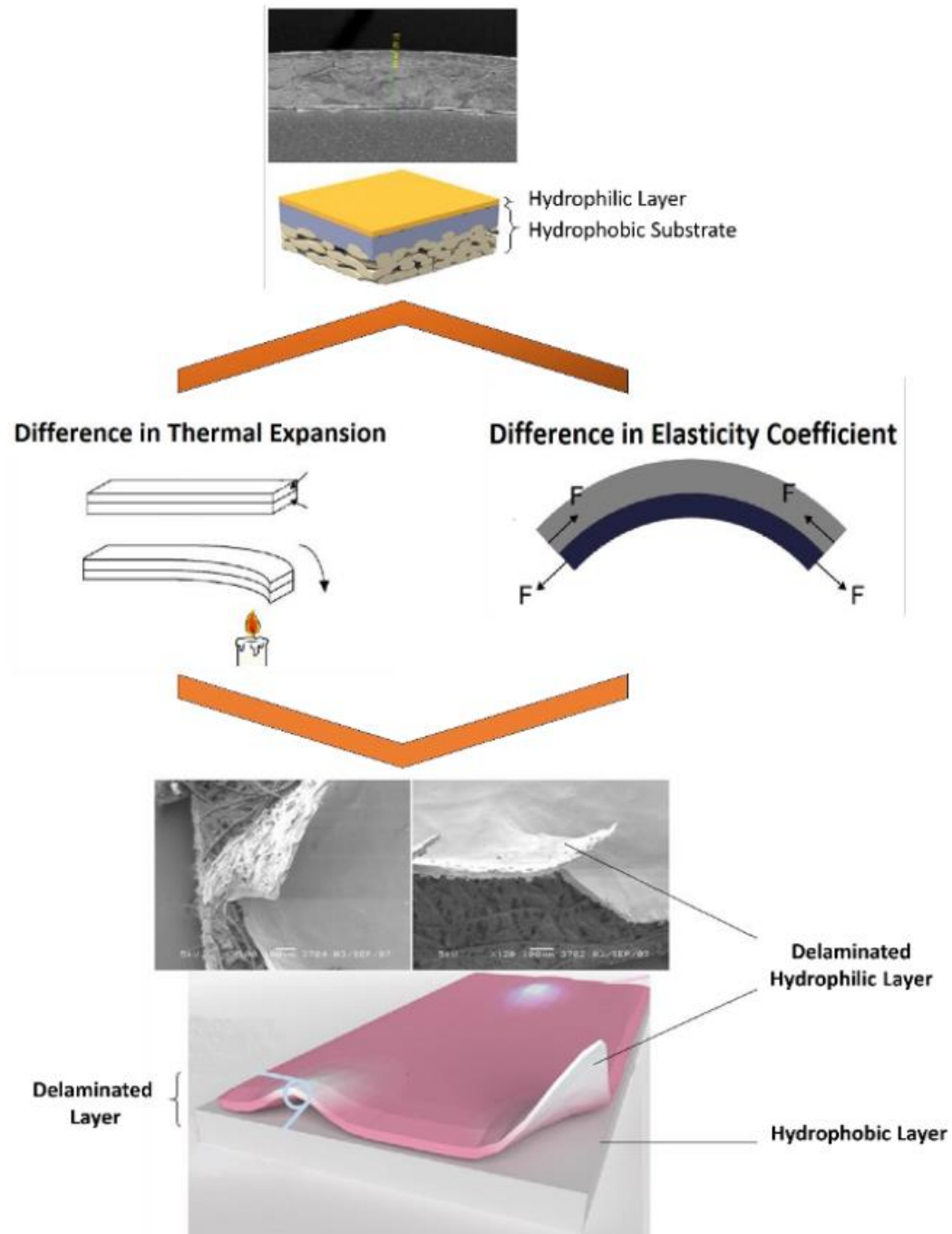


Figure 2. 1 Schematic illustration of delamination of Janus membranes [95].

Another major challenge is fabricating the Janus membranes through phase inversion due to the possibility of phase and structural changes between the layers. This problem occurs

especially when various coagulation rates are used to generate the two layers. A distinct layer with weak linkages between the hydrophobic and hydrophilic layers is typically formed when they solidify at different rates. The membrane's mechanical stability and performance are severely compromised by this inadequate interfacial bonding, which can cause delamination when the membrane is in operation. To address this issue, choosing appropriate dope compositions and ternary phase inversion process needs to be considered. The phase inversion rates of the hydrophilic and hydrophobic layers ought to be carefully compared. By aligning the two layers' coagulation behaviors, this analysis improves the membrane's structural integrity and lowers the chance of delamination. A lack of synchronization between the layers might result in the weakening of interfacial connections, which increases the membrane's vulnerability to mechanical failure in practical applications [96], [97].

To improve the adhesion between the omniphobic layer and hydrophilic layer in Janus membranes, pre-treatment processes can be employed. These processes create a strong connection between the hydrophilic coating and the omniphobic surface. Studies have shown that active spots on the omniphobic layer are necessary for a hydrophilic dope solution to adhere to it. The omniphobic surface of a hydrophilic layer cannot be directly coated without pre-treatment because the omniphobic substrates impede the establishment of active bonding sites and resist many liquids [98], [99]. A possible solution to this problem is forming fluorocarbon sites on the omniphobic surface; however, this process necessitates a high activation energy, usually reached at temperatures of about 90°C. Before applying the hydrophilic coating, plasma etching creates active spots on the surface, making it a more successful tactic. The hydrophilic and omniphobic layers showed strong

adhesion in a pre-treatment study that used this plasma etching; no delamination was seen during DCMD tests. The MD performance was high and stable when this method was used instead of previous Janus membrane production procedures [83].

2.2.2 Limitations in Vapor Transport Across the Janus Membranes

Another problem with Janus membranes is their dense interface morphology, which restricts vapor transport during MD applications and is frequently followed by delamination. Lowering membrane flux is a result of the coating layer's compact interface, which tends to decrease effective surface area. For example, Wang et al. [100] added chitosan to a hydrophilic PVDF membrane, which led to a 15% reduction of flux (from 31 LMH to 26 LMH) in comparison to the unmodified PVDF, even if the antifouling and antiwetting properties were improved. Similarly, Lin et al. [101] improved the antifouling and anti-wetting capabilities of a porous hydrophobic PTFE membrane by applying a hydrophilic hydrogel; nevertheless, the compactness and pore blockage caused a flux reduction from 30 LMH to 23 LMH in DCMD. Using co-extrusion techniques or modifying the concentration and composition of the dope solution are two ways to address problems with both dense interfaces and delamination. To reduce delamination, Zuo et al. [102] employed co-extrusion and various dope compositions. In order to improve the porosity, flux, and density of the interface, they introduced alumina nanoparticles into the inner layer, resulting in flaws in the polymer matrix. Nevertheless, overuse of nanoparticles decreased top-layer adhesion, separation performance, and mechanical strength. Therefore, to get the best possible structure and substrate adherence, careful balancing is needed during the design of Janus membranes.

2.2.3 Microdefect Formation in the Hydrophilic Membrane Layer

In addition to delamination, the coating of an omniphobic or hydrophobic layer with a hydrophilic layer can result in the production of microdefects, which can create microchannels that decrease the rejection of salt in membranes. To address this challenge, hydrophilic layers are frequently dried and hydrated; however, these processes may cause errors in actual testing. Wenzel theory suggests that hydrophilicity can be increased by increasing surface roughness in the hydrophilic layer. For instance, Chew et al. [98] coated a PDA layer on a PVDF substrate, resulting in an improved performance in wetting and fouling tests, but SEM analysis revealed microvoids that compromised membrane performance. To address these microdefects, Ag nanoparticles were used to coat the hydrophilic layer as shown in **Fig. 2.2**, successfully preventing microchannel formation and maintaining performance during 96-hour DCMD tests.

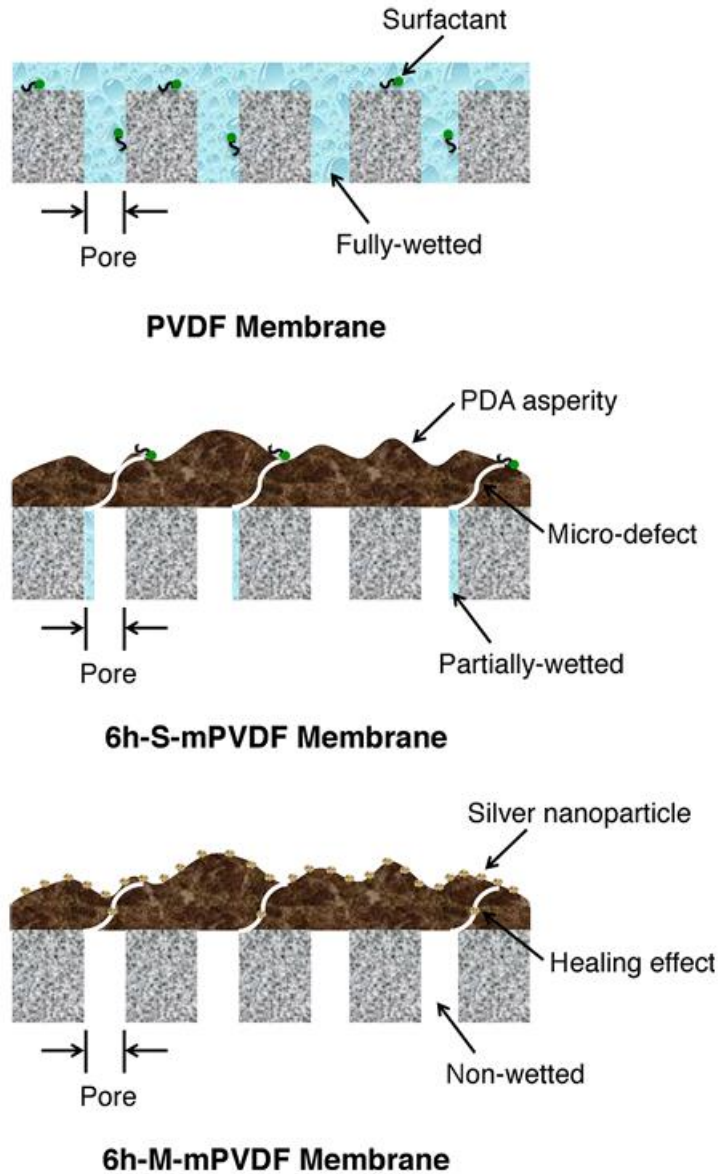


Figure 2. 2 Schematic illustration of Ag nanoparticles dispersion to resist wetting behavior of Janus Membranes [98].

2.2.4 Scaling Problems in Janus Membranes

Scaling is another major issue that affects the Janus membranes' long-term performance during MD. This problem is an important area of concern for both industrial and research applications since they can not only severely impair the membranes' lifespan but also

reduce their efficiency. To investigate the efficiency of Janus and hydrophobic membranes during scale generation in a high SDS feed water, Yin et al. [103] conducted a DCMD test. NaCl, gypsum scales, and amorphous silica were present in the feed solution at different amounts. Three different kinds of membranes were tested: PVA/PVDF-SiNP-FAS Janus membrane, PVDF-SiNP-FAS superhydrophobic membrane, and hydrophobic PVDF membrane. The sliding test results showed that the water droplet stayed stationary on the surface even though the hydrophobic membrane had a high-water contact angle. On the superhydrophobic membrane, however, the droplet started to glide at a 17° angle. Janus membranes can be regenerated with a specific backwashing method to remove the scales that build up on the membrane surface. Zou et al. [92] evaluated the membrane's functionality after performing the regeneration of the Janus membranes. Based on three days of continuous operation, the experimental results showed that the membrane's water recovery was about half of what it would have been after 16 hours of testing. This result showed that scale formation on the Janus membrane changed the pore structure, leading to a decrease in water recovery and salt rejection over time by changing its stability and shape.

2.3 MD Performance Evaluation of Janus Membranes

Electrospun nanofibrous membranes typically exhibit higher permeate flux due to their higher porosity (%) and larger pore size, making them well-suited for MD applications [44]. For instance, Woo et al. [104] reported different Janus-type membranes with hydrophobic top surfaces made of PVDF-co-HFP electrospun nanofiber, and hydrophilic bottom surfaces made up of PVA, Nylon-6, and PAN nanofiber. The reported membranes showed a higher permeate flux in AGMD testing configuration up to $15.5 \text{ kg m}^{-2} \text{ h}^{-1}$ than

commercial hydrophobic membranes with $5 \text{ kg m}^{-2} \text{ h}^{-1}$. Similarly, Kong et al. [105] constructed a Janus electrospun dual-layered membrane with a hydrophobic top layer of PVDF-co-HFP with ZIF-71 and a hydrophilic layer of PSF nanofibrous membranes. The reported membrane shows an asymmetric wettability of WCA on the hydrophobic side 147.6° while the hydrophilic side exhibited a lower WCA of 118° . This asymmetric feature of the membrane was attributed to a higher permeate water flux of $26.3 \text{ kg m}^{-2} \text{ h}^{-1}$ with a salt rejection of 99.99% during the DCMD test. Khayet et al. [106] fabricated Janus composite membranes using polyetherimide (PEI) substrate which was modified with fluorinated surface-modifying macromolecules (SMM). The fabricated membranes demonstrated a higher flux in DCMD, more than double that of commercial PTFE membranes. Su et al. [107] prepared dual-layer hollow fiber membranes by incorporating graphite particles and multi-walled carbon nanotubes (MWNT) by dry-jet wet-spinning method. The flux was enhanced from 41.2 to $66.9 \text{ kg m}^{-2} \text{ h}^{-1}$ in DCMD. Zhao et al. [108] developed a novel covalent organic framework (COF) membrane that allows for precise water transport and phase change interfaces. These membranes demonstrated outstanding anti-fouling and anti-wetting properties with a higher flux at the feed concentration of 3.5% and feed temperature was maintained at 85°C . Their design demonstrates the potential of gradient membranes in developing MD technology regarding the use of waste heat in desalination applications. Meng et al. [109] fabricated Janus membrane by modifying PVDF membranes by bio-inspired PDA/PEI coating which makes the hydrophilic layer, and a forcespun nanofiber hydrophobic layer on the other side. By increasing the PDA/PEI layer thickness the WCA decreased from 124.6° to 31.3° , and the rough hydrophobic nanofiber layer enhanced the LEP to 136.4 kPa. The optimal membranes demonstrated a

DCMD flux of $25.3 \text{ kg m}^{-2} \text{ h}^{-1}$ with a salt rejection of $>99.99\%$. Figoli et al. [110] developed Janus membranes by dip-coating commercial PA membranes that had hydrophilic characteristics with a UV-curable perfluoropolyether (PFPE) hydrophobic coating followed by polymerization. The WCA of the hydrophobic layer was measured at 150° , while the hydrophilic PA layer was $\sim 45^\circ$, and achieved LEP up to 2.05 bar. The optimized membrane exhibited a distillation flux of $11 \text{ kg m}^{-2} \text{ h}^{-1}$ with a salt rejection of 99.3% under 0.6M NaCl feed solution. Cheng et al. [111] were fabricated composite dual-layer PTFE membrane by coating a dense hydrophilic polyurethane layer. The reported membranes exhibited high water recovery and exhibited a distillation flux of $23 \text{ kg m}^{-2} \text{ h}^{-1}$ while maintaining $\sim 100\%$ salt rejection. In another study, Li et al. [112] fabricated Janus membrane by layer-by-layer coating of Teflon® AF1600 and polydopamine (PDA) on a plasma-treated PTFE/PP hydrophilic membrane. The hydrophobic top layer was exhibited with a WCA of $\sim 145^\circ$ while the bottom hydrophilic layer showed $\sim 33.5^\circ$. The produced membranes maintained a stable flux of $19.7 \text{ kg m}^{-2} \text{ h}^{-1}$ for 50 hours with a salt rejection of $>99.9\%$ in DCMD.

Table 2. 1 MD performance evaluation of previously reported Janus membranes

Hydrophobic layer	Hydrophilic layer	MD configuration	Flux (kg m⁻²h⁻¹)	Rejection (%)	Ref.
PP	DA/PEI deposition	DCMD	6.12	>99	[51]
PVDF	Ultemk/Al ₂ O ₃	VMD	24.4	-	[102]
PVDF	PVA-GA	DCMD	25	-	[103]
PVDF/HFP	Nylon-6	AGMD	15.5	99.2	[104]
Forcespun PVDF nanofiber	DA/PEI deposition	DCMD	25.3	>99.99	[109]
PTFE	PU	DCMD	23	~100	[111]
PTFE- PP/Teflon AF1600	PDA/PEI	DCMD	19.7	>99.9	[112]
PVDF/PVP	PVDF/PVA	DCMD	7.5	>99	[113]
PVDF	Commercial PET	AGMD	15.2	>99.95	[114]

PTFE	Cellulose Acetate	DCMD	20	-	[115]
PVDF/Cloisite I5A	PVDF/PAN/ Cloisite NA+	DCMD	21.6	-	[116]
PVDF	EDA/PEI	DCMD	5	~100	[117]
fluorinated SMM	PEI	AGMD	14.9	>99.4	[118]
PVDF	PDA-PEI	DCMD	15	>99.9	[119]
PH-0.5CNF	PH-0.5JC	WGMD	71.72	>99.99	This Work
PH-0.5CNF	PH-0.5JC	WGMD	78.42	99.93	This Work
PVDF	ZnO	WGMD	38.31	~100	This Work

CHAPTER 3

MATERIALS AND METHODOLOGY

3.1 Introduction

This chapter presents a detailed overview of the experimental procedures and methodologies used in this research. It also elaborates on the specific materials employed and the systematic strategies implemented to achieve the research objectives, ensuring the study's reliability and reproducibility. By carefully documenting each step, this section provides a clear and precise account of the processes involved, enabling future researchers to fully comprehend and replicate the study.

3.2 Fabrication of Electrospun Janus Membranes

3.2.1 Materials

Poly(vinylidene fluoride-co-hexa-fluoropropylene) ($M_w \sim 400,000 \text{ g mol}^{-1}$); *N,N*-dimethylformamide (DMF) (anhydrous, 99.8%), Carbon Nanofibers (CNF), acetone, ethanol, and isopropyl alcohol were purchased from Sigma-Aldrich, USA. Humic acid (HA) was purchased from Sigma-Aldrich, Switzerland. Sodium sulfate ($M_w = 142.04 \text{ g mol}^{-1}$) was purchased from Honeywell, Fluka, India. Calcium chloride (anhydrous, $\geq 98.0\%$, $M_w = 110.98 \text{ g/mol}$) was purchased from Riedel-de Haën, Germany. Sodium chloride (99.8%) was purchased from Chem-Lab, Belgium. Ball-milled submicron biomass-derived jute carbon (JC) was collected from the Interdisciplinary Research Center for Hydrogen and Energy Storage (IRC, HES), King Fahd University of Petroleum and Minerals, Saudi Arabia. The JC was synthesized based on previously reported literature [103]. The real seawater was arranged from the Gulf Sea, Saudi Arabia. The chemicals

were not further purified and used as received. For all experiments, deionized water (DI) was utilized, obtained from a Milli-Q Plus system (Millipore, Bedford, MA, USA). The commercially available PVDF membrane was purchased from TISCH Scientific.

3.2.2 Dope Solution Preparation

A clear and homogeneous PVDF-co-HFP (PH) polymer dope solution of 17% (w/v) was prepared into a mixed solvent of DMF and Acetone in a 1:1 ratio to fabricate the pristine PH electrospun nanofibers membrane. For the fabrication of single-layered hydrophilic membranes, first, jute carbon (0.1, 0.5, and 1.0 wt%) was dispersed into a solvent mixture (DMF: Acetone = 1:1). To achieve a homogeneous mixture of carbon particles the dispersion was subjected to a high intensity ultrasonication (Sonics Vibra Cell) for 30 minutes. Following sonication, 17% (w/v) of PH polymer pellets was added to the solution, and the mixture was stirred at 50 °C for 12 hours to ensure a complete dissolution and uniform distribution of the components. To remove any entrapped air bubbles, the dope solution was kept in an oven at 50 °C for 6 hours before being transferred into the syringe for electrospinning. A similar procedure was followed for preparing the dope solution to fabricate the hydrophobic CNF composite PH electrospun membranes with the concentration of 0.1, 0.5, and 1.0 wt% respectively.

3.2.3 Dope Solution Viscosity

In dual-layer membranes, the dope solution's viscosity is a crucial factor in determining how well the layers adhere to one another and delaminate [120]. Furthermore, it can affect the membrane morphology and overall desalination performance by altering the fiber diameter and pore size in electrospun nanofibrous. The viscosity of the dope solutions was

measured by a viscometer (LICHEN, MODEL: NDJ-9S) after filling the cell with the sample solution.

3.2.4 Single-Layered and Dual-Layered Electrospun Membrane Fabrication

The schematic of the fabrication process of the developed membranes is shown in **Figure 3.1a**. For the fabrication of single-layered and dual-layered membranes, the electrospinning machine (MECC NANON, Japan) parameters remained unchanged, apart from the required voltage. The electrospinning process was conducted with a fixed tip-to-collector distance of 15 cm, and a rotating metal drum which was wrapped with aluminum mesh (grit size- 3 μm) to serve as the fiber collector. The electrospinning parameters are shown in **Table 3.1**.

Table 3. 1 Electrospinning Parameters

Parameters	Values
Machine Model	MECC NANON, Japan
Syringe Diameter	16.5 mm
Feed Rate	1 mL/h
Drum Rotation	150 rpm
Spinneret Width	100 mm
Spinneret Speed	50 mm/s
Spinneret to Drum Distance	15 cm
Relative Humidity	30-35%
Temperature	25°C

To fabricate the single-layered membranes, the dope solution was first electrospun onto an aluminum mesh, and then the membranes were carefully placed onto A4-sized tracing paper. The membranes were allowed to undergo complete solvent evaporation in a vacuum oven for 12 hours at 60 °C. After evaporation, the membranes were subjected to hot-pressing using a lightweight household iron in between the tracing paper to avoid direct contact with the membrane surface. The hot-pressed temperature was kept below the melting point of PVDF-co-HFP (150 °C), and the iron was moved gently across the membranes to avoid any thermal degradation of the electrospun nanofibers. To fabricate the PH-CNF/PH-JC dual-layered Janus membranes, the PH-JC solution was the first electrospun to serve as a bottom hydrophilic layer, followed by electrospinning of PH-CNF nanofibrous membranes as the top hydrophobic layer. A similar procedure was followed as described above to have the final dual-layered Janus membranes with different concentrations of filler materials. The digital image of the prepared membranes with varying carbon concentrations is depicted in **Figure 3.1b** and the Janus membrane is shown in **Figure 3.1c** with top and bottom layers. It can be seen from **Figure 3.1b**, the pristine PH membrane exhibits a smooth and even surface, while incorporating the carbon content of 0.1 wt% and 0.5 wt% into the polymer matrix resulting in membranes with smooth and even surfaces due to the optimal balance between solution viscosity and electrospinning process parameters. However, when the carbon content was increased to 1.0 wt% (for both PH-1.0JC and PH-1.0CNF membranes), the surfaces became uneven. This is attributed to the rise in solution viscosity caused by the higher carbon loading. The higher viscosity reduces the fluidity of the solution, preventing the continuous stretching of the electrospinning jet. Moreover, the increased carbon content led to particle aggregation

within the solution, further impacting the uniformity of the fiber formation. The combination of these factors results in incomplete stretching and solidification of the jet at the electrospinning needle tip, producing uneven surface characteristics. The composition of all the prepared electrospun membranes, their designation, dope solution viscosity, and the required voltage are shown in **Table 3.2**.

Table 3. 2 Membrane Composition, Viscosity and Required Voltage for Electrospinning

Membrane ID	Membrane Types	PVDF-co-HFP (wt%)	DMF: Acetone	Carbon Nanofibers (wt%)	Biomass Carbon (wt%)	Viscosity (cP)	Required Voltage (kV)
PH	Single Layer	17	1:1	-	-	426	12.0
PH-0.1JC	Single Layer	17	1:1	-	0.1	502	11.0
PH-0.5JC	Single Layer	17	1:1	-	0.5	887	9.5
PH-1.0JC	Single Layer	17	1:1	-	1.0	1099	9.0
PH-0.1CNF	Single Layer	17	1:1	0.1	-	632	11.5
PH-0.5CNF	Single Layer	17	1:1	0.5	-	996	10.5
PH-1.0CNF	Single Layer	17	1:1	1.0	-	1223	10.0
PH-0.5CNF/PH-0.1JC	Dual Layer	17	1:1	0.5	0.0	996	11.0
		17	1:1	0.0	0.1	502	11.5
PH-0.5CNF/PH-0.5JC	Dual Layer	17	1:1	0.5	0.0	996	9.5
		17	1:1	0.0	0.5	887	10.5
PH-5.0CNF/PH-1.0JC	Dual Layer	17	1:1	5.0	0.0	996	9.5
		17	1:1	0.0	1.0	1099	10.0
PH-1.0CNF/PH-0.5JC	Dual Layer	17	1:1	1.0	0.0	1223	9.5
		17	1:1	0.0	0.5	887	9.0
PH-1.0CNF/PH-1.0JC	Dual Layer	17	1:1	1.0	0.0	1223	10.5
		17	1:1	0.0	1.0	1099	10.0

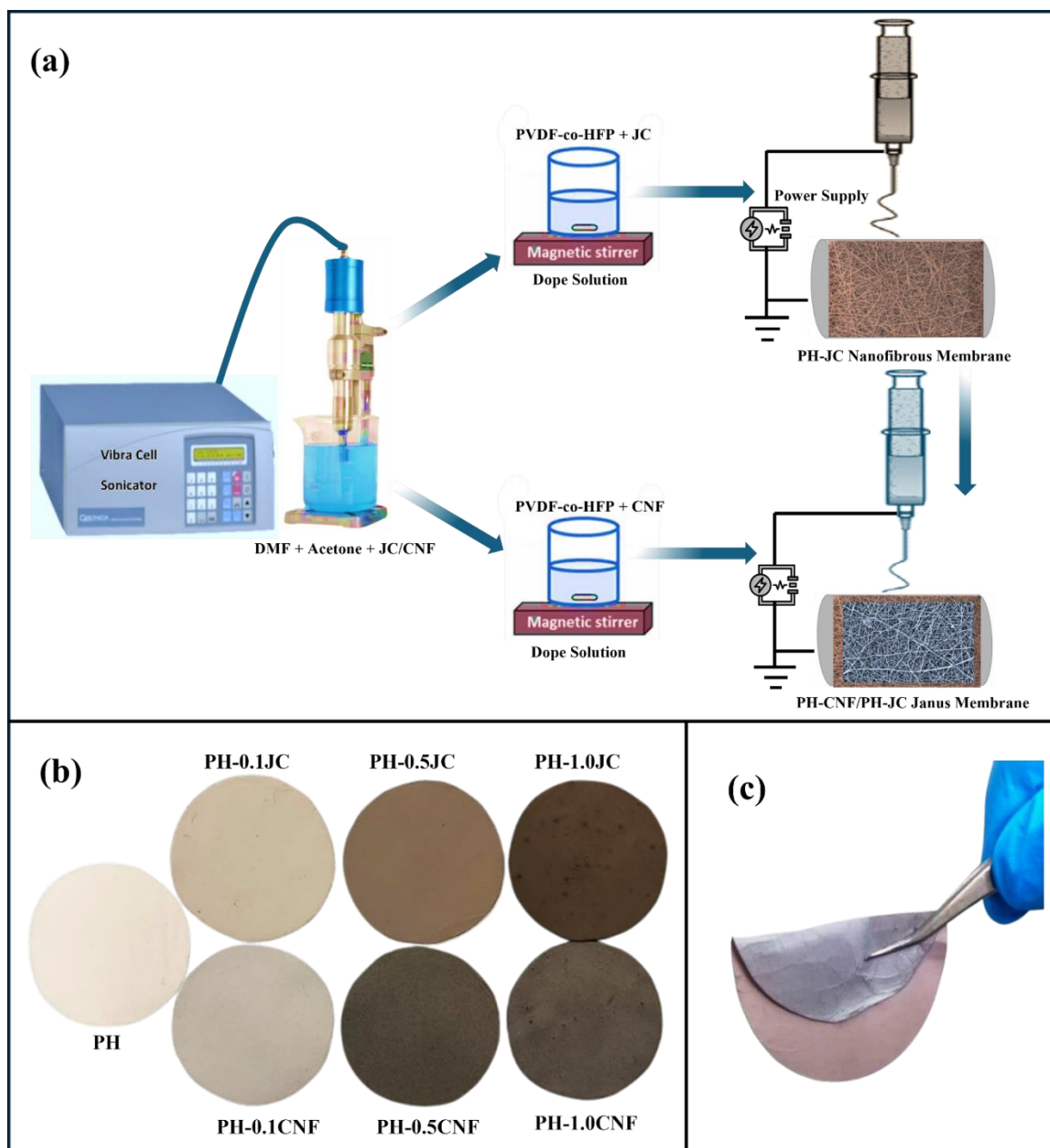


Figure 3. 1 (a) Schematic of the preparation of the electrospun nanofibrous single-layered dual-layered membranes; Digital image of (b) the prepared PH membranes composited with various concentrations of JC and CNF; and (c) Janus membrane showing the top and bottom layer.

3.3 Fabrication of PVDF Janus Membranes via Sputtering

3.3.1 Materials

Polyvinylidene Fluoride (PVDF) powder with $M_w = \sim 534,000$, lithium chloride (LiCl), N, N-dimethylformamide (DMF), iso-propyl alcohol ($\geq 99.9\%$), and ethanol ($\geq 99.9\%$), were purchased from Sigma-Aldrich, USA. Sodium chloride (NaCl, 99.8%) was purchased from ChemLab, Belgium, for preparing the feed solutions. The commercial PVDF membrane used in this study purchased from TISCH Scientific. Deionized (DI) water was supplied by a laboratory-scale system from Merck Millipore.

3.3.2 Preparation of PVDF Membranes

In this study, two different substrates were selected for fabricating PVDF membranes: a smooth glass (G) surface and a textured sandpaper (SP) substrate. A locally purchased SiC-based SP with a 400-grit size was used, prior to membrane casting, the SP was carefully cleaned. Both substrates were thoroughly prepared and placed horizontally to facilitate manual membrane casting using a film-casting doctor's blade. A precise amount of PVDF powder (17 wt.%) was dissolved in DMF (81 wt.%) containing 2 wt.% LiCl as pore former and stirred at 250 rpm while maintaining a temperature of 40 °C for 24 hours. The degassed polymer mixture was manually cast onto the selected substrates with a 250- μm casting film thickness. The fabricated membranes in this study were produced via a nonsolvent-induced phase separation (NIPS) method as shown in **Fig. 3.2a** using the prepared dope solution. Immediately after casting, the thin film was immersed in a coagulation bath filled with deionized water to complete the NIPS process. The membrane sheet, formed through precipitation in the coagulation bath, was retrieved after 10 minutes and transferred to a fresh deionized water bath for 12 hours to remove residual solvent. The hydrated

membranes were then air-dried between filter papers at room temperature for at least 24 hours before being subjected to further modification, characterization and testing.

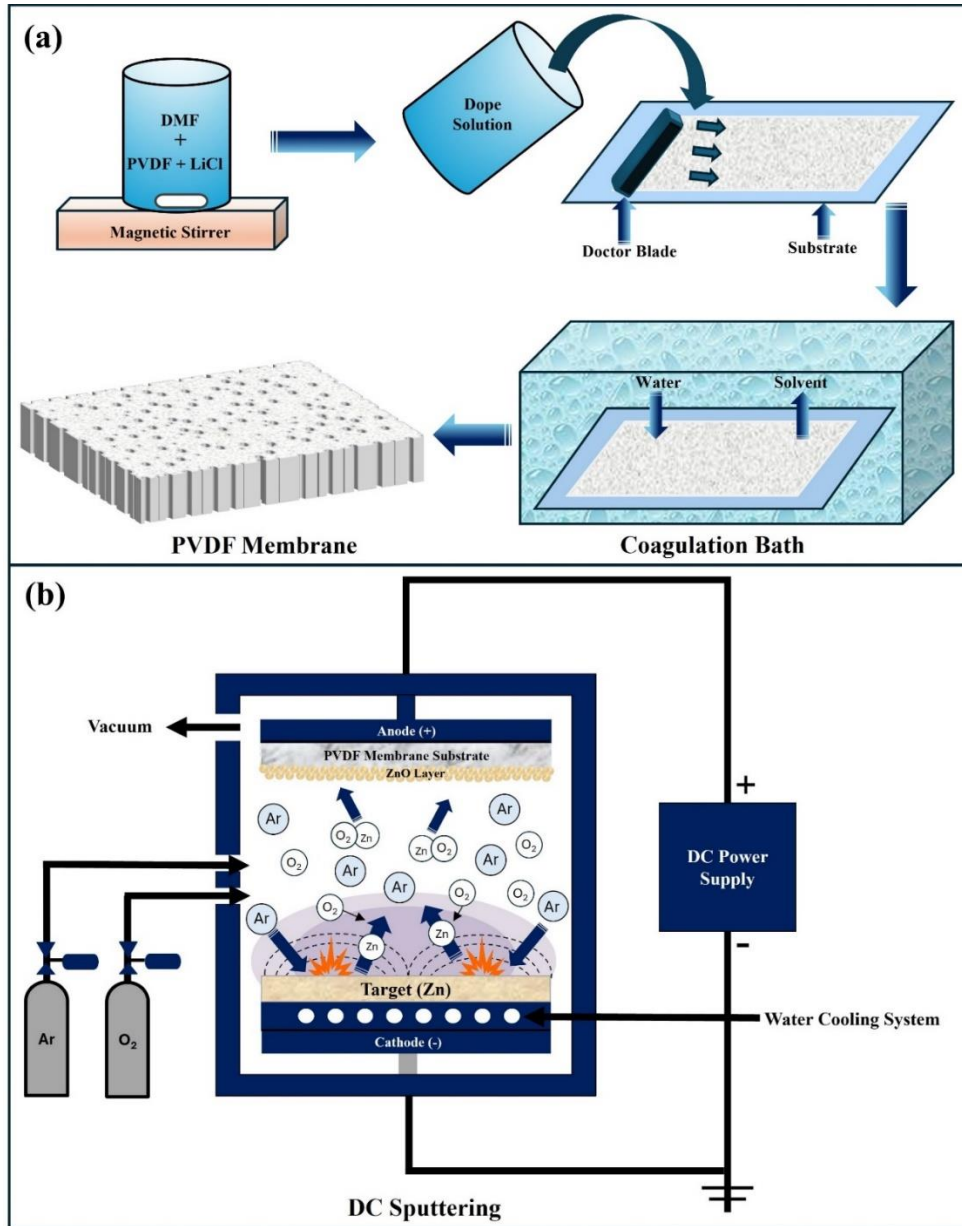


Figure 3. 2 Schematic illustration of (a) fabrication of PVDF membranes via phase inversion method; (b) sputtering of Zn atoms on the PVDF membrane surface in an oxygen atmosphere.

Table 3. 3 The fabricated membranes designation, their composition and duration of sputtering

Membrane ID	Substrate	Membrane Composition		Solvent	Casting Thickness (μm)	Sputtering Duration (min)
		PVDF (wt%)	LiCl (wt%)	DMF (wt%)		
G0	Glass	17	2	81	250	0
G5	Glass	17	2	81	250	5
G10	Glass	17	2	81	250	10
G12	Glass	17	2	81	250	12
G15	Glass	17	2	81	250	15
SP0	sandpaper	17	2	81	250	0
SP5	sandpaper	17	2	81	250	5
SP10	sandpaper	17	2	81	250	10
SP12	sandpaper	17	2	81	250	12
SP15	sandpaper	17	2	81	250	15

3.3.3 Sputtering on PVDF Membrane Surface

The prepared pristine PVDF membranes were employed in DC magnetron sputtering (NSC – 400 sputter coater) for the deposition of hydrophilic ZnO coating on the skin layer to make an asymmetric wettability as shown in **Fig. 3.2b**. A target material of zinc (Zn), 99.99% purity, was used as a cathode material in the system. For converting Zn into ZnO, an oxidizing atmosphere was created inside the deposition chamber by introducing argon (Ar) and oxygen (O_2) gases. Before deposition, the chamber was evacuated to the base

pressure of 8.69×10^{-5} torr. Afterward, Ar and O₂ were injected into the deposition chamber at the flow rate (sccm) of 35:35 at room temperature. The deposition was carried out at different time intervals by applying constant power. The composition of all the developed membranes, their ID used in this report, and sputtering duration are shown in **Table 3.3**. The substrate table was rotated during deposition to achieve a uniform coating. The details of the sputtering parameters are given in **Table 3.4**. MD experiments were carried out with the membrane surface facing the textured surface towards the feed side and the sputtered surface facing to the permeate side.

Table 3. 4 Deposition parameters of ZnO thin film

Sputtering Parameters	Values
Base pressure	8.69×10^{-5} torr
Working pressure	5.28×10^{-3} torr
Ar:O ₂ flow rate	35:35 (sccm)
Power	50 W
Sputtering duration	5, 10, 12, and 15 mins
Target to substrate distance	18.5 cm
Rotation	1.55 rpm

3.4 Membrane Characterization and Measurements

3.4.1 Morphology, Structural Integrity and Crystallinity Measurements

The surface morphology of the developed membranes was investigated by using a field emission scanning electron microscope (FE-SEM), supplied by FEI Quanta 250 FEG,

USA. The samples were first sputter-coated with gold for 50 seconds using a Cressington Sputter Coater to enable high-resolution imaging. The working distance was kept ~ 10 mm for the surface morphology, ~ 11.5 mm for the cross-sectional view, and the accelerating voltage was kept constant at 15 kV. Energy Dispersive Spectroscopy (EDX) (SILICON DRIFT 2017, USA) was employed to analyze the elemental composition of the clay particles and the composite membranes. Atomic Force Microscope (AFM, Agilent 5500, USA) was used to evaluate the surface roughness of the developed membranes using Si_3N_4 cantilever beam in contact mode with a resolution of 10 nm in an area of $5 \times 5 \mu\text{m}^2$, and at a scanning rate of 0.8 Hz.

The chemical structure of the developed membranes was assessed using FTIR (Fourier Transform Infrared) spectroscopy in ATR (Attenuated Total Reflectance) mode, employing a diamond crystal for 32 scans over a range of 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1} on an iS50 Nicolet Thermo Fisher Scientific instrument from Massachusetts.

X-ray diffraction spectra were obtained to analyze the crystalline structure of the sputtered membranes. An Ultima IV Rigaku X-ray diffractometer (Kuraray Company Ltd, Japan) was utilized, operating at a scanning rate of 1° min^{-1} , covering a range from 5° to 80° to capture the 2θ values. The diffraction patterns were recorded using monochromatic $\text{CuK}\alpha$ radiation (Wavelength = $1.54056 \text{ \AA}$) at 30 mA and 40 kV.

3.4.2 Surface Wettability Analysis

The WCA measures the membrane's wettability by revealing how a water droplet interacts with its surface. A goniometer equipped with a sessile drop method and real-time image

processing software (DM-501, Kyowa Interface Science Co. Ltd., Japan) was used to measure the WCA of all the prepared membranes. An image of the water droplet was captured by a digital camera at room temperature. An average of four measurements is reported for each membrane sample to minimize measurement errors due to chemical interaction between the water droplet and membrane surface.

Liquid Entry Pressure (LEP) is the minimum pressure needed for a liquid to penetrate a membrane's pores, influenced by the membrane hydrophobicity, liquid surface tension, pore size, and structure [121], [122]. The LEP for all the prepared membranes was evaluated using dead-end specially designed equipment. A round piece of membrane with an active surface area of 4.90 cm^2 was attached to the LEP chamber, the reservoir was filled with 5 mL of distilled water. Nitrogen gas was introduced and increasing the gas pressure caused the water to rise and contact the membrane surface. The LEP point was measured with the first water droplet formation. Four measurements were taken to minimize the inaccuracies, and the average results were reported.

3.4.3 Membrane Intrinsic Characteristics

The mean pore size (MPS) and the pore size distribution (PSD) of the fabricated electrospun membranes were measured by a Porometer 3G (Quantachrome instrument, USA) using the dry-wet flow method. The mass transfer resistance is significantly influenced by the thickness of the membrane [123]. The thickness of all developed membranes was measured using a constant force thickness indicator ($\pm 0.0001 \text{ mm}$) from Mitutoyo (Litematic VL-50A, Japan) at 10 distinct places within the membranes, and the average membrane thickness is reported.

The porosity for all the prepared membranes was measured using gravimetric analysis, by weighing the membrane samples at both dry and wet states before and after they were soaked in isopropanol for 2 hours. After being immersed in isopropanol the membrane samples were fully saturated, and any surplus solvent was removed using filter paper. The wetted sample was then weighed and the porosity, ε (%), was calculated using the following equation (1).

$$\varepsilon (\%) = \frac{\frac{M_W - M_d}{\rho_i}}{\frac{M_W - M_d}{\rho_i} + \frac{M_d}{\rho_m}} \times 100\% \quad (\text{Equation 1})$$

Where M_W is the mass of the wet membrane, M_d is the mass of the dry membrane. ρ_i and ρ_m are the density of iso-propanol (0.785 kg/m³) and polymer of the membrane respectively.

Even though MD does not require any external pressure, the higher mechanical strength of a membrane is crucial to maintaining a stable performance in the long run. The prepared membranes were tested by Amatek LD10 Universal machine, China to evaluate their tensile strength and elongation at breaking (%). All the tests were performed at a rate of 0.1 mm/min with a 300N load cell.

The Thermogravimetry analysis (TGA) was carried out in an inert nitrogen gas atmosphere (flow rate = 50 mL/min) using a Shimadzu TGA/DTA simultaneous measuring instrument, DTG-60/60H (Kyoto, Japan). The test was performed at a temperature range of 50–800 °C with a heating rate of 10 °C min⁻¹.

3.5 Water Gap Membrane Distillation Experiment

A custom-built MD system was used to conduct WGMD experiments to assess the performance of all fabricated electrospun nanofibrous single-layered and dual-layered membranes as shown in **Fig. 3.3**. The system was fully automated and equipped with comprehensive instrumentation for precise computer-controlled operation. The main instruments of this system are an MD cell and two recirculating water tanks- one supplies hot feed solution, and another one feeds the cold water to the MD module. Brass material was used for the condensation plate which was placed onto the coolant side. A high-density polyethylene (HDPE) was used to support the membrane which has an effective membrane surface area of $7.316 \times 10^{-4} \text{ m}^2$, creating a 5 mm gap that was later filled with distilled water. Flowmeters from Omega (FL50000) were installed and used to monitor the flow rates of hot and cold feeds into the MD cell. The hot feed solution was prepared by dissolving sodium chloride with a concentration of 70 g L^{-1} in DI water, making the solution highly saline (70,000 ppm). A weighing balance (Radwag, PS2100.R2.M) was used to measure the permeate flux and the salt rejection was calculated through software that was connected directly to the conductivity meter (Hanna HI5321). All the measured data were taken from software throughout the experiments; hence, the possibility of errors will be negligible. The performance of the tested samples was measured in terms of flux ($\text{kg m}^{-2} \text{ h}^{-1}$) and salt rejection (%).

The permeate flux ' J_p ' in $\text{kg m}^{-2} \text{ h}^{-1}$ was measured by the following Equation:

$$J_p = \frac{M}{At} \quad (\text{Equation 2})$$

Where “M” is the mass (kg) of the total permeate water, “t” is the time (h) taken to collect the permeate, and “A” is the effective membrane area (m²) respectively.

The following equation calculated the salt rejection percentage, R (%):

$$SR (\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100 \% \quad (\text{Equation 3})$$

Where C_f and C_p (measured in parts per million, ppm) represent the feed concentration and permeate concentration respectively.

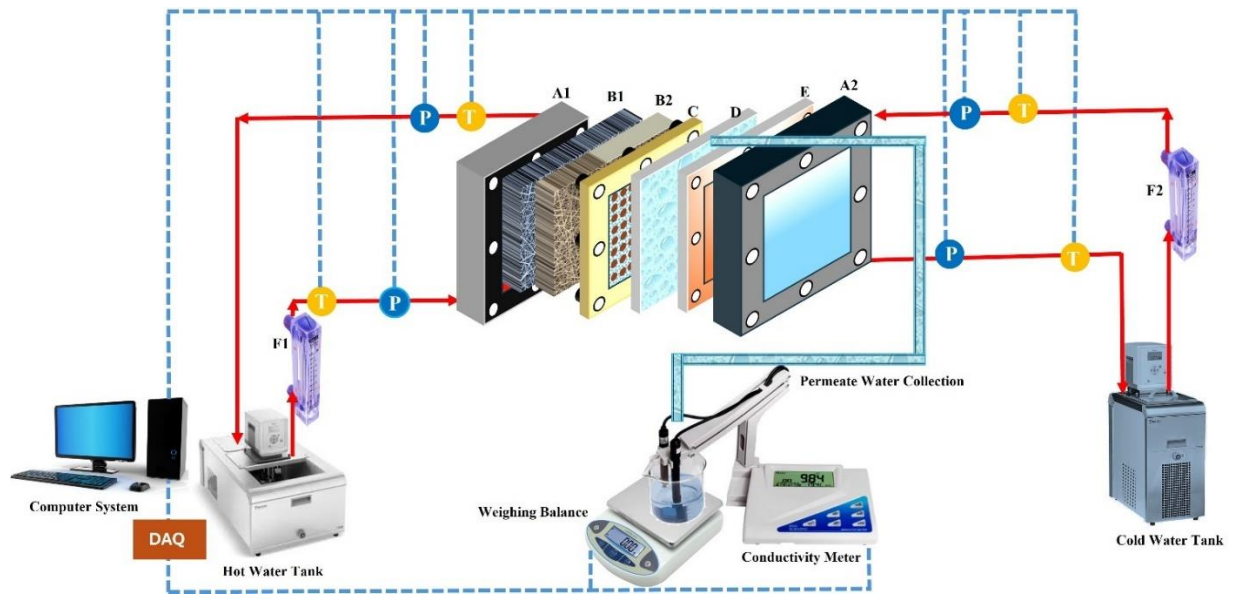


Figure 3. 3 Schematic setup for WGMD.

(A1, A2) Feed water and Cold-Water Chamber Frame, (B1, B2) Hydrophobic and Hydrophilic Membranes respectively; (C) Acrylic Spacer, filled with distilled water; (D) Permeate Water; (E) Condensation Brass Plate; (F1, F2) Flow Meter for Hot water and cold water respectively; (P) Pressure Gauge; (T) Temperature Gauge; DAQ = Data Acquisition System.

Table 3. 5 WGMD Experimental Conditions

Test Parameters	Values
Hot Feed Salinity (C_f)	70 g/L (NaCl)
Feed Temperature (T_f)	70 ± 0.5 °C
Feed Flowrate (F_f)	0.8 ± 0.1 L min ⁻¹
Coolant Water	Normal Tap Water
Coolant Temperature (T_c)	20 ± 0.2 °C
Coolant Flowrate (F_c)	1.8 ± 0.1 L min ⁻¹
Water Gap Distance	5 mm
Effective Membrane Surface	7.316×10^{-4} m ²

CHAPTER 4

BIOMASS CARBON AND CARBON NANOFIBERS

INTEGRATED JANUS MEMBRANES FOR MEMBRANE

DISTILLATION

4.1 Introduction

Despite the advancements in fabricating dual-layer Janus membranes, there remains a need for simpler fabrication processes to produce high-performance Janus membranes for MD applications. In this study, we developed novel dual-layered Janus membranes by combining Polyvinylidene fluoride-co-hexafluoropropylene (PH) with a hydrophilic bottom layer composed of pre-synthesized biomass-derived jute carbon nanoparticles (JC) followed by a hydrophobic top layer integrated with hydrophobic CNF by a simple electrospinning technique. It is noted that non-functionalized carbon nanomaterials like carbon nanofibers (CNF) are hydrophobic and biomass-derived nanocarbon, which is prepared at low temperatures, generally exhibits hydrophilicity due to the presence of abundant oxygen-containing functional groups. Initially, single-layered membranes—hydrophilic PH/JC and hydrophobic PH/CNF—were fabricated separately via electrospinning, with various concentrations of JC and CNF materials integrated into the PH polymer matrix. To fabricate the dual-layered membranes, the PH/JC layer was electrospun first, followed by the electrospinning of the PH/CNF layer on top. The fabricated hydrophilic and hydrophobic surfaces using a layer-by-layer electrospinning

approach ensure strong interfacial adhesion through fiber entanglement between layers, which enhances membrane durability and eliminates the risk of delamination. The effect of hydrophilic and hydrophobic carbon particle concentrations on membrane morphology, intrinsic characteristics, and performance in WGMD were thoroughly investigated. To the best of our knowledge, this is the first report to fabricate a layer-by-layer electrospun Janus membranes composed of hydrophilic and hydrophobic carbon materials incorporated with the PH membrane, creating asymmetric wettability for a robust WGMD performance.

4.2 Morphology and Elemental Analysis

The morphology of the pre-synthesized JC particles has been investigated by SEM as shown on **Fig. 4.1a1** (inset- WCA). The micrographs show that the shape of the JC particles is smaller and rounded. Particle size analysis using ImageJ software revealed that the JC particles had a diameter of <500 nm. Such submicron particles can be homogeneously distributed to the PH polymer solution. As seen in **Fig. 4.1(a2-a4)**, elemental analysis was performed using EDS analysis. The spectrum verified that carbon was a dominant element while a small amount of oxygen was present. Carbon compounds generated from biomass typically contain oxygen. The SEM micrographs of the CNF are displayed in **Fig. 4.1b1** (inset-WCA), with an average fiber diameter of ~ 100 nm. EDS analysis in **Fig. 4.1(b2-b3)** revealed that carbon is the only element in CNF.

The SEM images presented in **Fig. 4.1(c1-c2)** reveal that the pristine electrospun PH nanofibrous membrane features a smooth and uniform fiber arrangement with an average diameter of 619.89 nm (**Fig. 4.1c3**). As shown in **Fig. S1 (a1-a3)**, the EDS analysis confirms the presence of only two elements in the pristine PH membranes—carbon and fluorine, as anticipated. In contrast, the incorporation of carbon particles into the PH

polymer matrix increases fiber diameter. This increase is due to carbon particles having a high surface area and can interact with PH polymer chains by van der Waals forces. These interactions between the polymer chains and the carbon particles restrict the mobility of the polymer chains and agglomeration of the particles within the polymer matrix, leading to an increase in the polymer solution's overall viscosity as illustrated in **Fig. 4.3a**. The high viscosity makes it difficult to stretch the polymer solution during the electrospinning process, resulting in a larger fiber diameter. It was observed that an increase in the concentration of either JC or CNF particles in the PH polymer matrix leads to an increase in average fiber diameter. As shown in **Fig. 4.1(d1-d2)**, for the hydrophilic PH-0.5JC membrane surface, JC particles observed to aggregate on the membrane surface and adhere to the fibers, leading to an average fiber diameter of 677.24 nm, as shown in **Fig. 4.1d3**. The EDS analysis of the PH-0.5JC membrane, as depicted in **Fig. S1 (b1-b4)**, revealed that the JC particles were distributed across the membrane surface. This distribution is reflected in the elemental composition of the membranes, with a carbon content of 55.4%, which is higher than the fluorine content of 40.9%, and the presence of a small amount of oxygen (3.7%) suggests the membrane's hydrophilicity. Similarly, the fabricated hydrophobic membrane surfaces composed of PH and various concentrations of CNF exhibit a larger fiber diameter. This enlargement in the diameter suggests the successful incorporation of the CNF particles into the PH polymer matrix during the preparation of the composite solution. As shown in **Fig. 4.1(e1-e2)**, the membrane composed of PH-0.5CNF displays that the CNF particles are well-entangled and integrated with the PH fibers, leading to a larger fiber diameter of 641.71 nm compared to pristine PH fibers as shown in **Fig. 4.1e3**. The elemental analysis further supports the well-distributed CNF particles in the PH

polymer matrix, revealing a higher carbon content (56.9%) relative to fluorine (43.1%) as seen in **Fig. S1 (c1-c3)**. Additionally, the inclusion of CNF particles into the PH polymer matrix enhances the membrane's hydrophobicity, making it more conducive for facilitating the passage of water vapor across the hydrophobic surface. **Fig. S2** presents SEM images of the composited PH membranes containing 0.1 wt% and 1.0 wt% of JC and CNF particles, respectively. Since the composition and electrospinning parameters were kept consistent across all single-layered and dual-layered membrane fabrications, it is anticipated that the surface morphology of the carbon-doped PH membranes would be similar for each concentration. Therefore, SEM imaging was not performed on the single-layered membranes with varying carbon concentrations, as the morphology is expected to remain comparable. A significant challenge to the widespread usage and long-term stability of Janus membranes in practical applications is delamination. Due to the Janus design, the layers must be constructed from different materials, which often leads to poor interlayer adhesion and increases the risk of delamination over time. In this study, we described above in the fabrication section that the Janus layers are made up of one electrospun hydrophilic layer on the bottom, followed by another electrospun hydrophobic layer on top. From the cross-sectional SEM image, as shown in **Fig. 4.1(f1-f3)**, the fibers from both layers are well entangled and adhered to each other, making it difficult to separate. This entanglement and interfacial adhesion of the fiber's arrangement make the Janus membrane more mechanically stable which is described in the later section, and suitable for longer periods of MD applications. **Fig. S3** presents the cross-sectional SEM images of pristine PH; PH-0.5JC; and PH-0.5CNF membranes respectively.

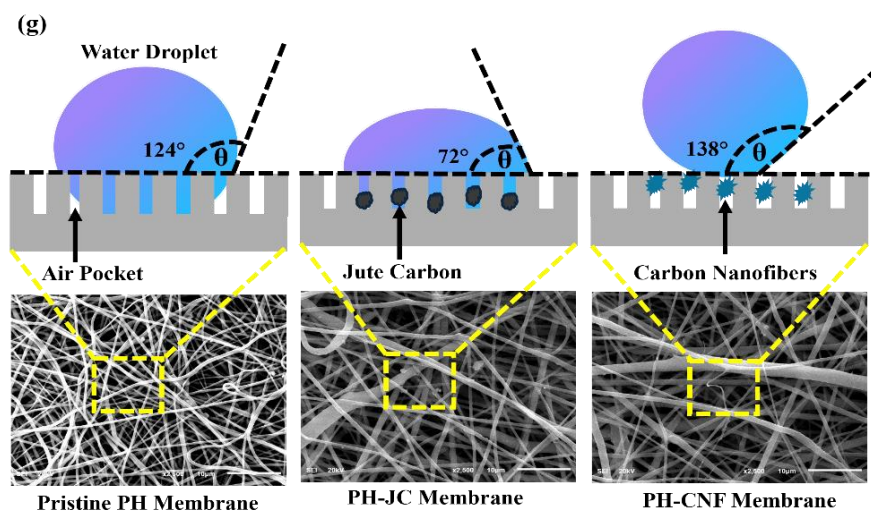
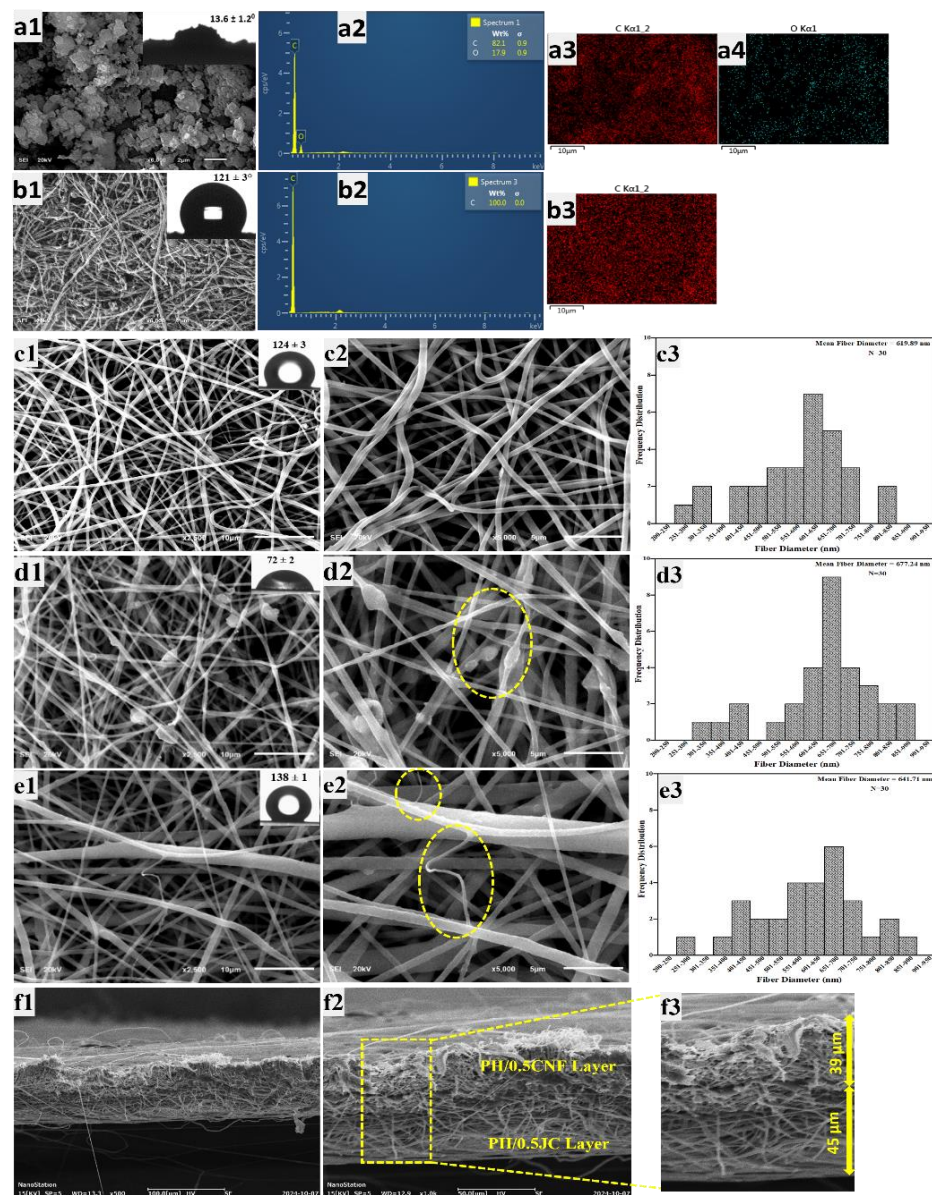


Figure 4. 1 SEM images of (a1) JC nanoparticles (inset- WCA), (b1) CNF (inset- WCA); and EDS spectrum and mapping for (a2-a4) JC nanoparticles and (b2-b3) CNF respectively; SEM images of the fabricated membranes for (c1-c2) PH, (d1-d2) PH-0.5JC, and (e1-e2) PH-0.5CNF (inset-WCA) respectively at different magnifications; Distribution of fiber diameters of (c3) PH, (d3) PH-0.5JC, and (e3) PH-0.5CNF; (f1-f3) Cross-sectional SEM image of the PH-0.5CNF/PH-0.5JC membrane; and (g) Schematic illustration of water droplets on developed electrospun PH and PH-CNP nanofibrous membranes.

4.3 Crystallinity and Structural Integrity Analysis

4.3.1 XRD Analysis

The XRD patterns of the JC nanoparticles are shown on **Fig. 4.2a**. The patterns display an intense and broad peak from $2\theta = 15^\circ$ and 30° , centered around 25° , which corresponds to d_{002} , indicating the semi-graphitized nature of the carbon [124], [125]. Additionally, the weak and broad diffraction peak of d_{101} around 43° is associated with the a-axis of the graphitic structure [124], [126]. Moreover, sharp peaks between 15° and 30° suggest the presence of a small amount of crystalline cellulose within the carbon [127], [128]. **Fig. 4.2b** presents the XRD pattern of CNF, with standard peak positions observed at approximately 25° , 42° , 44° , 54° , and 78° , corresponding to the d_{002} , d_{100} , d_{101} , d_{004} , and d_{110} planes, respectively. The presence of the three prominent peaks of d_{002} , d_{100} , and d_{101} indicates a graphitic structure composed primarily of sp^2 -hybridized carbon atoms. Because of its high non-polarity, this structure has less attraction for polar molecules like water, which leads to hydrophobic properties. As shown in **Fig. 4.2c**, for the pristine PH membrane the peaks observed at $2\theta = 18.3^\circ$ and 20.6° correspond to diffractions from d_{020} and $d_{200/110}$. The peak at $2\theta = 18.3^\circ$ indicates the non-polar α -phase and the peak at $2\theta =$

20.6° suggests the polar β -phase. The incorporation of CNF particles into the PH membranes resulted in a peak shift from 20.6° to 20°, which corresponds to the non-polar α -phase. This peak shift suggests an increased water-repellent surface, which indicates the membrane hydrophobicity. However, the incorporation of JC/CNF particles into the PH polymer matrix reduces crystallinity, as evidenced by the diminished intensity of the peak.

4.3.2 FT-IR Analysis

The surface functionality and elemental bonding of the fabricated electrospun nanofibrous membranes were analyzed by ATR-FTIR, as shown in **Fig. 4.2d**. The chemical structure of the pristine PH membrane exhibits CH₂ symmetric and asymmetric vibrations at 2980 cm⁻¹ and 3030 cm⁻¹ respectively, which is also seen in the CNF-incorporated hydrophobic membranes, confirming the PH structure was maintained in the PH/CNF membranes. Further, the peaks observed at 1065 cm⁻¹, 1175 cm⁻¹, and 1400 cm⁻¹ indicate the C-F wagging, CF₂ stretching, and CH₂ deformation respectively [129]. The spectrum of the PH/JC membrane displays several characteristic functional groups. The peaks were observed at 1650 cm⁻¹ for C=O stretching, 2860 cm⁻¹ and 2920 cm⁻¹ for sp³ and sp²-hybridized carbon of JC particles respectively. The broad-absorption spectrum displays between 3300-3600 cm⁻¹, indicating the O-H stretching vibration. The presence of the oxygen-containing functional groups in the PH/JC membranes suggests their hydrophilic nature. In contrast, the PH/CNF membrane does not show similar peaks for O-H functional groups, which is consistent with its mostly hydrophobic character due to the nature of CNF.

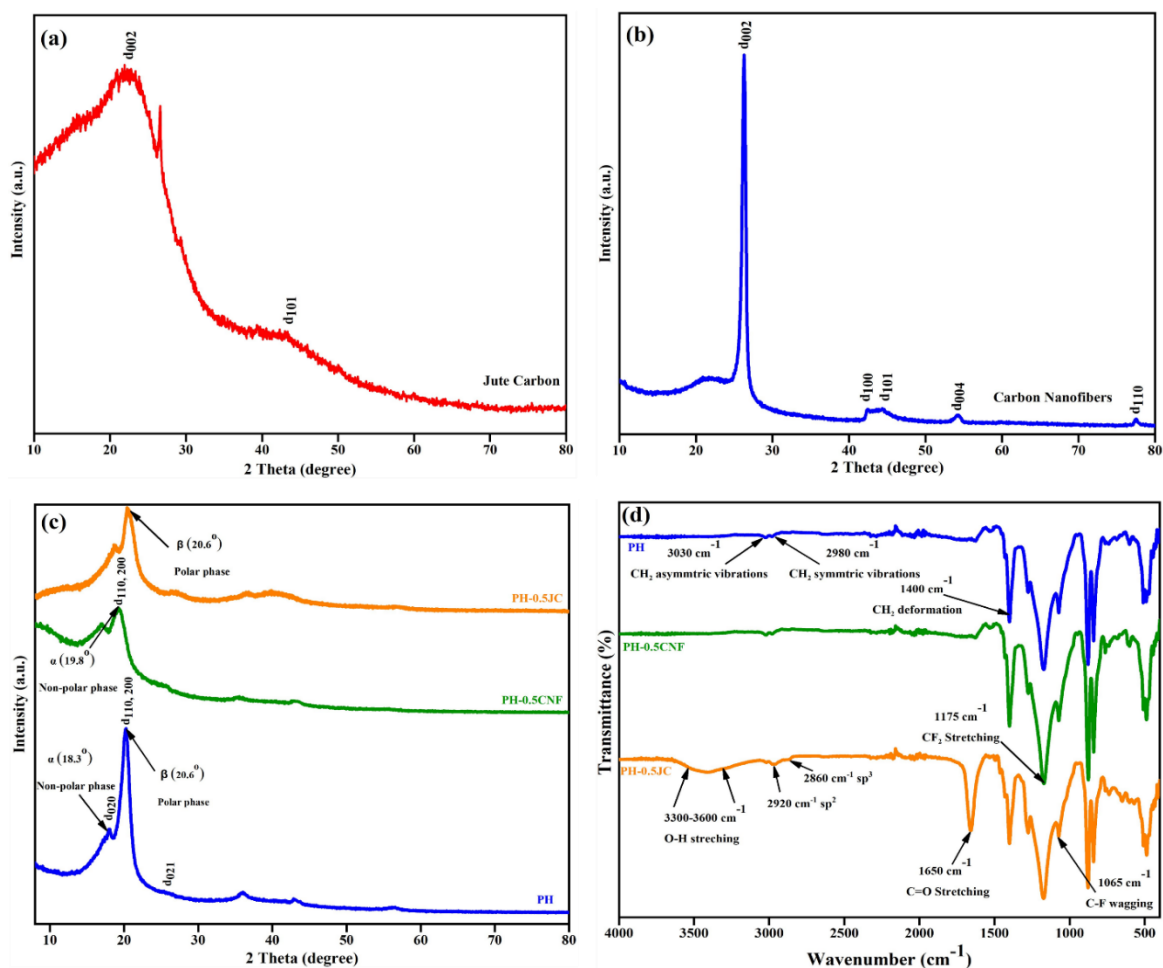


Figure 4. 2 X-ray Diffraction of (a) JC nanoparticles, (b) CNF; (c) the fabricated electrospun nanofibrous membranes respectively; and (d) ATR-FTIR spectrum of the fabricated electrospun nanofibrous membranes.

4.4 Surface Wettability Analysis

4.4.1 Water Contact Angle (WCA)

The WCA of the synthesized JC nanoparticles was measured at $13.6 \pm 1.2^\circ$ (inset **Fig. 4.1a1**) and the CNFs were measured at $121 \pm 3^\circ$ (inset **Fig. 4.1b1**). The WCA of all the fabricated electrospun nanofibrous membranes is illustrated in **Table 4.1**. The average

WCA of pristine PH nanofibrous membrane was measured at $124 \pm 3^\circ$. In loading JC particles from 0.1 wt% to 1.0 wt%, the WCA decreased gradually from $104 \pm 2^\circ$ to $63 \pm 2^\circ$, suggesting a transition towards a more hydrophilic surface of the membranes. This behavior can be attributed to the hydrophilic nature of the synthesized JC nanoparticles. Conversely, when hydrophobic CNF particles were added to the PH polymer matrix, a progressive increase in the WCA was observed, rising from $132 \pm 1^\circ$ to $145 \pm 1^\circ$ as the particle content increased from 0.1 wt% to 1.0 wt%. This trend reflects the enhancement of the hydrophobic properties of the composite PH/CNF nanofibrous membrane surface. However, the composited dual-layered PH membranes, incorporating different concentrations of JC and CNF particles exhibit distinct WCAs corresponding to hydrophilic and hydrophobic surfaces, respectively as illustrated in **Figure 4.3b**. The significant WCA difference makes an asymmetric wettability across the membrane, resulting in the formation of Janus-type membranes. The higher delta in WCA enhances the distinct functional properties of each side, with the hydrophobic layer repelling water and facilitating water vapor transportation while the hydrophilic layer promotes water absorption, optimizing the membrane's overall performance in WGMD. As shown in **Figure 4.1g**, JC-incorporated membranes turn into hydrophilic surfaces due to the presence of abundant oxygen groups on JC particles, which attract the polar water molecules. Conversely, the increased hydrophobicity of the CNF-incorporated membrane is attributed to the non-polar properties of the CNF particles due to the absence of hydroxyl or carboxyl functional groups, which prevents liquid infiltration into the membrane pores, keeping the surface dry, and allowing an easy passage for the water vapor to enhance MD performance.

4.4.2 Liquid Entry Pressure (LEP)

LEP is an important parameter that determines the hydrophobicity of a membrane by measuring the pressure at which liquid enters its pores [130]. Because of surface tension, MD hydrophobic membranes prevent water from passing through them. Higher LEP values are essential for long-term MD performance because they indicate the minimal pressure required for water to enter the pores. The membranes' pore size, shape, and hydrophobicity affect the LEP. According to the Young-Laplace equation, increasing the mean pore size of the membranes results in lower LEP values. Conversely, larger pore sizes facilitate the liquid to an easy and faster penetration through the membranes [122]. The average LEP values for all the developed membranes are illustrated in **Table 4.1**. The pristine PH membrane exhibits a LEP value of 105 ± 4 kPa. However, the incorporation of JC particles into the PH polymer matrix causes a notable decrease in LEP values. For instance, increasing the concentration of the JC particles from 0.1 wt% to 1.0 wt% in the PH polymer matrix lowers the LEP values from 99 ± 5 kPa to 72 ± 3 kPa. The decline in the LEP values for hydrophilic membranes is primarily due to their strong affinity towards the water molecule, which lowers the resistance of liquid infiltration into the membrane pores. Conversely, the opposite trend is observed with the CNF-incorporated hydrophobic PH membranes. Increasing the CNF concentrations from 0.1 wt% to 1.0 wt%, resulted in increased LEP values from 97 ± 6 kPa to 135 ± 5 kPa. The improvement in the LEP values corresponds to the membrane hydrophobicity and this causes the lower mean pore size of the membranes due to the denser fiber structure. The hydrophobic membranes typically exhibit higher LEP values due to their water-repellent surface properties which resist liquid infiltration into the membrane pores. However, no clear trend was observed in the dual-

layered membranes. This is because the Janus membrane thickness is subdivided into hydrophobic and hydrophilic layers almost equally. Among the Janus membranes, the lowest LEP (97 ± 6 kPa) was observed in the membrane composed of PH-0.5CNF/PH-1.0JC, where the highest LEP value (116 ± 5 kPa) was recorded for PH-1.0CNF/PH-0.5JC membrane.

Table 4. 1 Bulk Properties of the Developed Nanofibrous Membranes

Membranes	Contact Angle (°)		LEP (kPa)	MPS (μm)	Bubble Point Pressure (bar)	Thickness (μm)	Porosity (%)
	Feed Side	Permeate Side					
PH	124 ± 3	124 ± 3	105 ± 4	1.15	0.71	74 ± 4	82.14 ± 0.42
PH-0.1JC	104 ± 2	104 ± 2	99 ± 5	1.20	0.67	81 ± 2	84.12 ± 0.35
PH-0.5JC	73 ± 5	73 ± 5	83 ± 5	1.29	0.65	87 ± 3	86.89 ± 0.60
PH-1.0JC	63 ± 2	63 ± 2	72 ± 3	1.33	0.63	97 ± 6	81.74 ± 0.40
PH-0.1CNF	132 ± 1	132 ± 1	111 ± 6	1.19	0.81	77 ± 7	83.36 ± 0.55
PH-0.5CNF	139 ± 3	139 ± 3	117 ± 7	1.09	0.83	84 ± 5	85.55 ± 0.35
PH-1.0CNF	145 ± 1	145 ± 1	135 ± 5	0.85	0.86	87 ± 4	78.82 ± 0.42
PH-0.5CNF/PH-0.1JC	138 ± 2	103 ± 2	113 ± 7	1.07	0.79	79 ± 2	86.10 ± 0.50
PH-0.5CNF/PH-0.5JC	138 ± 1	72 ± 2	112 ± 5	1.28	0.67	84 ± 7	89.89 ± 0.73
PH-0.5CNF/PH-1.0JC	139 ± 1	64 ± 1	97 ± 6	1.15	0.73	91 ± 5	86.29 ± 0.35
PH-1.0CNF/PH-0.5JC	143 ± 3	69 ± 2	116 ± 5	1.18	0.71	93 ± 6	81.82 ± 0.65
PH-1.0CNF/PH-1.0JC	144 ± 1	62 ± 1	109 ± 6	0.91	0.85	96 ± 4	83.58 ± 0.80

4.5 Membrane Intrinsic Properties Analysis

4.5.1 Pore Size and Pore Size Distribution

In MD, the mean pore size (MPS) and pore size distribution (PSD) are important factors that significantly influence the resistance of wetting and permeate flux [102][131]. Although larger pores can increase the permeate flux, there is a chance of membrane wetting, especially when their size distribution is not uniform [131]. Therefore, a membrane with relatively small pores and a uniform PSD is preferred to ensure high vapor permeability while minimizing wetting. The pore size distribution promotes mass transfer by Knudsen and viscous diffusion while improving the wetting resistance of the membrane [102]. The membranes with uniform PSD and smaller pore sizes generally offer better mechanical strength and resist structural deformation, which enhances stability over longer run MD operation. Smaller pores can also reduce foulant accumulation into the membrane surface by blocking larger particles, however very small pores can risk clogging without proper pre-treatment. In contrast, larger and non-uniform pores may lead to lessening mechanical stability, higher fouling rates, and lower separation efficiency. To address these challenges, fabricating the membranes with uniform PSD is required to ensure consistent performance in harsher MD operating conditions with fouling components. The MPS of all the fabricated membranes are illustrated in **Table 4.1** with their bubble point pressure. As shown in **Figure 4.4a**, the MPS results reveal that the pristine single-layered PH membrane shows an MPS of 1.15 μm with narrow PSD between 1.04 μm to 1.19 μm , (**Figure S4a**). The single-layered JC-incorporated hydrophilic membranes exhibited an increase in MPS from 1.12 μm to 1.33 μm with an increase in JC concentrations from 0.1 wt% to 1.0 wt% respectively. All these membranes demonstrated narrow PSD as shown in

Figure S4b. Conversely, the single-layered hydrophobic PH membranes composed of CNF exhibit the opposite trend in the case of MPS. Increasing CNF concentrations from 0.1 wt% to 1.0 wt% decreases the MPS from 1.03 μm to 0.85 μm , these membranes also exhibit a narrow PSD as shown in **Figure S4c**. The smaller pore size of these hydrophobic membranes may be attributed to the highly dense PH fiber arrangement together with CNF, making slightly smaller pore diameters, evidenced by the cross-sectional SEM image as shown in **Figure 4.1(f1-f3)**. In dual-layered membranes, the top hydrophobic layer is in direct contact with the feed solution during MD, so the intrinsic characteristics of this layer significantly affect the overall membrane performance. As described in **Table 4.1**, the MPS of the fabricated dual-layered membranes ranges from 0.91 μm to 1.28 μm . As shown in **Figure S4d**, the PSD of the PH-1.0CNF/PH-1.0JC membrane exhibits a wider distribution (0.54 μm to 1.24 μm). This variation in the pore size can be attributed to the non-uniform fiber distribution resulting from higher viscosity and higher concentrations of nanoparticles in the solution. However, the PSD in the remaining concentration of Janus membrane structure demonstrated nominal pore sizes around 1.15 μm with narrow distribution, ideal for efficient vapor transport in MD. The MPS of the commercial PVDF membrane used in this study was measured at 0.22 μm .

4.5.2 Porosity & Thickness

Membrane porosity is enhanced by increasing the pore size and pore number density [132], [133], maintaining uniform thickness [132], and enlarging the channel size within the sublayer [134], all of which contribute to an improvement in permeate flux during MD [131]. Electrospun nanofibrous membranes exhibit higher porosity primarily due to their random fiber deposition, and high surface area-to-volume ratio. The Thickness and

porosities of all the developed membranes are summarized in **Table 4.1**. The pristine PH membrane displays a porosity of $82.14 \pm 0.42\%$, with a mean thickness of $74 \pm 4 \mu\text{m}$. From the single-layered membranes, it can be observed that increasing the carbon concentrations (either JC or CNF) in the PH polymer matrix gradually increases the membrane thickness and porosity respectively as described in **Table 4.1**. As the concentration of the JC particles in the single-layered hydrophilic PH membranes increases from 0.1 wt% to 0.5 wt%, the membrane thickness increases from $81 \pm 2 \mu\text{m}$ to $87 \pm 3 \mu\text{m}$. This increase in JC loading also results in a corresponding increase in porosity, rising from $84.12 \pm 0.35\%$ to $86.89 \pm 0.60\%$. A comparable trend is observed in CNF-incorporated PH membranes, where the thickness increases from $77 \pm 7 \mu\text{m}$ to $84 \pm 5 \mu\text{m}$ as the CNF content increases from 0.1 wt% to 0.5 wt.%, corresponding to an increase in the porosity from $83.36 \pm 0.55\%$ to $85.55 \pm 0.35\%$ respectively. The exception is observed in the case of higher concentration (1.0 wt%) of carbon fillers incorporated into the PH polymer matrix. For both PH-1.0JC and PH-1.0CNF membranes, the membranes show a decreased porosity despite being thicker at higher carbon concentrations. The increased concentrations of carbon particles can result in clogging the membrane pores by aggregating on the fibers surface which may be the cause of this decrease in the porosity. The average thickness of the dual-layered membranes is marginally higher than that of the single-layered membranes, as depicted in **Figure S5**. The highest thickness observed in the PH-1.0CNF/PH-1.0JC dual-layered membrane was measured at $96 \pm 4 \mu\text{m}$, while its porosity was $83.58 \pm 0.80\%$. The porosity of the dual-layered membranes ranges from $81.82 \pm 0.80\%$ to $89.89 \pm 0.73\%$, where the PH-1.0CNF/PH-0.5JC membrane shows the lowest and the PH-0.5CNF/PH-0.5JC membrane exhibits the highest porosity respectively. As depicted in **Figure 4.1f3**, the thickness of the

hydrophobic top layer of PH-0.5CNF was measured at 39 μm whereas the hydrophilic bottom layer of PH-0.5JC was measured at 45 μm . Although the electrospinning parameters and volume of the solution remained similar for both layers, the CNF-incorporated layer exhibited denser morphology as shown in **Figure 4.1(f1-f3)**, attributed to the reduced thickness and marginally lower MPS. The asymmetric wettability of the Janus membrane counterbalances the combination of a larger thickness and a smaller pore size, greatly improving vapor transport. As a result, the Janus membrane's improved flux performance is a direct consequence of the synergistic effects of the hydrophobic and hydrophilic layers, demonstrating an important role that the hydrophilic JC layer plays in improving flux performance. However, from **Fig. S5 and Fig. S6**, it can be inferred that the thickness and porosity of the dual-layered membranes, composed of varying carbon concentrations in both layers, do not follow a specific trend. Overall, the electrospun nanofibrous membranes demonstrate a higher porosity which highlights the inclusion of carbon-based additives significantly influences the structural and intrinsic properties of the membranes, contributing to their suitability for MD applications.

4.5.3 Mechanical Analysis

The mechanical properties of the fabricated electrospun membranes were investigated as shown in **Fig. 4.3c**. It can be observed that the pristine PH membrane displays lower tensile strength and extension (%) compared to the dual-layer Janus membrane. The PH-0.5CNF/PH-0.5JC membrane exhibits the highest tensile strength, approximately double that of the pristine PH membrane, with an extension of 144% before breakage. The membrane is composed of 0.5 wt% CNF shows the highest extension (170%) with a young modulus of 3.05 MPa, whereas the membrane with 0.5 wt% JC demonstrates the lowest

extension of 117% before fracturing the membrane, showing the young modulus of 2.53 MPa. The higher strength in the developed composite membranes can be attributed to the good compatibility of CNF with the PH fiber matrix in the nanocomposite.

4.5.4 Thermal Analysis

The prepared electrospun membranes exhibit distinct thermal stability due to incorporating varying concentrations of carbon particles into the PH polymer matrix. As shown in **Fig. 4.3d**, the pristine PH membrane starts decomposition at 431 °C, whereas the hydrophilic PH-0.5JC single-layered membrane begins to degrade at 426 °C. The earlier onset of decomposition of the PH-0.5JC membrane can be attributed to the release of CO and CO₂, likely due to the breakdown of oxygen-containing functional groups and the oxidation of carbon within the membrane matrix. In contrast, the PH-0.5CNF single-layered hydrophobic membrane exhibits the highest decomposition onset starting from 447 °C. Generally, CNF displays excellent thermal stability and can act as a barrier that slows the diffusion of volatile degradation products from the PH polymer matrix. This phenomenon can delay the onset of thermal decomposition of PH-0.5CNF. The dual-layered Janus PH-0.5CNF/PH-0.5JC membrane decomposes at 438 °C, falling between the decomposition temperatures of the single-layered hydrophobic and hydrophilic membranes.

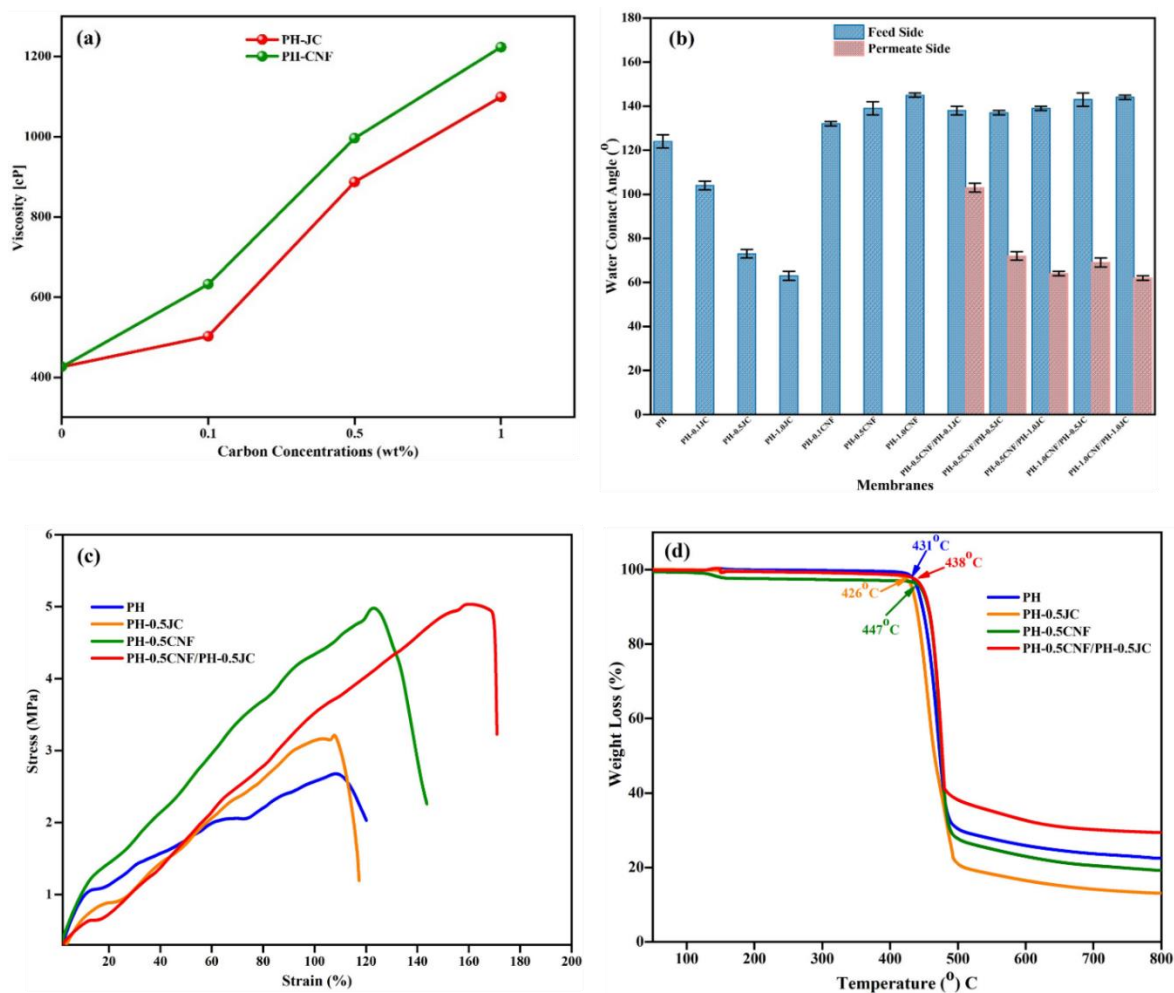


Figure 4. 3 (a) Viscosity of the prepared dope solution, (b) WCA, (c) Mechanical Strength, and (d) Thermogravimetric analysis of the fabricated membranes.

4.6 WGMD Performance Analysis

4.6.1 Pristine PVDF-co-HFP Membrane

All the fabricated electrospun nanofibrous membranes were tested using a WGMD setup. The experimental conditions of the WGMD system are provided in **Table 3.5**. As shown in **Fig. 4.4b**, the pristine PH membrane displays a flux of $27.35 \text{ kg m}^{-2} \text{ h}^{-1}$ with a salt rejection of 98.78%. As seen in **Figure S7a**, the membrane demonstrated a stable

performance throughout 24 hours of the operational period, with no significant changes observed.

4.6.2 Effect of Jute Carbon on Single-Layered Membranes

The integration of JC nanoparticles into the PH polymer matrix imparts hydrophilicity on the membrane surface. In MD, hydrophilic membranes typically exhibit lower permeate flux and reduce salt rejection due to their susceptibility to pore wetting. The hydrophilic membranes have a strong affinity towards the water molecules, causing the liquid to infiltrate and fill the membrane pores. This infiltration significantly obstructs the effective vapor transport passage, resulting in a lower permeate flux. Furthermore, the wetting phenomenon exacerbates the issue of salt rejection, the presence of liquid within the membrane pores allows for partial salt passage, thereby reducing the membrane's ability to reject salt effectively. As displayed in **Figure 4.4b**, the single-layered hydrophilic PH/JC membrane with 0.1 wt% JC exhibited a flux of $24.87 \text{ kg m}^{-2} \text{ h}^{-1}$ and a salt rejection of 96.35% which is lower than the pristine PH membranes, further increasing the JC content to 0.5 wt%, decreasing the permeate flux of $23.24 \text{ kg m}^{-2} \text{ h}^{-1}$ with a salt rejection 95.69%. At 1.0 wt%, the flux dropped to the lowest value of $20.81 \text{ kg m}^{-2} \text{ h}^{-1}$ with a salt rejection of 89.87% after 24 hours of the WGMD test. The WGMD performance of single-layered hydrophilic membranes declines over time as illustrated in **Figure S7b**. The reduced flux and salt rejection suggest the impact of continuous pore wetting of the prepared PH/JC hydrophilic membranes over 24 hours of operating time.

4.6.3 Effect of Carbon Nanofibers on Single-Layered Membranes

Carbon nanofibers are generally hydrophobic materials as evidenced by their higher WCA of $121 \pm 3^\circ$ (inset- **Fig. 4.1b1**). Carbon nanofibers' intrinsic characteristics include their

non-polarity and the absence of functional groups that can repel water and are suitable as hydrophobic filler materials for membranes used in MD applications. All fabricated hydrophobic PH membranes incorporated with CNFs demonstrate enhanced performance in WGMD, showing superior permeate flux and salt rejection, attributed to their inherent resistance to pore wetting. The hydrophobic properties of the membranes repel the water molecules, preventing liquid from infiltrating the pores and maintaining a dry, air-filled structure necessary for efficient vapor transport. The ability of the vapor to pass through the membrane more effectively facilitates higher flux because the vapor channels are kept dry by wetting resistance. Additionally, the absence of liquid in the pores reduces the passage of salts throughout the hydrophobic membrane structure due to a dry surface. As shown in **Figure 4.4b**, the single-layered hydrophobic PH/CNF membranes demonstrate superior performance compared to the pristine PH membranes. Incorporating a small amount of CNF particles (0.1 wt%) into the PH polymer matrix results in a permeate flux of $36.17 \text{ kg m}^{-2}\text{h}^{-1}$ and a salt rejection rate of 99.23%. A further increase in CNF concentration to 0.5 wt% leads to a substantial improvement of flux of $48.35 \text{ kg m}^{-2} \text{ h}^{-1}$, which is approximately 77% higher than that of pristine PH membranes. This membrane also maintains the highest salt rejection close to 100% among all the developed membranes after 24 hours of MD operation as shown in **Figure 4.4b**. This increase in the flux is attributed to several key parameters including the higher WCA, higher LEP, larger mean pore size, and higher membrane porosity. However, the opposite trend was observed when the CNF concentration increased to 1.0 wt%, the permeate flux drastically reduced to $34.56 \text{ kg m}^{-2} \text{ h}^{-1}$. This decline is likely due to the pore blockage of the membrane caused by the excessive loading of the CNF particles, which prevents an easy passage for the water vapor.

Additionally, the PH-1.0CNF membrane exhibits a slightly lower salt rejection of 99.97% than the PH-0.5CNF membrane, which may be attributed to the pore wetting, causing transportation of the dissolved solids. Nevertheless, all hydrophobic PH/CNF membranes consistently show a high salt rejection ($>99.9\%$), attributed to their excellent anti-wetting properties. As shown in **Figure S7c**, all the prepared PH/CNF hydrophobic membranes exhibit a stable performance in terms of flux and salt rejection throughout 24 hours of WGMD operating time.

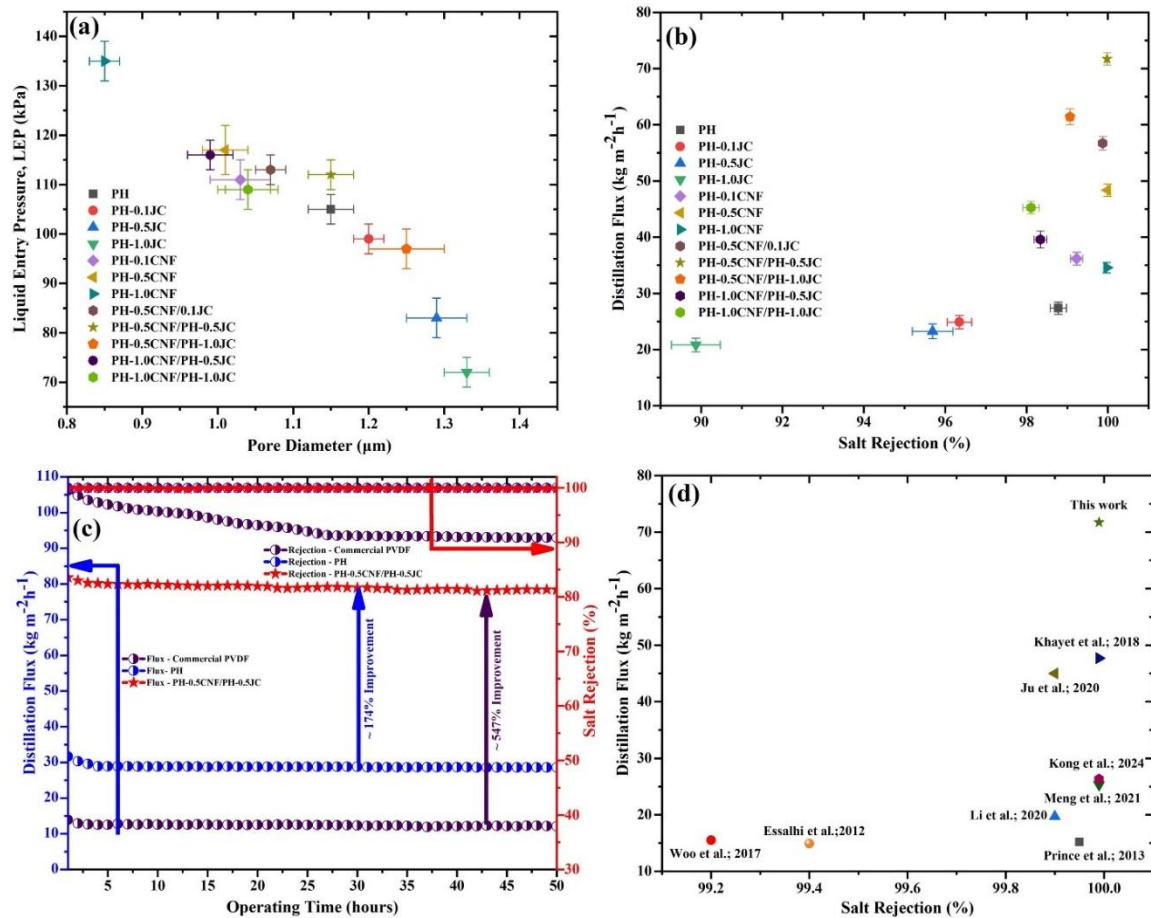


Figure 4. (a) LEP as a function of pore diameter; (b) Distillation flux and salt rejection for all the developed membranes; (c) Long-term stability performance with real seawater;

and (d) comparison of Janus MD performance (this study) with previous reports [104], [109], [112], [114], [118], [135], [136], [137].

4.6.4 WGMD Performance of the Janus Membranes

One of the major challenges in fabricating Janus membranes is precise control over the thickness of the individual layers. The ratio of hydrophilic to hydrophobic layer thickness is an important factor in determining the transport behavior of the membrane and in customizing its performance for a certain application. For instance, to enable effective separation, membranes intended for oil-in-water demulsification usually have a thin hydrophilic layer on top of a thicker hydrophobic layer. Conversely, fog harvesting needs a thicker hydrophilic layer with a thin hydrophobic layer to capture and channel the water more efficiently. However, for MD, both layers are relatively thicker to optimize water transport while maintaining high selectivity.[138] In this study, the hydrophobic and hydrophilic layer thicknesses were kept thicker only by changing the carbon concentrations on each layer. The thickness of the individual hydrophobic and hydrophilic layers on the Janus membrane was half of their respective single-layered membranes. This innovative equal-layered structure Janus electrospun membranes exhibit enhanced performance in WGMD, which strategically combines the top hydrophobic PH/CNF layer and the bottom hydrophilic PH/JC layer. During WGMD of the Janus membranes, half of the hydrophobic layer faces the feed solution which repels the water molecules and facilitates considerably more water vapor to pass through the membrane surface by effectively rejecting the salts. Meanwhile, on the permeate side, the gap between the spacer and condensation plate is filled with stagnant water that contacts the remaining half of the hydrophilic layer. This

design promotes rapid infusion and condensation of water vapor, thereby improving the efficiency of a distillation process significantly. Additionally, the asymmetric structure helps to mitigate the membrane scaling and fouling, which resists contaminant accumulation on the membrane surface. This synergistic combination of enhanced vapor transportation, effective salt rejection, and faster vapor condensation results in a Janus membrane that outperforms conventional single-layered membranes. As depicted in **Fig. 4.4b**, all the developed dual-layered Janus electrospun membranes exhibit a superior permeate flux compared with the single-layered membranes. Among the prepared Janus membranes, the PH-0.5CNF/PH-0.5JC membrane demonstrates the highest flux of $71.72 \text{ kg m}^{-2} \text{ h}^{-1}$, representing an improvement of approximately 162% compared to the pristine PH membranes, and maintained a higher salt rejection of 99.98% after 24 hours of WGMD operation. This performance enhancement can be attributed to the effective distribution of CNF particles onto the hydrophobic layer which effectively repels the water molecules and creates an easy passage for water vapor to transport. Simultaneously, on the other hand, a uniform distribution of 0.5 wt% JC particles in the hydrophilic layer accelerates the water vapor condensation, resulting in a higher WGMD performance. The incorporation of 0.5 wt% CNF into the hydrophobic layer improves the membrane's mechanical stability and thermal resistance, while maintaining sufficient hydrophobicity. This is critical in preventing pore wetting, keeping the surface dry and ensuring robust WGMD performance. Similarly, the integration of 0.5 wt% JC particles in the hydrophilic layer provides the necessary water uptake on the permeate side and enhances the vapor flux due to its oxygen containing functional groups, as evidenced by the ATR-FTIR analysis. Moreover, the optimal loading of 0.5 wt% of carbon content ensures that the viscosity of the

electrospinning solution was well-balanced, enabled uniform fiber formation and reduced the surface irregularities. In contrast, higher loading of carbon content i.e. 1.0 wt% in the polymer matrix, resulting in excessive viscosity, leading to uneven fiber formation, particle aggregation on to the membrane surface that compromised the membrane performance in WGMD. In the case of, lower loading of carbon content i.e. 0.1 wt% on PH polymer matrix, results in insufficient functionalized carbon materials, thereby reducing the hydrophobic or hydrophilic properties required to achieve effective asymmetric wettability, leading to lower flux. The PH-1.0CNF/PH-0.5JC membrane exhibits the lowest flux of $39.58 \text{ kg m}^{-2} \text{ h}^{-1}$ with a relatively lower salt rejection of 98.34%. This can be attributed to the higher concentration of CNF particles on the top layer, leading to pore blockage that prevents easy water vapor transportation. Among the dual-layered membranes, the PH-0.5CNF/PH-1.0JC membrane also exhibited an excellent permeate flux of $61.42 \text{ kg m}^{-2} \text{ h}^{-1}$ while maintaining a salt rejection of 99.07%. The membranes composed of PH-0.5CNF/PH-0.1JC and PH-1.0CNF/PH-1.0JC exhibit permeate flux of $56.72 \text{ kg m}^{-2} \text{ h}^{-1}$ and $45.25 \text{ kg m}^{-2} \text{ h}^{-1}$ with salt rejection of 99.87% and 98.11%, respectively. As shown in **Figure S7d**, throughout the 24-hour WGMD operational period, a few of the dual-layered membranes experienced a slight reduction in flux and salt rejection in the first few hours in the case of a higher concentrated JC-incorporated hydrophilic layer. This reduction in the MD performance can be attributed to prolonged exposure to highly saline feed solutions. The membrane's pores may begin to experience slight wetting due to pore blockage which reduces the membrane's ability to selectively vapor transportation, resulting in a slightly lower flux and salt rejection. Due to demonstrating superior performance, the PH-0.5CNF/PH-0.5JC membrane was chosen as the optimum loading of the carbon fillers to

be tested further in harsh experimental conditions compared with the pristine PH membranes.

4.6.5 Long-Term Stability Test with Real Seawater

The long-term stability of the pristine PH membranes, Janus PH-0.5CNF/PH-0.5JC membranes, and commercial PVDF membranes were evaluated using real seawater as the feed solution. The salinity of the real seawater was measured at 46.4 g L^{-1} . The seawater was directly used without pretreatment in the WGMD setup with the previous set of experimental parameters. As shown in **Fig. 4.4c**, the desalination performance of the pristine PH membrane demonstrates a slight increase in flux compared with the more concentrated feed solution of 70 g L^{-1} . Although the flux of this membrane decreased slightly from $30.29 \text{ kg m}^{-2} \text{ h}^{-1}$ to $28.59 \text{ kg m}^{-2} \text{ h}^{-1}$ after 50 hours of operation, it maintained an impressive salt rejection rate of 99.99%. Similarly, the Janus PH-0.5CNF/PH-0.5JC membrane also exhibits a decreasing trend in flux with a reduction from $81.82 \text{ kg m}^{-2} \text{ h}^{-1}$ to $78.42 \text{ kg m}^{-2} \text{ h}^{-1}$, yet it has shown an excellent salt rejection of $>99.9\%$ after 50 hours operation. The WGMD process involves both water vapor and heat transfer, resulting in a highly concentrated salt in the solution at the interface of the evaporation due to the latent heat loss associated with vapor transfer. The latent heat loss in the interface causes a reduction of the temperature in the feed solution. Despite these challenges during long-term MD operations, the permeate flux with real seawater was observed to be higher on the Janus membrane, attributing to the higher vapor pressure on low concentrated feed solution, according to Raoult's Law [109]. Notably, the Janus PH-0.5CNF/PH-0.5JC membrane demonstrated approximately a 174% improvement in permeate flux compared to the pristine PH membrane. Furthermore, commercially available PVDF membranes

were also tested under identical WGMD experimental conditions with real seawater. As shown in **Fig. 4.4c**, the PVDF membrane revealed a lower permeate flux of $12.11 \text{ kg m}^{-2} \text{ h}^{-1}$ with a salt rejection of 90.84% after 50 hours of operation. In comparison, the developed Janus PH-0.5CNF/PH-0.5JC membrane showcased an exceptional enhancement, with ~547% improvement in flux over the commercially available PVDF membrane.

4.6.6 Antiscaling Stability

The scaling on the membrane surface during MD applications is a serious issue, as it can significantly impair the anti-wetting properties. To evaluate the anti-scaling stability of the developed pristine PH and the optimum Janus membranes in WGMD, the feed solution was prepared with 70 g L^{-1} of NaCl, 20 mM Na_2SO_4 (2.84 g L^{-1}), and 20 mM CaCl_2 (2.22 g L^{-1}). The WGMD performance of the pristine PH membrane was significantly decreased over 36 hours of operational time, exhibiting a flux of $13.01 \text{ kg m}^{-2} \text{ h}^{-1}$ while the salt rejection was 96.51% as shown in **Fig. 4.5a**. The decline performance may be attributed to the co-existence of Ca^{2+} ions and SO_4^{2-} ions in the feed solution, which formed CaSO_4 crystals at a thermal condition as displayed in **Fig. 4.5b**. Naturally, Calcium sulfate is hydrophilic and can effectively interact with water molecules by forming hydrogen bonds, thereby increasing the hydrophilicity of the membrane surface as evidenced by its WCA value of $79 \pm 2^\circ$ (inset- **Fig. 4.5b**) Conversely, the developed Janus PH-0.5CNF/PH-0.5JC membrane exhibits a stable WGMD performance and there was no obvious scale formation in the membrane surface as shown in the SEM image after performing anti-scaling test (**Fig. 4.5c**). The WCA value of $133 \pm 2^\circ$ (inset- **Fig. 4.5c**) further confirmed the membranes' hydrophobicity under harsh conditions, indicating the anti-scaling stability of the prepared novel Janus PH-0.5CNF/PH-0.5JC membrane. The integration of CNFs into the polymer

matrix offer a larger functionalized surface area, enhanced conductivity which enables the application of external electric fields or electrochemical reactions to prevent charged scaling salts particles as reported by the previous studies.[139],66,[141], [142] The elemental wt% analysis of the PH membrane surfaces as shown in **Figure S8(a1-a4)**, provides a quantitative measure of CaSO_4 scaling formation, further confirming the extent of depositon. On the other hand, the optimal Janus PH-0.5CNF/PH-0.5JC membrane does not form any scaling as evidenced by the elemental analysis as shown in **Figure S8(b)**.

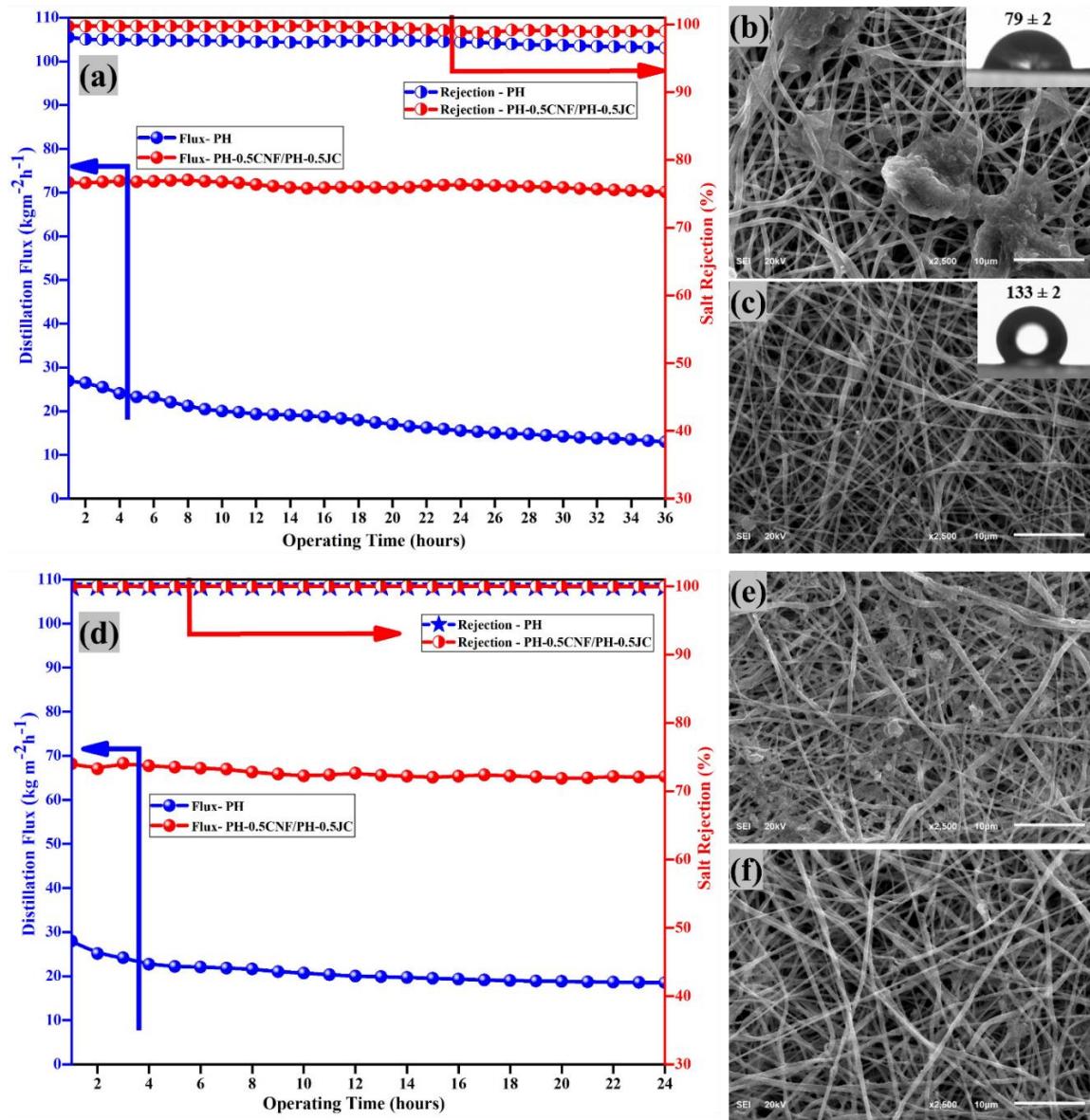


Figure 4. 5 (a) Anti-scaling stability of pristine PH and Janus PH-0.5CNF/PH-0.5JC membranes; SEM images after the anti-scaling test for (b) pristine PH membrane; and (c) PH-0.5CNF/PH-0.5JC membrane respectively; (inset- WCA after anti-scaling test); (d) Anti-fouling stability of pristine PH and Janus PH-0.5CNF/PH-0.5JC membranes; SEM images after the anti-fouling test for (e) pristine PH membrane; and (f) PH-0.5CNF/PH-0.5JC membrane respectively.

4.6.7 Antifouling Stability

The feed solution was prepared with 70 g L⁻¹ of NaCl and 100 mg L⁻¹ of organic Humic acid to evaluate the anti-fouling stability. As seen in **Fig. 4.5d**, the Janus PH-0.5CNF/PH-0.5JC membrane exhibits excellent anti-fouling stability compared with the pristine PH membrane. The PH membrane experienced a lower flux after 24 hours of the WGMD test since there was a foulant formation on the membrane surface as shown in **Fig. 4.5e**. The foulant layer on the PH membrane surface was further confirmed by the elemental analysis as shown in **Figure S9**. Conversely, there was no such foulant formation on the PH-0.5CNF/PH-0.5JC membrane as displayed in **Fig. 4.5f**, also confirmed by the presence of a minimal amount of nitrogen and oxygen on the membrane surface (**Figure S9**). However, both membranes maintained a higher salt rejection of >99.95% throughout 24 hours of WGMD operational time. The enhanced anti-fouling stability of the Janus membrane could be attributed to the smooth morphology of the CNF, which reduces the adhesion sites for foulants and minimizes their accumulation as reported by the previous studies [143][144]. Additionally, the conductive nature of the CNF prevents charged foulants and degraded organic pollutants from accumulating on the membrane surface.[139][140] The inherent hydrophobicity, interconnected open pore structure, and high porosity further facilitate the faster mass transfer while restricting the fouling, ensuring long-term operational stability under harsh conditions [143].

4.7 Results Comparison

A brief literature review of the Janus dual-layered membranes is presented in **Fig. 4.4d**. The figure compares the previously reported membranes' bulk properties and their MD performance with this present study. For instance, Khayet et al. previously reported dual-

layered electrospun membranes using a hydrophobic layer of PVDF and a hydrophilic layer of polysulfone (PSF). In this study, the performance of DCMD was evaluated by varying the thickness of the hydrophilic layer. Increasing the thickness of the PSF layer leads to a more open structure which exhibits a higher tendency for wetting compared to the PVDF layer. This change in thickness reduced the liquid/vapor path distance, resulting in a higher permeate flux. The DCMD permeate flux of the fabricated dual-layered membranes reached values of $47.7 \text{ kg m}^{-2} \text{ h}^{-1}$ with a higher salt rejection of 99.99% with a feed concentration of 30 g L^{-1} of NaCl, maintaining a feed temperature of 80°C and coolant temperature of 20°C [102]. In another study, Meng et al. reported a novel sandwich-like Janus membrane to evaluate in DCMD, featuring a microporous PVDF membrane with a PDA/PEI hydrophilic coating on one side and a nanofiber hydrophobic layer on another side. The contact angle decreased from 145.2° to 31.3° with increasing the PDA/PEI deposition time, resulting in a higher permeate flux of $25.3 \text{ kg m}^{-2} \text{ h}^{-1}$ and salt rejection of $>99.99\%$ at 60°C with a feed concentration of 35 g L^{-1} NaCl.[109] Notably, the developed novel Janus membranes in this study outperformed the previously reported membranes in the literature. The results underscore the superior performance of the developed novel Janus Membranes, highlighting its potential as a promising candidate for commercial water desalination applications.

CHAPTER 5

SPUTTERING-ASSISTED SURFACE ENGINEERING OF JANUS PVDF MEMBRANES FOR MEMBRANE DISTILLATION

5.1 Introduction

In this study, two different substrates including sleek glass and sandpaper were chosen to cast the phase inversion PVDF membranes. Later, Janus PVDF membranes were fabricated through a surface engineering approach utilizing ZnO coating via DC magnetron sputtering in an oxygen atmosphere, using a Zn target. Unlike conventional techniques that rely on chemical modifications or multilayer assembly to make asymmetric wettability of the Janus membranes, this method enables the direct surface engineering of the prepared PVDF membranes with a minimal change in their bulk properties. The Zn atoms bombard from the target under a controlled plasma atmosphere, react with oxygen to create a ZnO layer on the membrane's top layer. The deposition of ZnO introduces hydrophilicity to the skin surface of the PVDF membranes while preserving their inherent hydrophobicity of the bottom (textured) surface, resulting in a Janus structure with asymmetric wettability.

Delamination is a major challenge in developing Janus membranes through conventional multilayer fabrication techniques especially while exposing them in an extended period for MD operation. Delamination mainly occurs due to the poor adhesion between the layers,

mismatch with the polymer blending or solvent utilized during fabrication, and poor chemical grafting. In our previous study, we developed a delamination-free Janus membrane using a sequential electrospinning approach, where distinct carbonaceous materials were strategically integrated on both surfaces of the membrane to achieve asymmetric wettability [145]. In contrast, here in this study we observed that sputtering offers a delamination-free approach on PVDF phase inversion membranes, as the ZnO coating is physically bonded to skin surface under highly vacuum and energetic conditions. The strong adhesion between this ZnO coating and PVDF layers ensures long-term stability under highly saline conditions without the risk of interfacial detachment, demonstrating the modified membranes a superior alternative to the chemical grafting or polymer blending approaches. Additionally, these solvent-free and scalable techniques maintain the membrane integrity while allowing them for a precise control over surface wettability. The prepared unmodified and modified membranes were tested by a custom built WGMD setup with a highly saline feed solution of 70 gL^{-1} of NaCl. The optimal modified membranes demonstrated a remarkable distillation flux while maintaining higher salt rejection with real seawater for an extended period of WGMD operation. To the best of our knowledge, this is the first study to employ ZnO sputtering on a PVDF membrane surface to fabricate Janus membranes with asymmetric wettability, specifically designed for MD applications. By finely tuning sputtering conditions, the surface properties of the membrane can be optimized for improved MD performance, demonstrating the effectiveness of sputtering techniques for next-generation desalination applications.

5.2 Morphological Analysis

The glass and sandpaper substrates were selected to imprint their unique surface patterns onto the membrane during NIPS process. The surface morphology of the unmodified and sputtered modified PVDF membranes were analyzed using SEM. The PVDF membranes cast on glass substrate demonstrated a relatively dense and smooth surface on the bottom layer as shown in **Fig. 5.1a1**. This structure is attributed to the rapid phase separation occurring during NIPS process with the glass substrate, resulting in instantaneous demixing and making the skin layer denser [146]. Moreover, an excessive shrinkage of the membranes was observed during the phase inversion due to the rapid demixing, leading to more tortuous membrane structures [147] as shown in the cross-sectional SEM images in **Fig. 5.2(a2-e2)**. The denser morphology can hinder the membrane's performance and its suitability for the MD applications where higher porosity is expected. In contrast, **Fig. 5.1b1** highlights the structural variations in PVDF membranes cast on sandpaper substrate, resulting in distinct surface textures. The pristine SP0 membrane displayed an irregular pattern on the bottom surface with deep depressions surrounding flatter regions, suggesting that abrasive particles from the sandpaper affected the surface. The membrane surface contained concave structures, forming deep depressions without noticeable protrusions. These formations contribute to additional re-entrant structures that help repel solutes in the feed solution effectively during MD operation. And such asymmetric nanoscale pores extend the interaction time between the membrane and feed water, creating more vapor transport pathways.

However, surface images of the sputter-modified skin layers indicate a distinct alteration in surface morphology compared with the pristine G0 membrane, clearly demonstrating

the formation of the ZnO layer as shown in **Fig. 5.2(a1-e1)**. The formation of continuous ZnO film on the skin layer with varying time causes with distinct nanostructures, leading to a rougher surface. A previous study on ZnO nanostructured thin films revealed that varying sputtering time affected the surface morphology, exhibiting polycrystalline films with uniform surface height and particle sizes around 24 nm for 30 minutes sputtering duration [148]. The findings suggest that the sputtering parameters play an important role in defining the surface characteristics of ZnO-coated PVDF membranes, which can be tuned to achieve the required properties for specific applications. Additionally, the induced energy during sputtering may slightly etch the skin layer of the membrane, resulting in a formation of micro-cracks. These cracks can be identified as surface pore openings, leading to an increased effective porosity of the sputtered modified membranes.

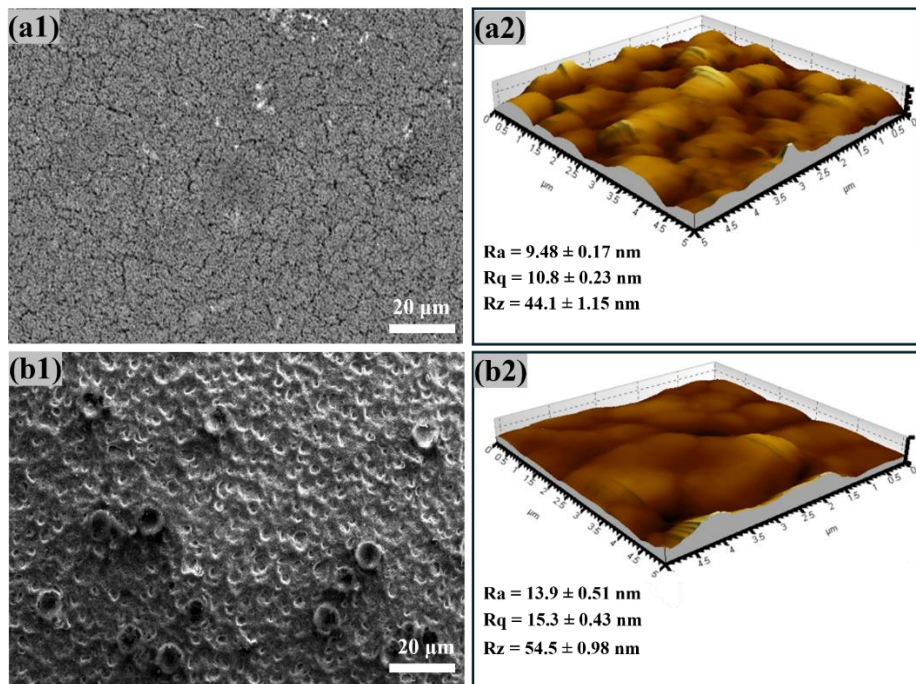


Figure 5. 1 Textured surface SEM images of (a1) G0, and (b1) SP0 membranes; 3D AFM images of the textured surfaces of (a2) G0, and (b2) SP0 membranes respectively.

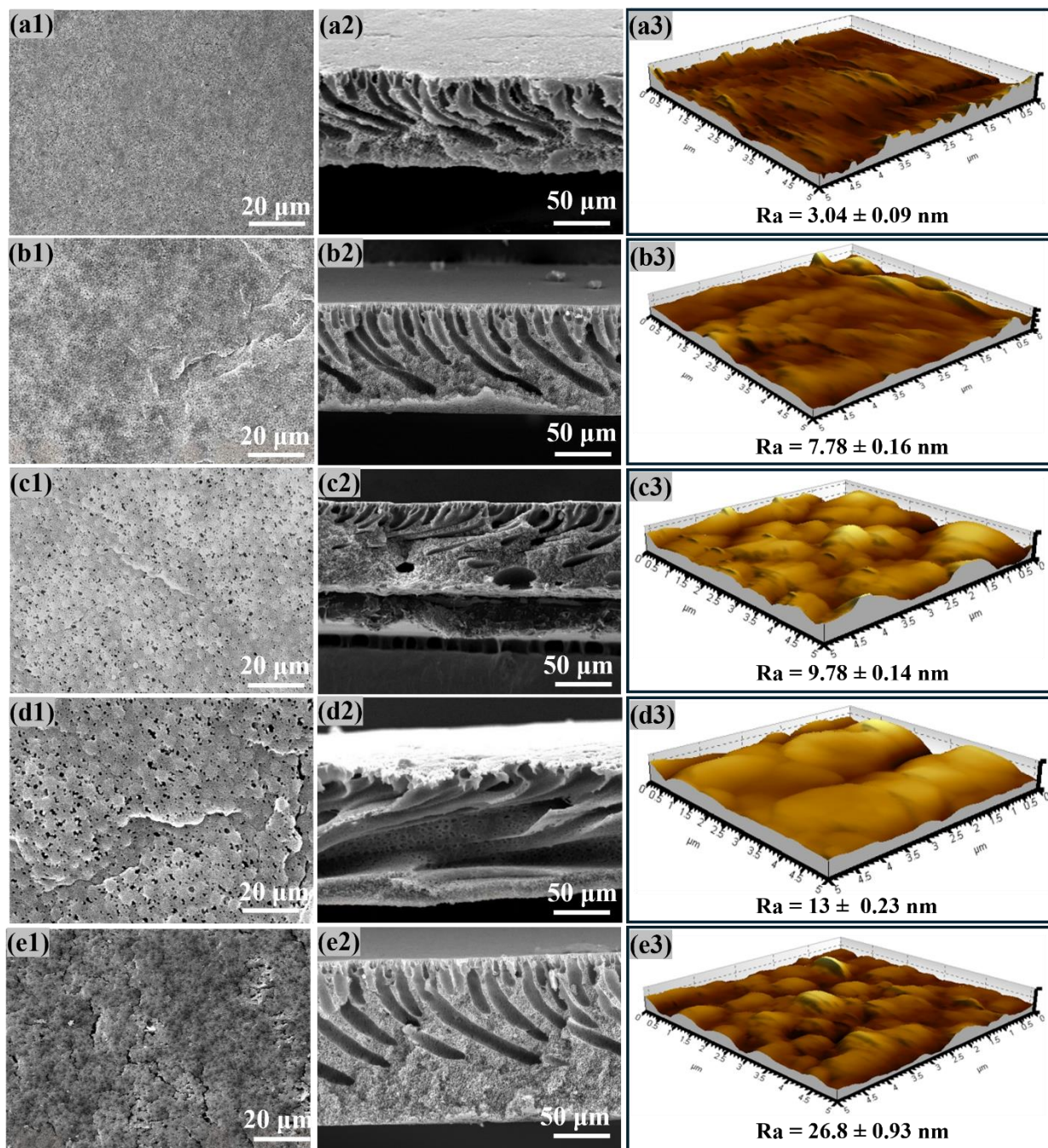


Figure 5. 2 (a1-e1) Skin layer surface SEM images, (b2-e2) cross-sectional SEM images, and (a3-e3) 3D AFM images of skin layer for G0, G5, G10, G12, and G15 membranes respectively.

In the sputter modified skin layer for both glass and sandpaper substrates membranes reveal a notable morphological variation influenced by sputtering duration and texture of the substrate. As the duration of sputtering time increases, the accumulation of ZnO layer is progressively increased on the membrane surface as evidenced by the surface morphology shown in **Fig. 5.2(b1-e1)** and **Fig. 5.3(b1-e1)**. Although the ZnO layer exhibits significant surface coverage, cross-sectional images reveal that its thickness remains minimal, measuring only a few nanometers. However, it is noted that surface morphology exhibits irregularly shaped ZnO nanoparticles, a phenomenon that needs further explanation. It is obvious from **Fig. 5.4(a1-b2)**, the sputtered modified layer exhibits a completely different morphology and structure on its surface. The selection of substrates and sputtering techniques are the key factors of the formation of irregular morphology of ZnO particles. Sputtering is a physical vapor deposition technique that often results in non-uniform nucleation and growth, producing a range of sizes and forms of particles. Surface diffusion dynamics during deposition have an impact on this non-uniformity. Particularly, greater surface roughness and irregular particle formation can result from enhanced surface diffusion caused by larger densities of zinc atoms [149]. Moreover, particle shape is significantly influenced by the substrates' natural roughness and texture. The roughness of membranes cast on sandpaper substrates is higher than that of membranes cast on glass substrates as shown in **Fig. 5.1a2 and b2**. This increased roughness can cause the deposited ZnO layer to become less uniform, which enhances the formation of particles with irregular shapes. Because there are more nucleation sites and anisotropic growth patterns brought on by the uneven surface, the inconsistencies in particle shape are more noticeable on rougher substrates. Furthermore, the conformality and homogeneity of the ZnO layer are

strongly influenced by the deposition process itself. Sputtering processes frequently produce non-uniform layers with variable particle morphologies, whereas atomic layer deposition (ALD) is recognized for providing highly uniform and conformal coatings. This discrepancy results from the fact that sputtering uses an intense particle bombardment that can produce non-uniform nucleation and growth, whereas ALD uses self-limiting surface reactions that provide fine control over layer thickness and uniformity [150]. However, the irregular ZnO layer formation makes the surface more hydrophilic, resulting in more water absorption in the permeate side to facilitate faster condensation during WGMD operation.

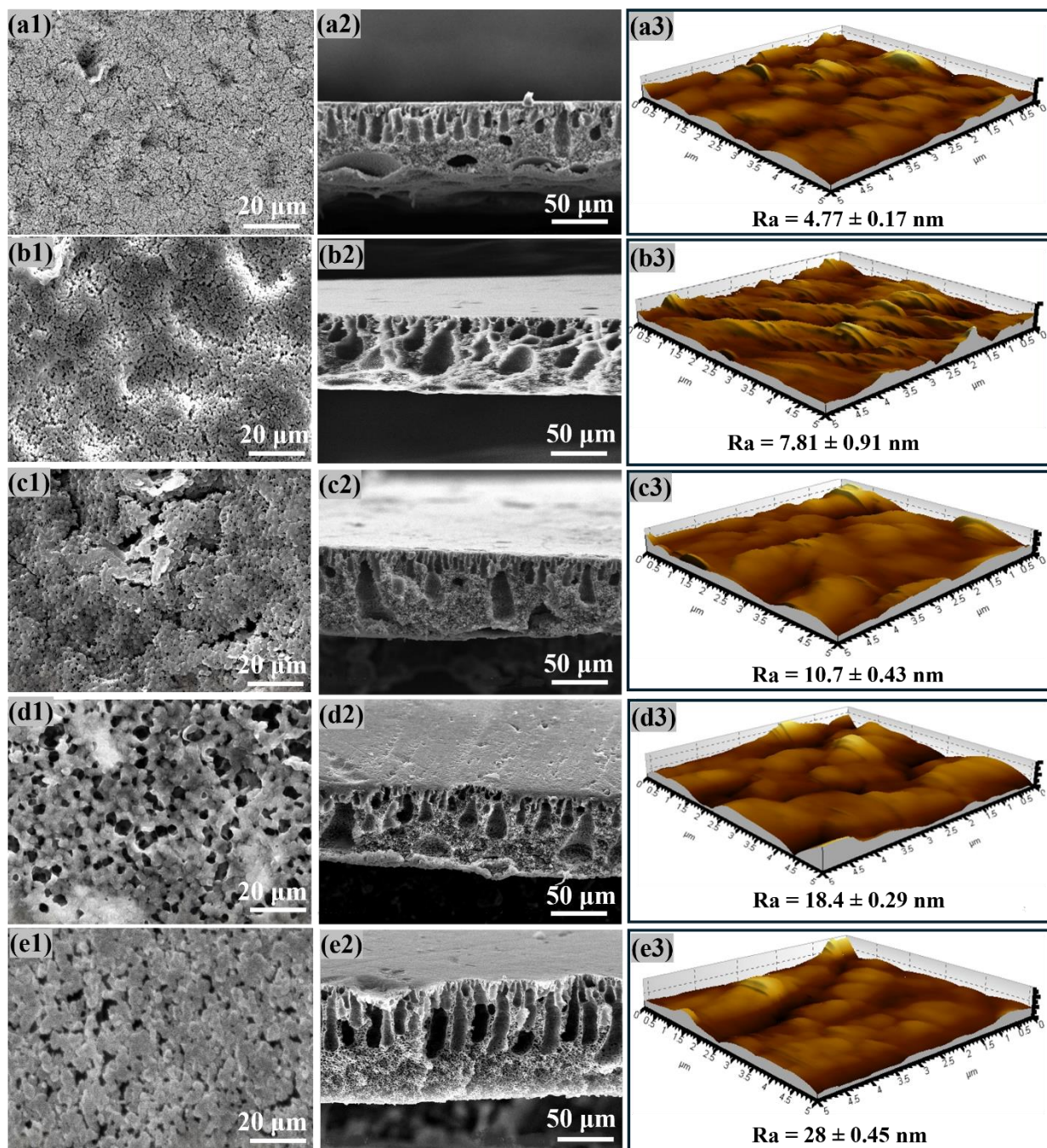


Figure 5. 3 (a1-e1) Skin layer surface SEM images, (b2-e2) cross-sectional SEM images, and (a3-e3) 3D AFM images of skin layer for SP0, SP5, SP10, SP12, and SP15 membranes respectively.

To assess the cross-sectional SEM images, all the prepared membranes were deliberately fractured with liquid nitrogen. As illustrated in **Fig. 5.2(a2-e2)** and **Fig. 5.3(a2-e2)**, the fabricated membranes exhibit an asymmetric structure attributed to the characteristic of NIPS technique used in membrane preparation. All the membranes demonstrated a finger-like microvoid structure under the skin layer due to the rapid demixing of DMF and non-solvent during phase inversion, while a spongy and porous layer is formed near the textured surface [151]. The cross-section of the sandpaper textured membranes exhibits several re-entrant structures and porous structures due to the delayed demixing and minimal shrinkage due to the textured support. The use of rough sandpaper surface during casting prevents excessive shrinkage and structural defects, maintained structural integrity, which provided stability during membrane formation. Furthermore, the cross-sectional images of sandpaper-cast membranes revealed a well-defined, straight finger-like structure. This morphology reduces tortuosity, providing a more direct pathway for water vapor transport through the membrane pores, thereby enhancing permeation efficiency. In contrast the glass-cast PVDF membranes experienced immediate demixing and significant shrinkage during phase separation due to the absence of support or texture surface. Additionally, the glass-cast membranes curled in the water coagulation bath, resulting in an elongated pore at an angle, ultimately leading to a denser and more tortuous structure [152].

The skin surface roughness of both unmodified and ZnO-modified membranes cast on a glass substrate was analyzed using AFM, as shown in **Fig. 5.2(a3-e3)**. Compared to the pristine G0 membrane, the modified membranes exhibited progressively higher roughness values with increasing sputtering duration. The G0 membrane displayed a relatively low average roughness (Ra) of 3.04 ± 0.09 nm on the skin layer, while the highest roughness

was observed in the G15 membrane, reaching 26.8 ± 0.93 nm. Similarly, the ZnO-modified membranes cast on sandpaper substrates exhibited higher surface roughness compared to the pristine SP0 membrane as demonstrated in **Fig. 5.3(a3-e3)**. The SP0 membrane had an average roughness of 4.77 ± 0.17 nm, whereas the SP15 membrane reached 28 ± 0.45 nm. This increase in roughness is attributed to the greater deposition of the ZnO coating on the surface. The AFM roughness parameters of all the modified membranes cast on glass and sandpaper substrates are illustrated in **Fig. S10**. Notably, sandpaper-cast membranes demonstrated slightly higher roughness than those cast on a flat glass substrate. This increased roughness introduces numerous air pockets on the G12 membrane surface compared with pristine G0 membrane as shown in **Fig. 5.4a2 and b2**, which can further enhance the ZnO layer's roughness, ultimately improving the hydrophilicity of the skin layer. The presence of Zn and O elements in the EDS analysis of the modified G12 membranes demonstrated that the sputtering of ZnO successfully deposited on the membrane surface as illustrated in **Fig. 5.4b3**.

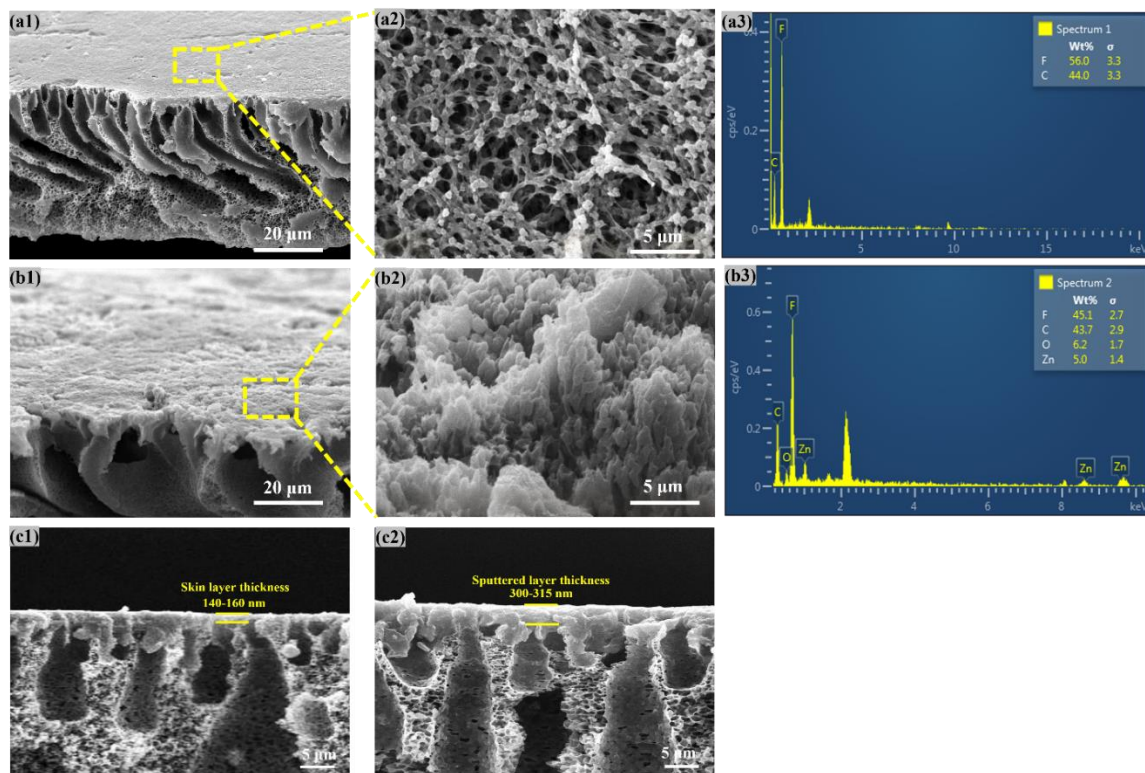


Figure 5. 4 (a1, b1) Cross-sectional images, (a2, b2) surfaces images at higher magnification; and (a3, b3) EDS spectrum of G0, and G12 membranes respectively; (c1, c2) skin layer thickness of SP0 and SP15 membranes respectively.

5.3 Structural Integrity, Crystallinity and Thermogravimetric Analysis

The elemental interaction between the PVDF and sputtered ZnO nanoparticles were analyzed by ATR-FTIR as shown in **Fig. 5.5(a-b)**. The pristine SP0 membrane exhibits asymmetric and symmetric CH_2 vibrations at 3043 cm^{-1} and 2984 cm^{-1} respectively [153], [154]. However, for SP15, the shift in CH_2 stretching vibrational peaks is attributed to the higher ZnO deposition, suggesting alterations in the chemical environment or molecular interactions between PVDF and ZnO, likely through hydrogen bonding or Van der Waals forces. Further, the deposition of ZnO can create stress or strain in the PVDF matrix, affecting bond angles and lengths which is attributed to the change in vibrational frequency

of functional groups. The spectrum observed at 1401 cm^{-1} , 1167 cm^{-1} , and 1065 cm^{-1} corresponds to the CH_2 deformation, CF_2 stretching, and C-F wagging respectively [129]. The intense peak of 485 cm^{-1} observed in **Fig. 5.5b** was due to the Zn-O stretching vibrations [155]. The observed changes in the FTIR peaks at 613 cm^{-1} , 760 cm^{-1} , 795 cm^{-1} , and 975 cm^{-1} in the modified PVDF membranes after ZnO sputtering suggest alterations in the polymer's crystalline phases. Specifically, the peaks at 613 cm^{-1} , 760 cm^{-1} , and 795 cm^{-1} are associated with the α -phase of PVDF, indicating its presence in the membrane. The peak at 975 cm^{-1} is linked to the β -phase, suggesting a partial transformation from the α -phase to the β -phase due to ZnO incorporation. This phase transition is likely induced by the interaction between PVDF and ZnO, which can influence the polymer's structural arrangement [156]. The broad absorption band detected between $3250\text{-}3600\text{ cm}^{-1}$ in the SP10 and SP15 membranes corresponds to the O-H stretching vibration, signifying the presence of oxygen-containing ZnO functional groups that enhance the hydrophilicity of the membrane's skin layer.

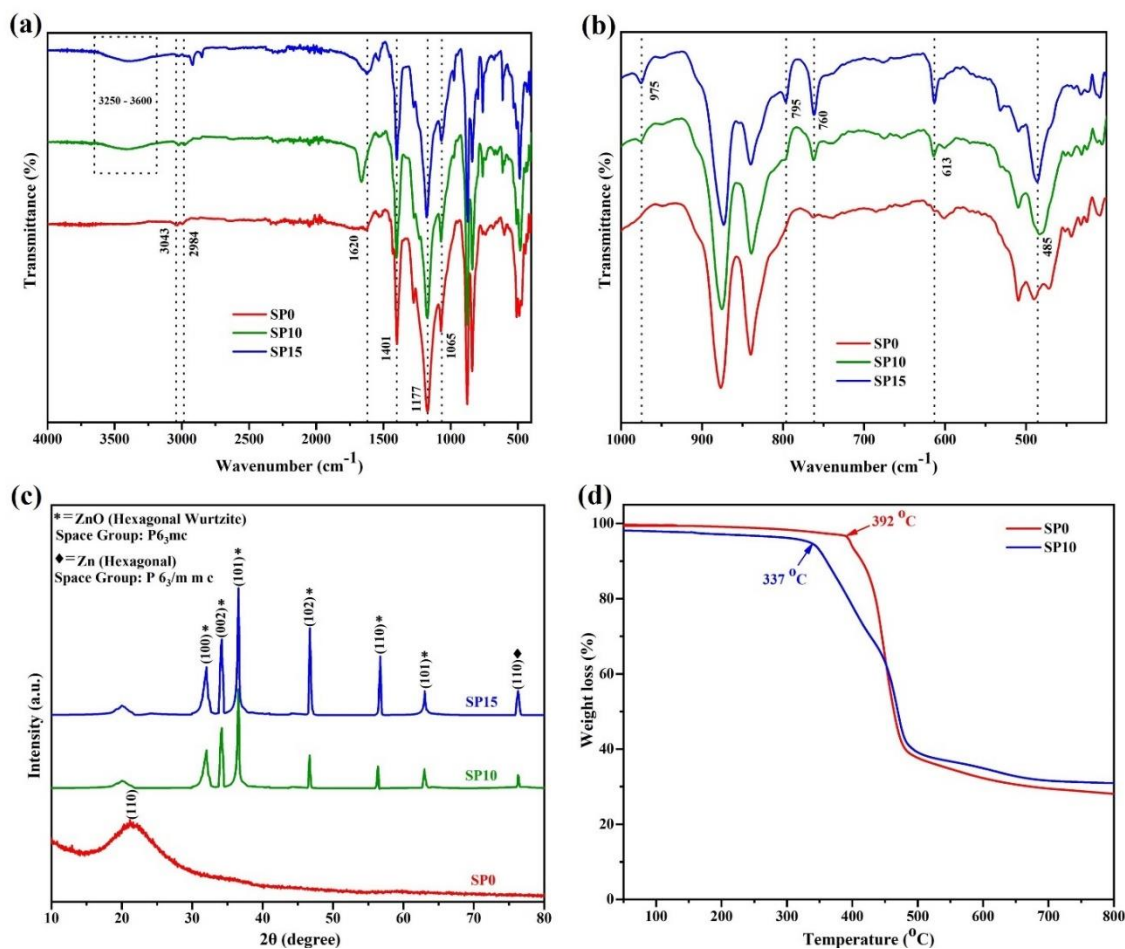


Figure 5. 5 (a, b) FTIR (c) XRD analysis of the pristine SP0, modified SP10, and SP15 membranes respectively; (d) Thermogravimetry analysis of SP0 and SP10 membranes respectively.

The XRD analysis, presented in **Fig. 5.5c**, reveals distinct crystalline characteristics of both the pristine PVDF membrane and the Zn-sputtered modified membrane. As can be seen, the pristine SP0 membrane exhibits the characteristics peak at 20.8° corresponding to (110) plane indicates the polar β -phase [157]. Upon 10 and 15 minutes of sputtering, the characteristic PVDF peak shifted to the left, indicating either stress relaxation or it may introduce tensile stresses on the membrane surfaces due to prolonged exposure [158]. The

XRD diffraction peaks of SP10 and SP15 membranes, observed at $2\theta = 32.05^\circ$, 34.2° , 36.57° , 46.7° , 56.74° , and 63.05° , correspond to the (100), (002), (101), (102), (110), and (101) planes, respectively. These peaks are aligned well with the characteristic diffraction pattern of ZnO (JCPDS card #31-1451), confirming its hexagonal wurtzite structure with the space group $P6_3mc$ [159], [160]. Additionally, diffraction peak at $2\theta = 76.4^\circ$ corresponds to metallic zinc (Zn), exhibiting a hexagonal close-packed (hcp) structure, associated with the (101) plane and the space group $P6_3/mmc$. The appearance of metallic Zn peaks is likely due to incomplete oxidation during the sputtering process, which can be attributed to limited oxygen interaction within the sputtering chamber. These findings suggest a successful integration of ZnO within the PVDF membrane surfaces and demonstrate the influence of sputtering duration on the membrane's crystalline structure and surface properties.

The TGA results demonstrate a change in the thermal degradation behavior of the modified SP10 membrane compared to pristine SP0 membrane. The onset decomposition temperature of the SP10 membrane occurs at approximately 337°C , whereas pristine SP0 membrane begins to degrade at around 392°C . The early onset degradation of SP10 membrane may be due to the catalytic effect of ZnO nanoparticles, which could facilitate the polymer chain breakdown at lower temperature. However, the modified membrane exhibits a lower weight loss (%) compared to the pristine membrane. This difference in weight loss (%) at elevated temperatures can be attributed to the residual ZnO nanoparticles that remain stable which facilitate the reduced overall polymer decomposition. Thus, the presence of ZnO on the membrane surface is likely to enhance thermal stability at elevated temperatures by acting as a heat barrier that is favorable for MD applications.

5.4 Surface Wettability Analysis

The WCA values for all the prepared sputtered membranes were evaluated on both the skin layer and the bottom textured surface using deionized water via the sessile drop method. As illustrated in **Figure 5.6a**, the membranes cast on a glass substrate exhibited WCA around $93 \pm 1^\circ$ on the bottom textured surface for G0-G15 membranes. In contrast, the WCA on the skin layer decreased progressively with increasing sputtering time. Notably, the skin layer of G0 had a WCA of 83° , while the lowest WCA, observed for G15 with $58 \pm 2^\circ$. Membranes subjected to 5 minutes of sputtering demonstrated a WCA of $75 \pm 2^\circ$, which further decreased to $69 \pm 1^\circ$ and $63 \pm 3^\circ$ after 10 and 12 minutes of sputtering, respectively. Similarly, as depicted in **Figure 5.6b**, the membranes cast on sandpaper demonstrated a higher WCA of approximately $124 \pm 3^\circ$ on the bottom textured surface for all prepared membranes (SP0-SP15) and $101 \pm 1^\circ$ on the skin layer of SP0. However, sputtering for varying durations resulted in a decrease in WCA on the skin layer. The membrane sputtered for 5 minutes exhibited a WCA of $84 \pm 2^\circ$, while the membranes with SP10 and SP12 demonstrate WCA of $68 \pm 2^\circ$ and $62 \pm 2^\circ$ respectively. The minimum WCA of $55 \pm 2^\circ$ was recorded after 15 minutes of sputtering. This reduction is attributed to the increased hydrophilicity resulting from the deposition of a more hydrophilic ZnO layer over time. As shown in **Fig. 5.2(c1-c5)** and **Fig. 5.3(c1-c5)**, the surface roughness of the skin layer increases with longer sputtering durations, providing more sites for water interaction. Depending on the membrane surface structure, water molecules may either rest on the peaks of the rough surface (Cassie-Baxter state) or infiltrate into the valleys (Wenzel state). In this case, a Wenzel state is more likely to occur, leading to a stronger affinity for water molecules and consequently a lower WCA on the skin layer [161]. Additionally, the

increased deposition of the ZnO layer enhances the formation of hydrogen bonds between the water and the membrane surface, further contributing to the reduction in WCA.

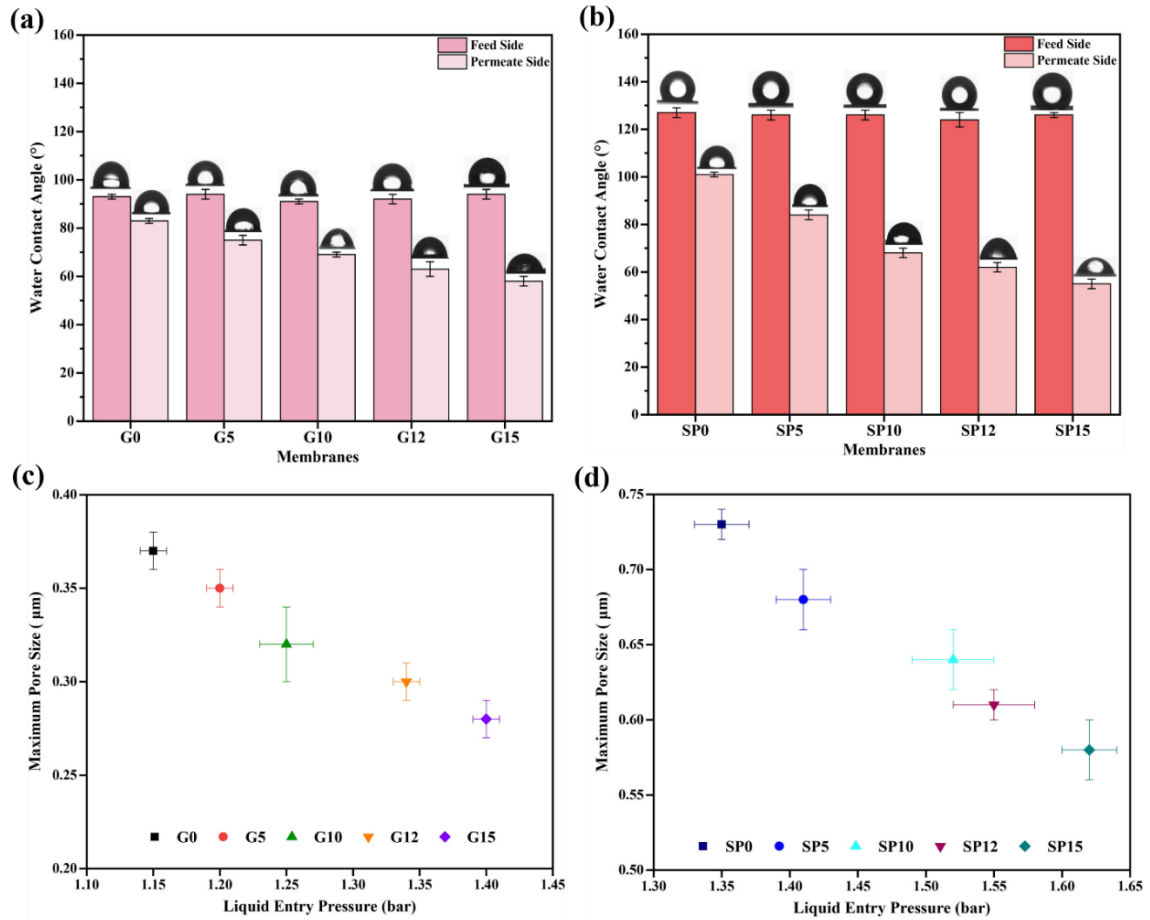


Figure 5. 6 WCA on the feed and permeate side of the prepared membranes cast on (a) glass and (b) sandpaper substrates respectively; LEP as a function of maximum pore diameter of the prepared membranes cast on (c) glass and (d) sandpaper substrates respectively.

LEP is a critical parameter that evaluates the hydrophobicity of a membrane by measuring the pressure at which liquid can penetrate its pores [130]. Due to surface tension, hydrophobic membranes used in MD effectively block water from passing through. Higher

LEP values are crucial for maintaining long-term MD performance, as they signify the minimum pressure necessary for water to enter the pores. The LEP is influenced by the pore size, shape, and hydrophobic characteristics of the membranes. The average LEP values for all the membranes developed are presented in **Table 5.1**. **Figure 5.6c and 5.6d** show the LEP values as a function of maximum pore size of all the developed membranes cast on glass and sandpaper substrates respectively. According to the Young-Laplace equation, an increase in the average pore size of the membranes leads to lower LEP values. In contrast, larger pore sizes allow for easier and more rapid liquid penetration through the membranes. García-Payo et al. [121] investigated the wetting characteristics of hydrophobic membranes and determined that LEP values between 0.5 and 1.5 bar are appropriate for MD applications, varying based on the surface properties and pore dimensions. From **Figure 5.6c**, it is evident that the pristine G0 membrane, cast on a glass substrate, demonstrates a lower LEP value of 1.15 ± 0.01 bar, accompanied by a maximum pore size of 0.37 ± 0.01 μm . In contrast, modifying the skin layer of the membranes through various sputtering durations results in a decrease in pore size and an increase in LEP values. Notably, the G15 membrane exhibits a higher LEP value of 1.40 ± 0.01 bar, with the lowest maximum pore diameter measured at 0.28 ± 0.01 μm . Similarly, membranes cast on a sandpaper substrate follow this trend. The lowest LEP value recorded for the SP0 membrane is 1.35 ± 0.02 bar, with a maximum pore diameter of 0.73 ± 0.01 μm . Conversely, the membrane subjected to 15 minutes of sputtering shows the highest LEP value of 1.62 ± 0.02 bar, along with the lowest maximum pore size of 0.58 ± 0.02 μm . Interestingly, the LEP values and maximum pore diameters of the modified membranes do not appear to be significantly affected by the deposition of ZnO layer, may be attributed to

the relatively thin coating on the membrane surface. This minimal changes in the LEP and pore size allows for the modification of the membrane surface to achieve asymmetric wettability without obstructing the existing pore structure. Optimizing sputtering parameters highlights the benefits of this surface modification for MD applications. The enhanced hydrophilic surface promotes the movement of stagnant water closer to the membrane interface, facilitating rapid condensation of vapor as it passes through the hydrophobic layer. This improved condensation process ultimately contributes to a higher distillation flux, making the modification highly effective for MD performance.

Table 5. 1 Properties of the sputter modified and unmodified membranes

Membranes ID	WCA (°)		LEPw (bar)	Mean Pore Diameter (μm)	Thickness (μm)	Porosity (%)	Tortuosity
	Feed Side	Permeate Side					
G0	93 ± 1	83 ± 1	1.15 ± 0.01	0.37 ± 0.01	97.24 ± 2.14	67.12 ± 0.82	2.63
G5	94 ± 2	75 ± 2	1.20 ± 0.01	0.33 ± 0.02	99.53 ± 1.12	72.32 ± 1.21	2.25
G10	91 ± 1	69 ± 1	1.25 ± 0.02	0.29 ± 0.02	106.31 ± 2.51	74.15 ± 0.95	2.14
G12	92 ± 2	63 ± 3	1.34 ± 0.01	0.28 ± 0.02	108.32 ± 1.18	79.34 ± 1.84	1.83
G15	94 ± 2	58 ± 2	1.40 ± 0.01	0.20 ± 0.02	125.41 ± 2.33	65.12 ± 0.74	2.79
SP0	127 ± 2	101 ± 1	1.35 ± 0.02	0.63 ± 0.02	121.21 ± 1.52	78.14 ± 1.10	1.90
SP5	126 ± 2	84 ± 2	1.41 ± 0.02	0.60 ± 0.01	126.52 ± 2.13	83.21 ± 0.89	1.64
SP10	126 ± 2	68 ± 2	1.52 ± 0.03	0.54 ± 0.03	128.12 ± 1.18	84.43 ± 1.05	1.58
SP12	124 ± 3	62 ± 2	1.55 ± 0.03	0.48 ± 0.02	134.61 ± 4.47	83.41 ± 0.51	1.63
SP15	126 ± 1	55 ± 2	1.62 ± 0.02	0.44 ± 0.01	141.42 ± 3.75	73.61 ± 1.13	2.17

5.5 Membrane Intrinsic Properties

5.5.1 Membrane Pore Diameter and their Distribution

Membranes featuring mean pore diameters (MPD) within the range of 0.05 to 1.0 μm are commonly employed in MD processes [162]. Pore size distribution (PSD) is a crucial factor that greatly affects both wetting resistance and permeate flux [102]. PSD influences mass

transfer via Knudsen and viscous diffusion while enhancing wetting resistance and determining flux [102]. While larger pores can enhance permeate flux, a non-uniform size distribution raises the risk of membrane wetting [163]. Therefore, membranes featuring relatively small pores and a narrow PSD are preferred, as they ensure high vapor permeability while reducing the likelihood of wetting. **Fig. S11** shows the minimum, mean and maximum pore sizes of the modified and unmodified glass and sandpaper cast membranes. The pristine G0 membrane exhibits an MPD of $0.37 \pm 0.01 \mu\text{m}$, while the minimum pore diameter is $0.30 \pm 0.01 \mu\text{m}$ and the maximum pore diameter is $0.39 \pm 0.01 \mu\text{m}$. The membranes modify with ZnO sputtering demonstrate the decrease in MPD. However, all membranes from G0-G15 had a common MPD in the range of 0.20-0.37 μm . The lowest MPD was observed in the case of G15 membrane, attributed to the higher deposition of ZnO, blocking the pores of the membrane surface. On the other hand, the membranes cast on sandpaper substrate demonstrated relatively larger MPD than the membranes cast on glass substrate ranging from 0.63-0.44 μm for SP0-SP15 membranes respectively as illustrated in **Table 5.1**. This is attributed to the textured membranes cast on sandpaper substrates having less shrinkage and additional pore openings on the surface due to texturing. However, it is noted that all the membranes prepared for this study demonstrated a narrower PSD. The PSD can be adjusted by changing the coagulation bath or by varying the concentration of PVDF and pore former composition in the casting solution [164]. However, irrespective of these conditions in variation in pore size in PVDF membranes with texture will depend on the formation of membrane on casting substrates. In this study, fine tuning of sputtering facilitates the formation of narrow PSD without changing the pore diameter significantly. Membranes with uniform PSD and smaller pore

sizes typically exhibit improved mechanical strength and resistance to structural deformation, contributing to stability during extended MD operations. Additionally, smaller pores help minimize foulant accumulation on the membrane surface by blocking larger particles; however, excessively small pores may become clogged without adequate pre-treatment. Conversely, larger and irregular pores can compromise mechanical stability, increase fouling rates, and lower separation efficiency. To address these issues, it is essential to fabricate membranes with a uniform PSD to maintain consistent performance under challenging MD conditions that may involve fouling or scaling components.

5.5.2 Membrane Thickness, Porosity, and Tortuosity

Membrane thickness, porosity and tortuosity are interconnected parameters that significantly influence the MD performance of phase inversion membranes. A thicker membrane generally resists the vapor transportation during MD due to the longer diffusion path, resulting in a lower flux despite maintaining higher porosity. In contrast, thin membrane can facilitate faster vapor transport due to shorter distance, however it can cost mechanical strength which may not be suitable for longer MD operation. Balancing thickness of the fabricated membranes is essential for MD. As illustrated in **Table 5.1**, all the unmodified and sputtered modified membranes had a thickness in the range of 97-141 μm . The membranes fabricated using sandpaper substrate exhibited a larger thickness compared to the glass substrate, can be attributed to additional features of the sandpaper substrate. It is noted that the modified membrane thickness slightly increases due to the deposition of ZnO layer over time, leading to a higher porosity.

Membrane porosity is the fraction of void space within the membrane that can improve with an increase in pore size and pore number density [132], [133], along with maintaining

uniform thickness [132] and expanding channel size within the sublayer [134], all of which contribute to enhanced vapor transport during MD [131]. As shown in **Table 5.1**, sputter-modified membranes exhibited a slightly higher porosity due to the increase in surface roughness on the skin layer as evidenced by the AFM results. This can be attributed to the formation of ZnO nanoparticles create micro/nanostructures, which effectively increases the surface area and apparent porosity. The membranes cast on sandpaper demonstrated higher porosity than those cast on glass substrates due to the difference in surface roughness and phase inversion kinetics. The pristine G0 membrane exhibits a porosity of $67.12 \pm 0.82\%$, while the SP0 membrane shows a significantly higher porosity of $78.14 \pm 1.10\%$. As sputtering time increases, the porosity of the G5, G10, and G12 membranes also rises to $72.32 \pm 1.21\%$, $74.15 \pm 0.95\%$, and $79.34 \pm 1.84\%$, respectively. However, further increasing the sputtering time to 15 minutes leads to a decline in porosity for membranes cast on both glass and sandpaper substrates. Among all samples, the SP10 membrane exhibits the highest porosity, which is further supported by SEM analysis. The enhanced porosity of the sandpaper membranes can further be justified by their multiple nucleation sites, which enhances solvent-non-solvent exchange and promotes pore formation. Additionally, the sandpaper can facilitate faster removal of solvent in the coagulation bath, which accelerates phase separation and creates more porous morphology. While the membranes cast on glass substrates slow down the solvent exchange rate, resulting in a lower porosity. Moreover, the additional surface feature of the sandpaper minimizes the membrane to shrink during phase inversion, whereas the non-adhesive glass substrates allow the polymer solution to contract more freely, resulting in a compact membrane structure. These combined effects contribute to the higher porosity of sandpaper-casted

membranes, making them more suitable for MD applications compared to glass-casted membranes.

In phase inversion PVDF membranes, tortuosity is essential since it has a direct impact on porosity and MD performance. It explains the complexities of pore pathways, where longer, curving channels with a greater amount of tortuosity increase transport resistance and decrease the permeate flux. Lower tortuosity, on the other hand, offers more direct vapor paths, improving permeability during MD. Porosity and tortuosity must be balanced; high porosity typically results in lesser tortuosity, which improves vapor movement, whereas excessive tortuosity can decrease flux while increasing the wetting resistance. An optimal structure with moderate tortuosity and high porosity can be achieved by adjusting the concentration of polymers, solvent exchange rates, and casting conditions. As can be described from **Table 5.1**, the membranes with higher porosity demonstrate the lower tortuosity and vice versa. In summary, balancing membrane thickness, porosity and tortuosity are three essential factors to maximize flux during MD operations while maintaining wetting resistance and structural integrity.

5.6 WGMD Performance Analysis

A systematic investigation of the WGMD performance of the prepared membranes was conducted to assess the effect of varying G/GO concentrations in the PVDF matrix. The experiments were performed using a highly saline feed solution of 70,000 ppm NaCl. The WGMD experimental conditions are described in **Table 3.5**. The PVDF membranes cast on glass and sandpaper substrates exhibited distinct surface morphology which influenced their WGMD performance. As shown in **Fig. 5.7a**, the pristine G0 membrane cast on glass substrate exhibits a flux of $13.51 \text{ kg m}^{-2}\text{h}^{-1}$ with a salt rejection of 99.66% after 24 h of

WGMD operation, whereas the pristine SP0 membrane exhibits a flux of $19.87 \text{ kg m}^{-2}\text{h}^{-1}$ with 99.97% salt rejection (**Fig. 5.7b**). The enhanced performance of the sandpaper casted membrane is attributed to their straight, finger-like porous structure with a lower tortuosity that facilitates a more direct vapor pathway by reducing mass transfer resistance. Whereas the glass-cast membranes exhibited excessive shrinkage and structural compaction with higher tortuosity, making it difficult to pass the vapor through membrane surface.

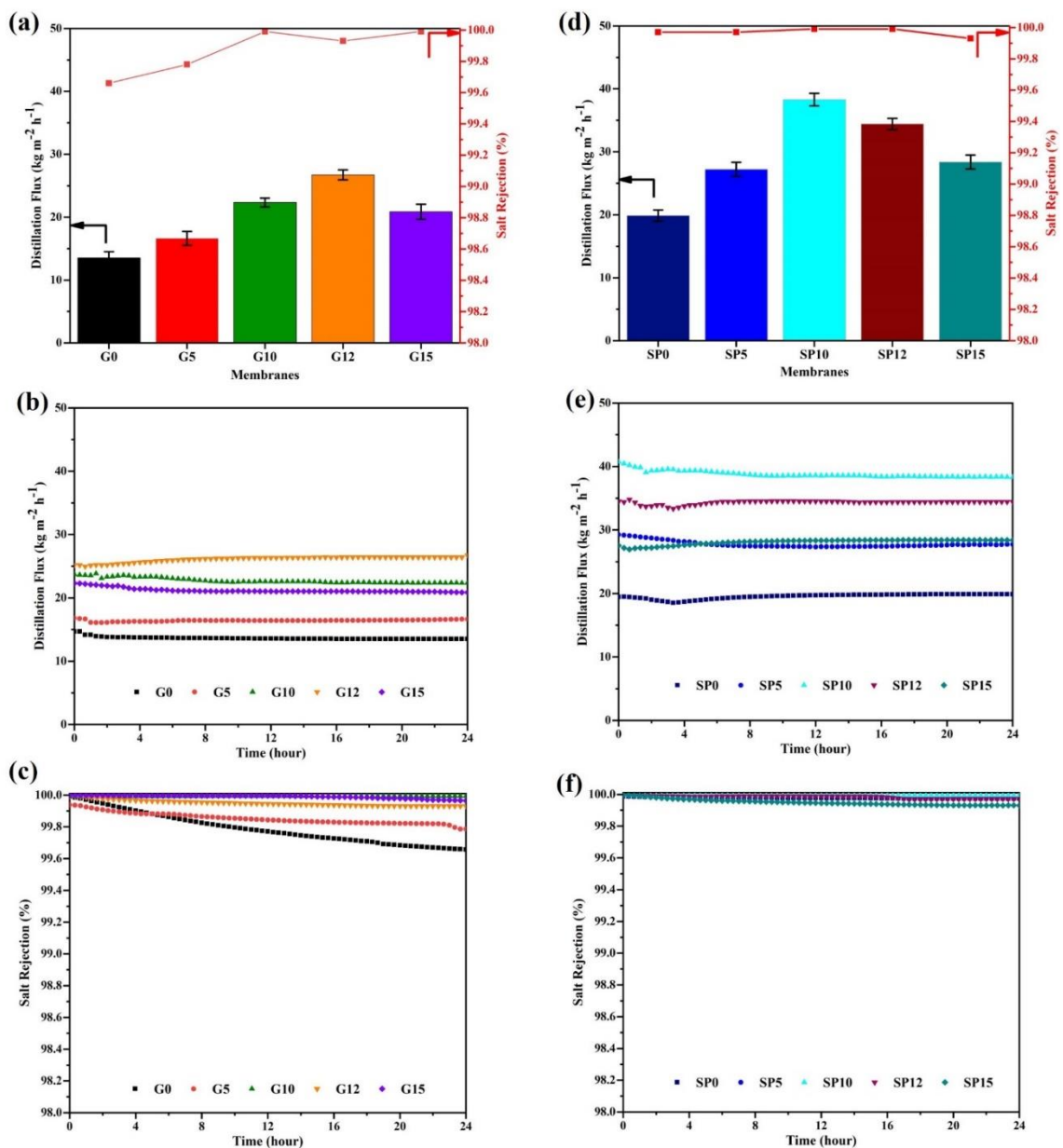


Figure 5. 7 WGMD performance evaluation of the prepared membranes cast on (a) glass and (d) sandpaper substrates; 24h stability of for flux and salt rejection analysis for (b, c) glass cast and (e, f) sandpaper cast membranes respectively.

In contrast, the sputtering of Zn in an oxygen atmosphere, resulting in the formation of ZnO layer onto the skin layer of the modified membranes. With increasing sputtering time, the ZnO layer thickened and formed a hydrophilic surface, making a Janus-like structure with asymmetric wettability of both surfaces. The asymmetric wettability of the membrane surfaces played an important role in enhancing the overall WGMD performance by promoting rapid water vapor condensation on the permeate side by reducing interfacial resistance, resulting in a higher permeate flux. Furthermore, the enhanced roughness due to the ZnO deposition on the sandpaper cast membranes promotes the trapping of air pockets, which in turn strengthens the capillary-driven condensation during WGMD process. The increased roughness facilitates water transport due to the enhanced interaction between the stagnant water and the ZnO layer on the permeate side, resulting in a more efficient heat and mass transfer throughout the membrane. As illustrated in **Fig. 5.7a**, the membranes subjected to sputtering for 5, 10, and 12 minutes demonstrated enhanced permeate flux values of 16.63, 22.33, and 26.73 kg m⁻² h⁻¹, respectively, while consistently maintaining a salt rejection rate exceeding 99.7% over a 24-hour WGMD operation. The increased flux is attributed to the presence of hydrophilic ZnO layer promotes rapid water absorption and condensation, reducing the thermal boundary layer effect and increasing the driving force for mass transfer. Additionally, the asymmetric wettability of the modified membranes can prevent concentration polarization and salt accumulation near the hydrophobic surface, demonstrated an enhanced performance in WGMD due to the

improved condensation kinetics and reduced fouling. A prolonged sputtering duration led to a decline in permeate flux ($20.86 \text{ kg m}^{-2}\text{h}^{-1}$) on the G15 membrane, which can likely be attributed to excessive ZnO deposition on the membrane surface. This excessive deposition may cause partially membrane pores blockage, thereby resisting vapor transport through the membrane surface. As a result, the reduced porosity and increased mass transfer resistance hinder the efficiency of the water vapor permeation, ultimately leading to a decrease in overall flux performance. On the other hand, the highest permeate flux was observed in the case of SP10 membranes with a value of $38.31 \text{ kg m}^{-2}\text{h}^{-1}$ while maintaining salt rejection of $>99.99\%$. Like the G15 membrane, the sandpaper membrane sputtered with 15 minutes also demonstrated a decline in the permeate flux of $28.40 \text{ kg m}^{-2}\text{h}^{-1}$ with a salt rejection of 99.93% . Moreover, it is noteworthy that all the prepared membranes exhibited a stable permeate flux and salt rejection throughout the WGMD operation as illustrated in **Fig. 5.7(c-f)**. Overall, the remarkable performance of the sandpaper-cast membranes with ZnO-modification can be attributed to their straight finger-like pore structure, lower tortuosity, higher surface roughness, and enhanced hydrophilicity. The combination of these parameters resulted in enhanced permeate flux and salt rejection in WGMD, demonstrating the effectiveness of surface engineering strategies in MD applications.

5.7 Performance Evaluation of Commercial PVDF Membranes via ZnO Sputtering

To evaluate the impact of surface modification on MD performance, commercially available PVDF membranes (denoted as CP0) were subjected to ZnO sputtering for durations of 10, 15, and 20 minutes (denoted as CP10, CP15, and CP20 respectively). The

bulk properties of both unmodified and modified membranes are summarized in **Table S11**. As expected, increasing the sputtering duration induced hydrophilicity on one surface due to ZnO deposition. However, the ZnO coating exhibited minimal influence on the membrane's pore diameter, thickness, and porosity, ensuring that the bulk characteristics remained largely unchanged. Despite this, the modified membranes demonstrated enhanced performance in WGMD under identical experimental conditions.

As illustrated in **Fig. 5.8a**, the pristine PVDF membrane (CP0) exhibited a distillation flux of $10.71 \text{ kg m}^{-2}\text{h}^{-1}$ while maintaining a salt rejection of 99.83% in a highly saline solution containing 70 gL^{-1} NaCl over 24 hours of WGMD operation. Upon increasing the sputtering duration to 10 minutes (CP10), the flux improved to $14.96 \text{ kg m}^{-2}\text{h}^{-1}$ with a slightly enhanced salt rejection of 99.86%. The optimal performance was observed for CP15 membranes, achieving a flux of $18.87 \text{ kg m}^{-2}\text{h}^{-1}$ and an exceptional salt rejection of 99.95%. However, further increasing the sputtering duration to 20 minutes (CP20) resulted in a reduced flux of $13.32 \text{ kg m}^{-2}\text{h}^{-1}$, likely due to excessive ZnO deposition causing partial pore blockage. Additionally, the CP20 membrane exhibited unstable salt rejection of 99.69%, possibly attributed to increased wetting on the permeate side, leading to liquid infiltration during WGMD operation. These findings highlight the potential of ZnO sputtering as an effective surface modification technique for enhancing the MD performance of commercial PVDF membranes. This approach presents a novel and sustainable strategy for improving commercial desalination processes, offering a scalable solution for high-salinity water treatment. The SEM images of the modified CP15 membrane after testing at various magnification (**Fig. 5.8c1-c3**) confirm that the membrane structure remained intact, with no visible damage or residue accumulation on the surface.

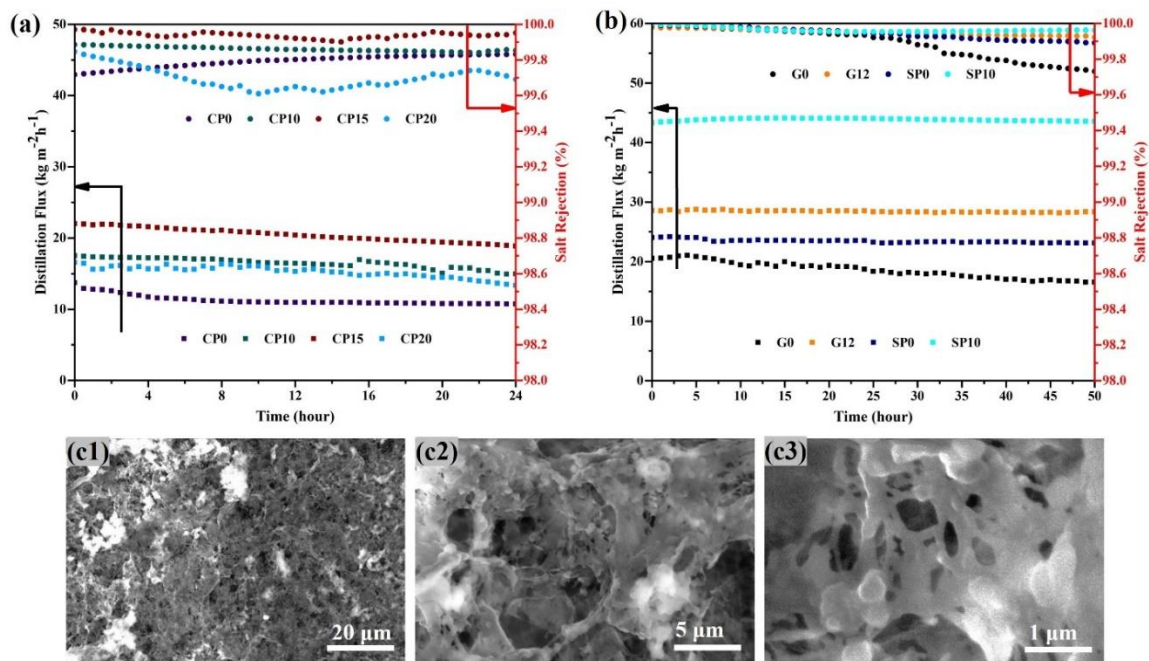


Figure 5. 8 WGMD performance of (a) unmodified and modified commercial PVDF membranes with 70 g L^{-1} of NaCl feed solution; (b) long term stability test with real seawater for the pristine and optimal membranes cast on glass and sandpaper substrates; (c1-c3) SEM images of CP15 membranes after WGMD test at various magnification.

5.8 Long-Term Stability Analysis

The long-term stability of the pristine G0 and SP0 membranes and the optimized G12 and SP10 membranes were evaluated using real seawater as a feed solution for 50 hours. The seawater, collected from the Gulf Sea in Dhahran, Khobar, Saudi Arabia, had a salinity of 41.76 g L^{-1} and was used without any pretreatment. All other experimental conditions were maintained as specified in **Table 3.5**. As shown in **Fig. 5.8b**, the pristine G0 and SP0 membranes exhibited a flux of $16.52 \text{ kg m}^{-2} \text{ h}^{-1}$ and $23.13 \text{ kg m}^{-2} \text{ h}^{-1}$ respectively, which are represented a slight increase compared to their performance with a highly concentrated 70 g L^{-1} NaCl solution. In contrast, the modified G12 and SP10 membranes demonstrated

significantly higher flux of $28.35 \text{ kg m}^{-2}\text{h}^{-1}$ and $43.52 \text{ kg m}^{-2}\text{h}^{-1}$, approximately 72% and 88% greater than that of the pristine G0 and SP0 membranes respectively while maintaining a higher salt rejection of >99.99%. However, a slight decline in flux was observed for all the membranes over an extended period of WGMD operation. This phenomenon is attributed due to the WGMD process which involves both water vapor and heat transfer, leading to an increase in salt concentration at the evaporation interface due to latent heat loss associated with vapor transport. This loss of latent heat causes a reduction in the temperature of the feed solution. Despite these challenges, the Janus membrane exhibited superior permeate flux when tested with real seawater, which can be attributed to the higher vapor pressure of the lower-concentration feed solution, in accordance with Raoult's Law [109]. However, a gradual decline in salt rejection over time was observed, likely due to the wetting tendency of PVDF membranes during extended operation. The feed solution concentration was measured at 51.82 gL^{-1} after 50 hours of WGMD operation, suggesting the membrane's effectiveness in concentrating the brine solution. This higher preconcentration of the brine solution is a crucial step for resource recovery by MD crystallization since it can facilitate the extraction of valuable minerals and salts including NaCl, Mg, Ca, and Li. However, due to the limitation of our MD module effective surface area of $7.316 \times 10^{-4} \text{ m}^2$, results in a moderate preconcentration of the brine solution. Expanding the membrane effective surface area on an industrial scale could significantly enhance the resource recovery, leveraging our approach to fabricate membranes for large-scale implementation.

CHAPTER 6

CONCLUSION AND RECOMMENDATIONS

6.1 Conclusion

This study presents the successful fabrication of high-performance Janus membranes with asymmetric wettability, effective for sustainable and long-term WGMD operation. Two different innovative strategies were employed to develop the Janus membranes — electrospun dual-layer Janus membranes by integrating distinct carbonaceous materials on both sides of the membrane surfaces to have asymmetric wettability and magnetron sputtering of ZnO on PVDF phase inversion membranes to overcome the critical challenges of Janus membrane delamination, wetting problem, and low permeate flux.

The electrospun Janus nanofibrous membranes were fabricated using hydrophobic carbon nanofibers and hydrophilic biomass-derived carbon nanoparticles that demonstrated excellent interfacial bonding and mechanical stability between the two layers. The asymmetric wettability of between the two layer enhances directional vapor transport from the feed side of the WGMD module while rapid condensation had occurred on the permeate since the hydrophilic layer helps the stagnant water comes closer to the surface, resulting in a twofold increase in the distillation flux compared to the pristine membranes. The optimized Janus membrane remarkably achieved a ~547% increase in permeate flux compared to the available PVDF membranes while tested with real seawater, maintaining an exceptional salt rejection and stable for a long term. The incorporation of different

carbon materials into the polymer matrix highlights the potentiality in improving both the anti-fouling and anti-scaling resistance during WGMD operation.

In parallel, the sputtering-assisted surface engineering strategy allowed deposition of ZnO nanolayers on the PVDF membrane skin layer, forming a hydrophobic–hydrophilic interface without the need for additional solvents, adhesives or chemical grafting. This fine-tuning deposition approach effectively preserved the membrane’s porosity and structure, but preventing the risk of delamination. The membrane with optimal sputtering durations significantly enhanced the distillation flux—up to 93% higher compared to the pristine PVDF membranes by maintaining ~100% salt rejection. Furthermore, the optimized membranes exhibited strong anti-wetting performance and stable for long-term operation using real seawater, highlighting their potentiality for brine pre-concentration and valuable resource recovery applications.

Overall, this study demonstrates that rational membrane design—through material selection, surface modification, and structural engineering—can substantially improve the MD performance and their stability for long-run operation. The obtained findings and results offer a sustainable and scalable pathway for developing next-generation Janus membranes, with strong potential for the application in real-world desalination plants, hypersaline brine treatment, and valuable resource recovery applications.

6.2 Future Recommendations

1. Exploring other Biomass sources

Investigation of the potential use of alternative biomass-derived carbon nanoparticles (for instance, date seeds, coconut shell, tree leaf, rice husk) to integrate into the hydrophilic layer of the Janus membranes.

2. Functionalization of Carbon Nanofibers or Alternative Hydrophobic Materials

Modifying carbon nanofibers to have more intrinsic hydrophobicity of the particles or searching for alternative hydrophobic nanomaterials to enhance hydrophobicity of Janus surface, anti-fouling behavior, and selective vapor transportation.

3. Sputtering with other metal oxides

Sputtering with other metal oxides like Experiment with other oxides like Al_2O_3 , TiO_2 , or Fe_2O_3 to compare their hydrophilicity on the PVDF membranes, their stability under different operational conditions.

4. Integration of photothermal materials

Incorporation of photothermal materials like polydopamine, plasmonic nanomaterials or MXenes to investigate solar-assisted MD for energy-efficient and sustainable desalination.

5. Coupling MD with crystallization

Further studying the potentiality of the developed membranes in MD crystallization (MDC) systems for valuable resource recovery from different concentrated brine solutions.

6. Designing of multi-layered Janus membranes

Developing of triple-layer or gradient layer membranes with fine tuning porosity to further optimize the trade-off between vapor transport and thermal conductivity.

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Journal Publications:

1. **Hossain Md. E.**, Ahmad Hilal, Mohammed Abdul Azeem MA, Lawal D.U., Aziz MA, Baroud TN, et al. “*Biomass-Derived Carbon and Carbon Nanofibers Integrated Electrospun Janus Membranes: A New Frontier in Membrane Distillation*”. *ACS Applied Materials & Interfaces*, **2025**; (<https://doi.org/10.1021/acsami.4c21554>).
2. **Hossain, Md. E.**; Azeem, M. A.; Obidara, T. O.; Lawal, D. U.; Spyrou, K.; Sakavitsi, V.; Baroud, T. N. Flake Shaped Hydrophobic Clay Nanoparticles Incorporated Electrospun Membranes for Desalination of Highly Saline Water. *Journal of Water Process Engineering* **2025**, 71, 107272. (<https://doi.org/10.1016/j.jwpe.2025.107272>).
3. **Hossain Md. E.**, Johan BA, Shah SS, Abdallah M, Rahman MR, Baroud TN, Aziz MA et al. “Effect of Carbon Nanomaterials Incorporated Polymeric Membrane Separators for Energy Storage Devices”. *Chemistry - An Asian Journal*. Wiley-VCH GmbH; 2025. (<https://doi.org/10.1002/asia.202401618>)
4. T. O. Obidara, Azeem MA, Lawal D.U., Konstantinos Spyrou, Sakavitsi Viktoria, **Hossain Md. E.**, Baroud TN, et al., “Enhanced performance of novel nano-enabled PVDF membranes with amino and chloro-based clay for membrane distillation”, *Separation & Purification Technology*, Jan. **2025**, (<https://doi.org/10.1016/j.seppur.2025.131435>)
5. Perdana MY, Johan BA, Abdallah M, **Hossain Md. E.**, Baroud TN, Drmosh QA, Aziz MA, et al. Understanding the Behavior of Supercapacitor Materials via Electrochemical Impedance Spectroscopy: A Review”. *The Chemical Record*. John Wiley and Sons Inc; **2024**. (<https://doi.org/10.1002/tcr.202400007>)

Supplementary Materials

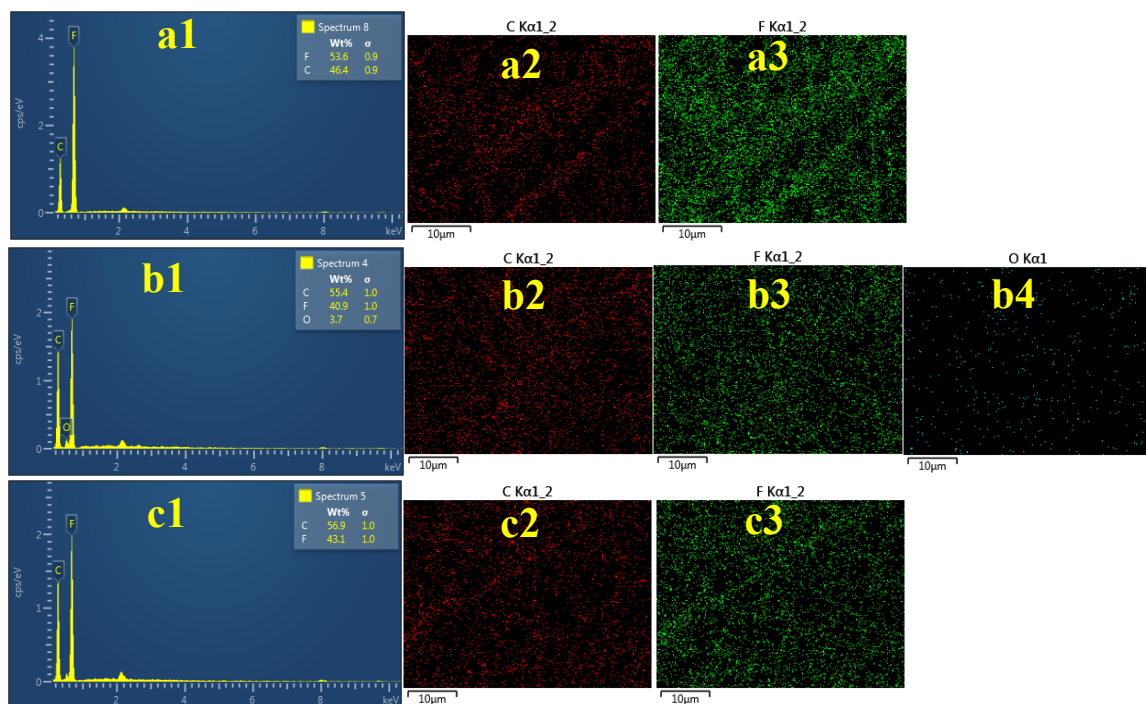


Figure S 1 EDS spectrum and mapping for the membranes (a1-a3) PH, (b1-b4) PH-0.5JC, and (c1-c3) PH-0.5CNF respectively.

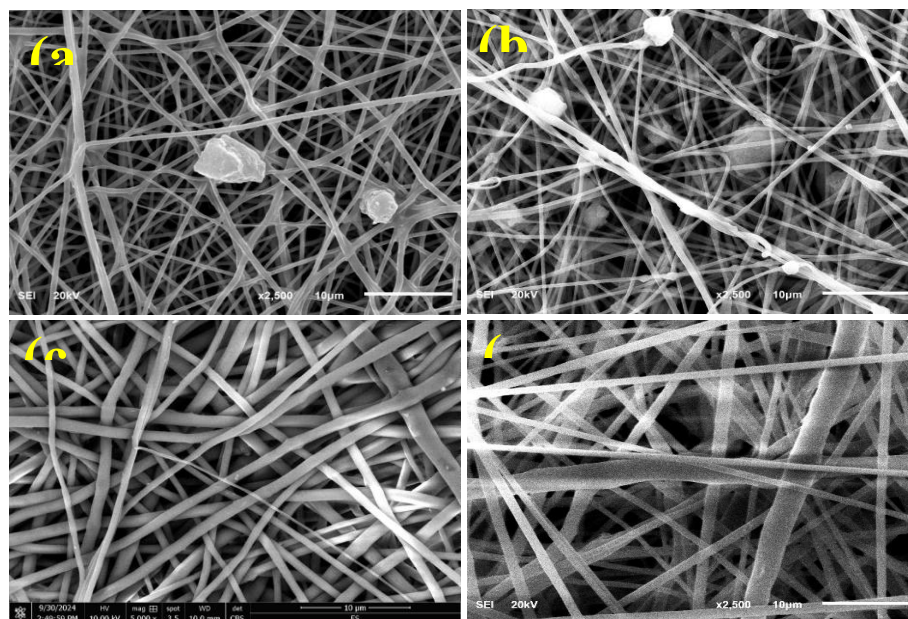


Figure S 2 SEM images of the composited PH membranes (a) 0.1wt% JC; (b) 1.0 wt% JC; (c) 0.1 wt% CNF; and (d) 1.0 wt% CNF respectively.

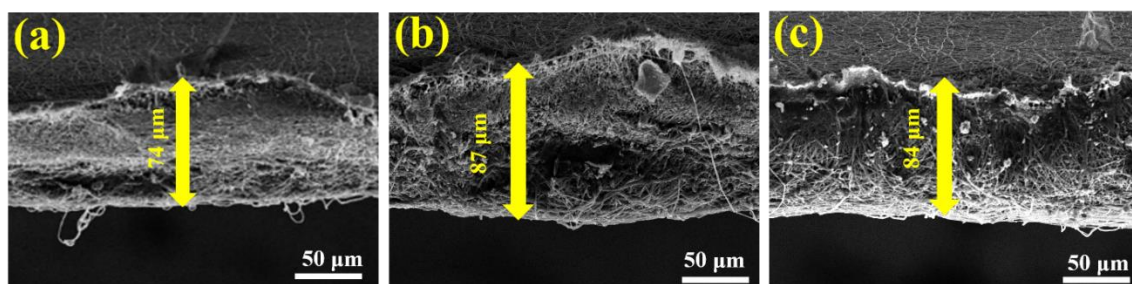


Figure S 3 Cross-sectional SEM images of (a) pristine PH; (b) PH-0.5JC; and (c) PH-0.5CNF membranes respectively.

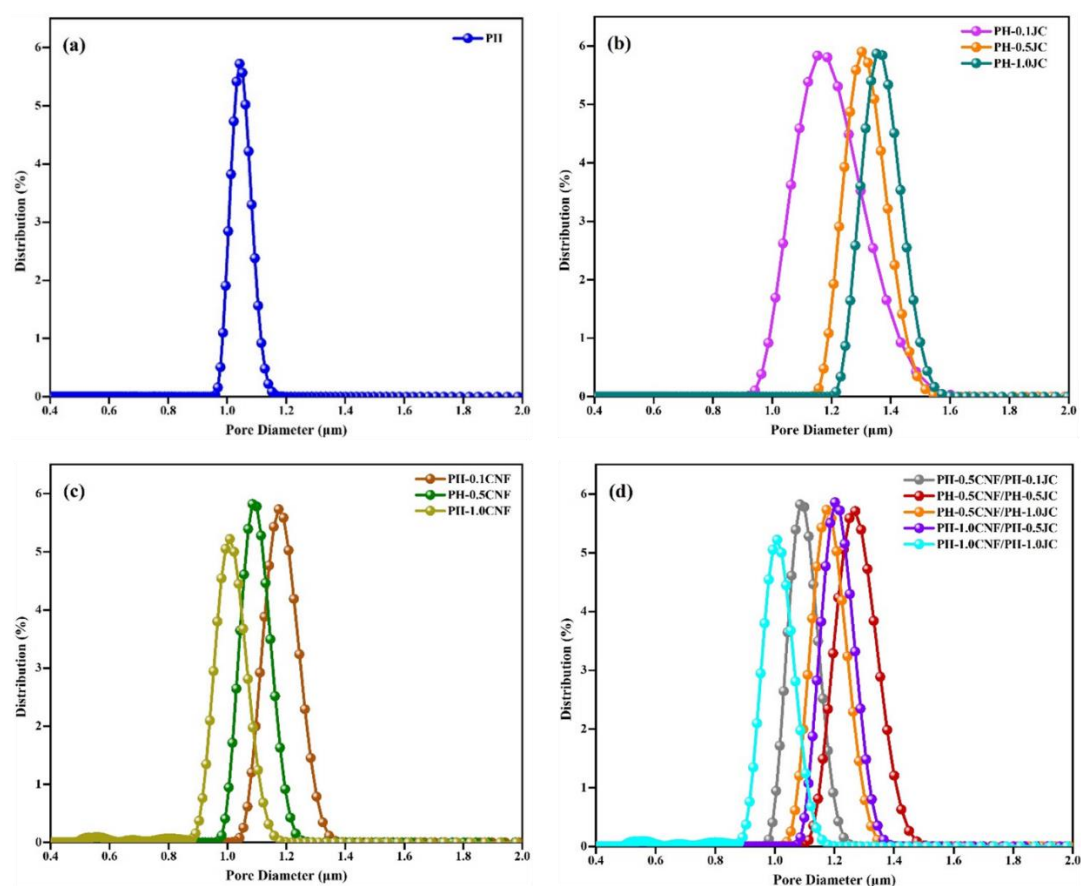


Figure S 4: Pore size distribution of (a) PH; (b) PH-JC; (c) PH-CNF; and (d) Janus PH-CNF/PH-JC membranes.

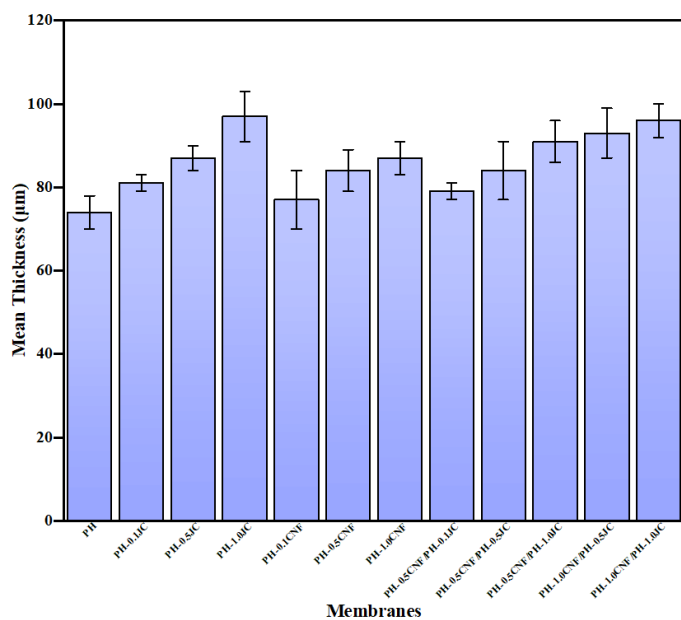


Figure S 5 Mean Thickness for all the developed electrospun nanofibrous membranes.

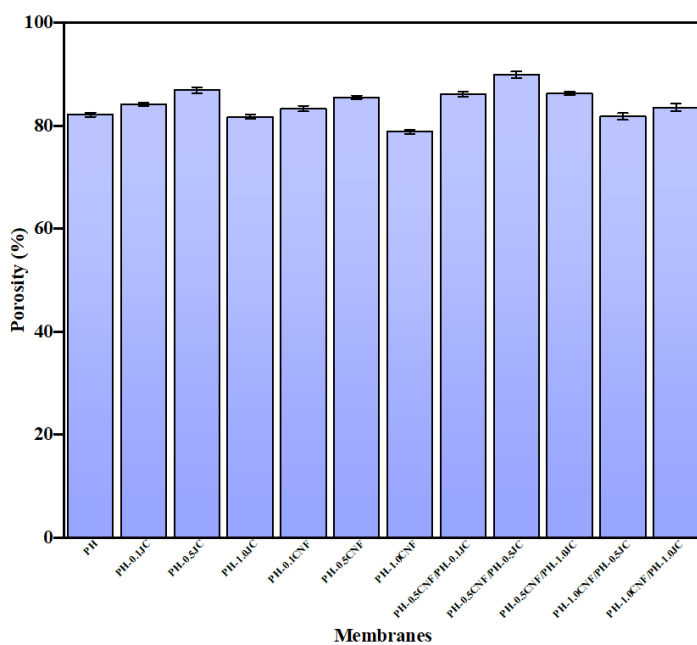


Figure S 6 Porosity (%) for all the developed electrospun nanofibrous membranes

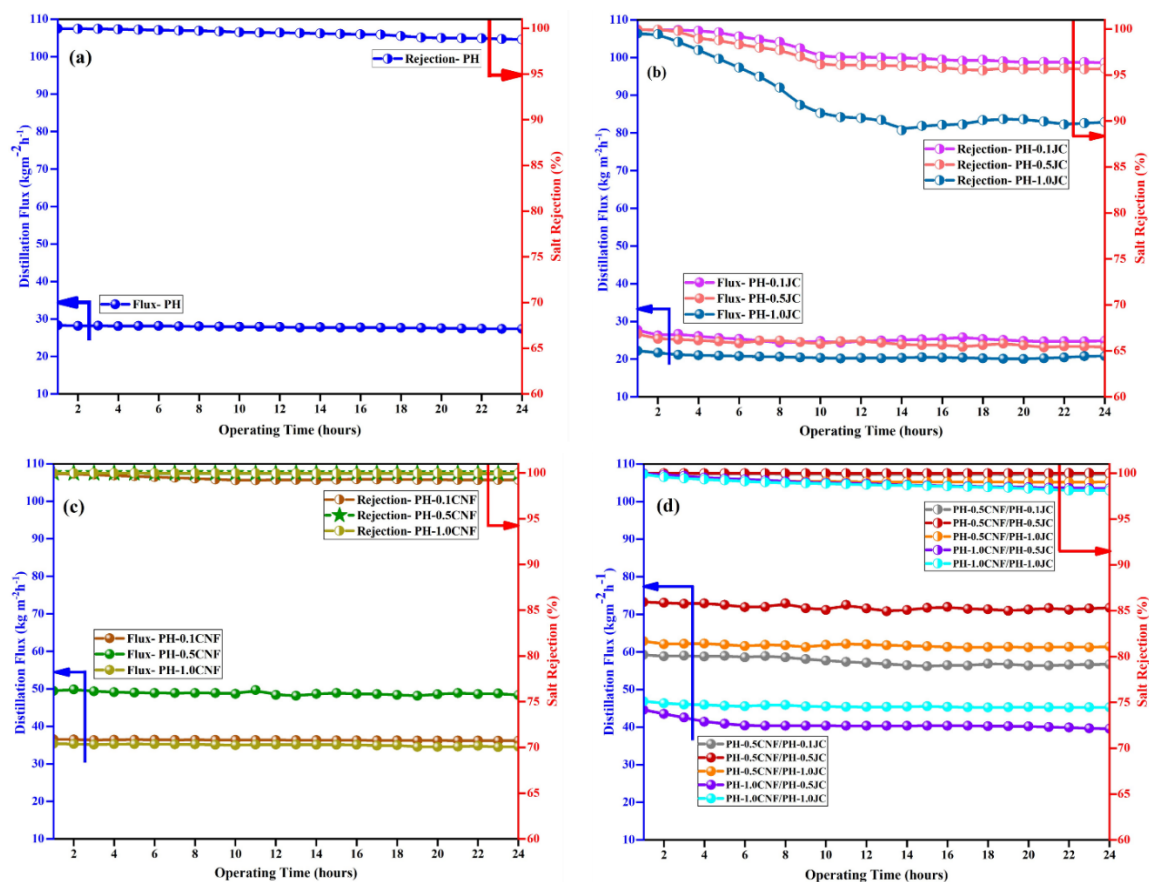


Figure S 7 The WGMD performance through 24 hours of operational time (a) PH membrane, (b) single-layered hydrophilic membranes, (c) single-layered hydrophobic membranes, and (d) dual-layered Janus membranes.

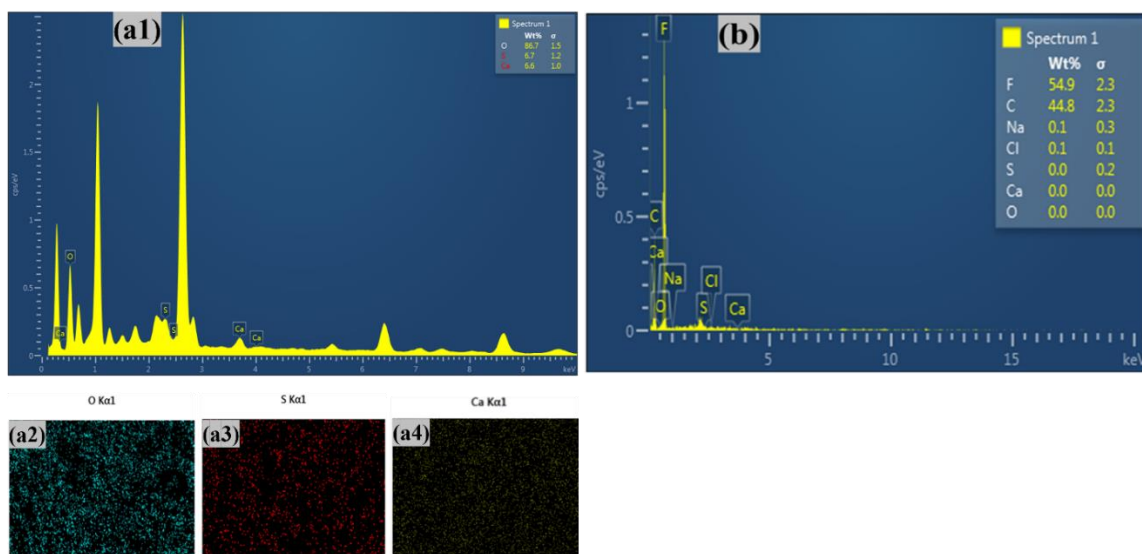


Figure S 8 EDS analysis after anti-scaling test for pristine PH membrane (a1) spectrum, (a2-a4) mapping, and (b) PH-0.5CNF/PH-0.5JC membranes respectively

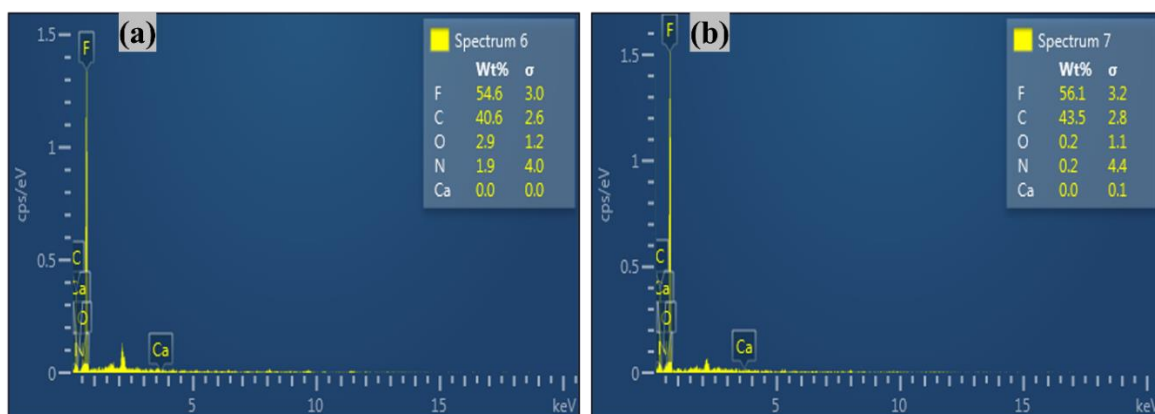


Figure S 9 EDS spectrum analysis after anti-fouling test for (a) pristine PH, and (b) PH-0.5CNF/PH-0.5JC membranes respectively.

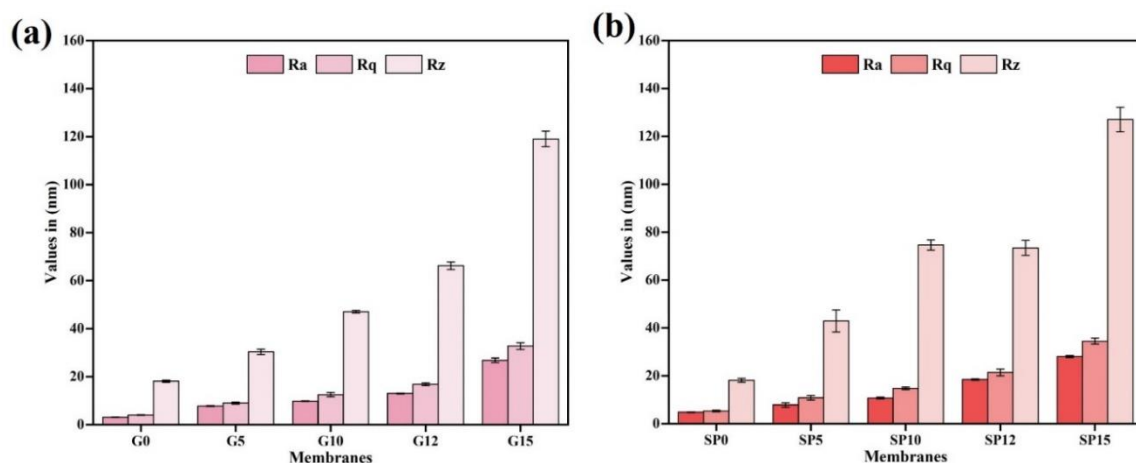


Figure S 10 Skin layer surface roughness parameters of all the prepared membranes cast on (a) glass and (b) sandpaper substrate respectively.

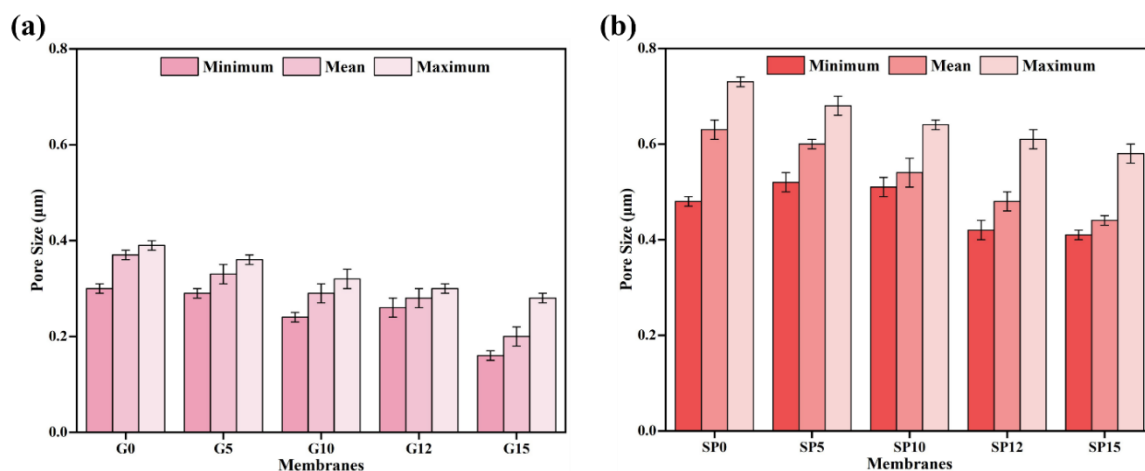


Figure S 11 Pore diameter of the prepared membranes cast on (a) glass and (b) sandpaper substrate respectively.