

**COVALENT ORGANIC FRAMEWORK (COF)
BASED MEMBRANES FOR DESALINATION AND
BORON REMOVAL**

BY

UMAR HUSSAINI NUHU

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COLLEGE OF GRADUATE & INTERDISCIPLINARY STUDIES

This thesis, written by **Umar Hussaini Nuhu** under the direction of his thesis advisor and approved by his thesis committee, has been presented and accepted by the Dean of College of Graduate & Interdisciplinary Studies in partial fulfillment of the requirements for the degree of **MASTER OF SCIENCE IN CHEMICAL ENGINEERING**



Dr. Saad F. Alafnan
Department Chairman



Dr. Suliman S. Al-Homidan

Dean of College of Graduate &
Interdisciplinary Studies

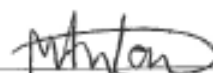
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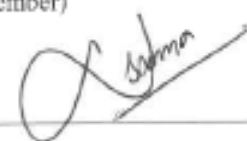
Dr. Umer Zahid
(Advisor)



Dr. Isam Al-Jundi
(Co-Advisor)



Dr. Mohammed Antar
(Member)



Dr. Usama Ahmed
(Member)



Dr. Niaz Ali Khan
(Member)

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2025

[This work is dedicated to my to My Dad, Alhaji Hussaini Nuhu and my Mom, Hajiya Bilkisu Abubakar, who are just too invaluable to me since the day I was born up to this very moment of my life, may Allah reward you all with paradise]

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LIST OF ABBREVIATIONS

BET	: Brunauer-Emmett-Teller
BSA	: Bovine serum albumin
FTIR	: Fourier-transform infrared spectroscopy
IP	: Interfacial polymerization
ISA	: Integrally skinned asymmetric
ICP-OES	: Inductively coupled plasma atomic emission spectroscopy
LMH	: Liter per square meter per hour
LMHB	: Liter per square meter per hour per bar
PA	: Polyamide
PPM	: Parts per million
RO	: Reverse osmosis
SA	: Sulphonic acid
SWCC	: Saline Water Conversion Corporation
TDS	: Total dissolved solids
TFC	: Thin film composite
TFN	: Thin film nanocomposite
TEM	: Transmission Electron Microscope

XRD : X-ray diffraction

XPS : X-ray Photoelectron Spectroscopy

ABSTRACT

Full name : Umar Hussaini Nuhu
Thesis Title : Covalent organic framework (COF)-Based Membranes for Desalination and Boron Removal
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Introducing well-structured and selective ionic channels into the polyamide (PA) layer of Reverse osmosis (RO) membranes during interfacial polymerization (IP) shows promise for boosting the Donnan and steric exclusion effects, thus enhancing performance. In this research work, we propose a novel method to rapidly synthesize water soluble sulfonic acid containing covalent organic framework (SA-COF) nanosheets and incorporated them during IP to precisely adjust ionic groups within the PA layer. The SA-COF's processability and charged nature enhance compatibility with PA, enabling a high loading (10 wt.%) without compromising membrane integrity. Additionally, SA-COF integration during IP results in PA membranes with reduced thickness, increased negative charge density, and increased hydrophilicity. Consequently, PA membranes containing 10 wt.% SA-COF, denoted as PA-COF₁₀, demonstrated exceptional water permeance (0.98 L/m²·h·bar), surpassing pristine PA membranes (0.39 L/m²·h·bar), while maintaining over 98% rejection for NaCl. Moreover, PA-COF₁₀ membranes exhibited outstanding operational stability and resistance to fouling. PA-COF₁₀ membranes exhibited a flux recovery rate of 93% after 35 fouling cycles with bovine serum albumin (BSA), compared to only 63% for pristine membranes. SA-COF was also systematically added to the membrane support to investigate its influence on boron rejection. The membranes fabricated by varying the SA-COF loading were tested under identical operating conditions, achieving around 86% at an optimal loading of 7wt.%. This synergistic enhancement of permeance, salt rejection and boron removal through charged SA-

COF integration offers a practical and eco-friendly approach for advanced desalination membrane development, facilitating rapid clean water production.

ملخص الرسالة

الاسم الكامل: عمر حسيني نوحو

عنوان الرسالة: لتحلية المياه وإزالة البورون (COF) الأغشية القائمة على الإطار العضوي التساهمي

التخصص: الهندسة الكيميائية

تاريخ الدرجة العلمية: مايو ٢٠٢٥

أثناء (RO) لأغشية التحلية بالتناضح العكسي (PA) يُظهر إدخال قنوات أيونية منتظمة البنية وانتقائية في طبقة البولي أميد وهداً كبيراً في تعزيز تأثيري دونان والاستبعاد الحجمي، مما يؤدي إلى تحسين الأداء. في هذا البحث، نقترح (IP) البلمرة البينية طريقة جديدة لتحليق صفائح نانوية من إطار عضوي تساهمي قابل للذوبان في الماء يحتوي على مجموعات حمض السلفونيك بشكل سريع، ودمجها أثناء عملية البلمرة البينية لضبط المجموعات الأيونية بدقة داخل طبقة البولي أميد. إن قابلية (SA-COF) وطبيعته المشحونة تعزز التوافق مع البولي أميد، مما يسمح بتحميل عالٍ (10% بالوزن) دون التأثير على SA-COF معالجة أثناء البلمرة البينية إلى أغشية بولي أميد ذات سماكة أقل، وكثافة شحنة SA-COF سلامة الغشاء. بالإضافة إلى ذلك، أدى دمج SA-COF، سالبة أعلى، وزيادة في محبة الماء. ونتيجة لذلك، أظهرت أغشية البولي أميد التي تحتوي على 10% وزناً من نفاذية ماء استثنائية (0.98 لتر/متر مربع ساعة بار)، متجاوزة الأغشية الأصلية (0.39، PA-COF10) والتي يشار إليها باسم علاوة على ذلك، أظهرت (NaCl) لتر/متر مربع ساعة بار)، مع الحفاظ على نسبة رفض تتجاوز 98% لكلوريد الصوديوم ثباتاً تشغيلياً ومقاومة ممتازة للتلوث، حيث سجلت معدل استعادة تدفق بلغ 93% بعد 35 دورة تلوث PA-COF10 أغشية بشكل منهجي إلى SA-COF مقارنة بـ 63% فقط للأغشية الأصلية. كما تمت إضافة (BSA) باستخدام ألبومين مصل البقر SA- الدعامة الداعمة للغشاء لدراسة تأثيره على رفض البورون. وتم اختبار الأغشية المصنعة باستخدام تحميلات مختلفة من تحت ظروف تشغيل متطابقة، حيث حققت نسبة رفض للبورون تقارب 86% عند تحميل أمثل يبلغ 7% وزناً. يمثل هذا COF المشحون نهجاً عملياً وصديقاً للبيئة لتطوير SA-COF التحسين التآزري في النفاذية ورفض الأملاح وإزالة البورون عبر دمج أغشية تحلية متقدمة، مما يسهل إنتاج مياه نظيفة بسرعة.

CHAPTER 1 INTRODUCTION

1.1 Background

Concerns about global water availability have been increasingly emphasized over the past few decades, often described in critical terms such as the "global water crisis" and "water scarcity"[1]. Two major factors contributing to this issue are economic expansion and population growth, which have led to the excessive use of traditional freshwater sources in different regions worldwide [2]. Water scarcity is typically defined as a situation where the overall annual renewable water supply ready for consumption drops below 1,000 cubic meters per person per year [3]. As of 2015, 28 countries, most of which are developing nations, were already facing water scarcity. This crisis is expected to worsen in the coming decades, as the population is being projected to reach about 9 billion by the year 2050. Estimates suggest that by then, 44 countries—home to roughly 2 billion people will likely experience severe water shortages [4, 5]. These projections (Figure 1) are assumed based on the fact that there will be no additional withdrawal of freshwater to accommodate the growing population as derived from estimates by FAO data on total renewable water resources (a combination of groundwater and surface water availability in each country) [6] and World Bank population projections for 2020 and 2050 [7].

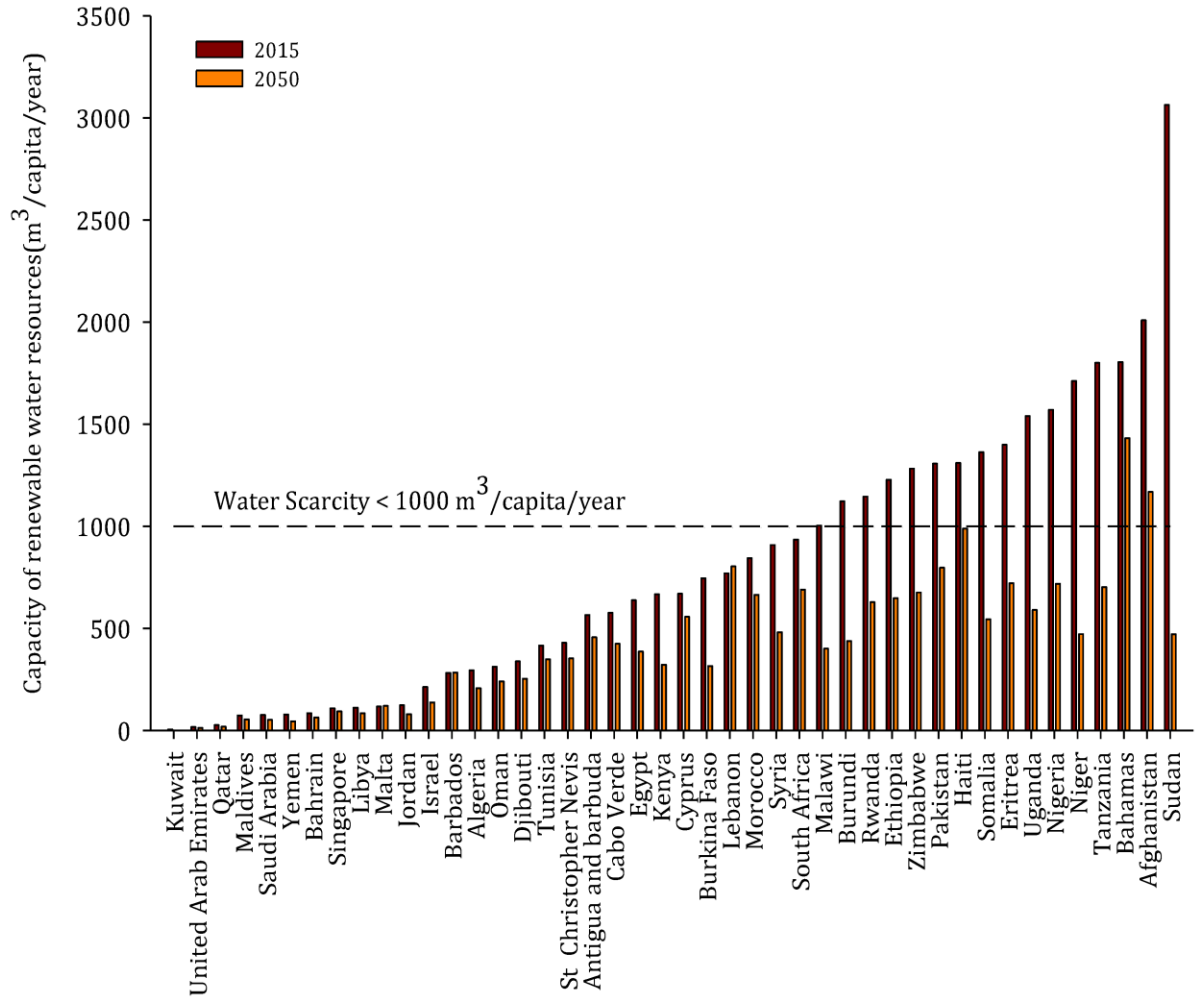


Figure 1: Projected countries to be hit with water scarcity by year 2050 [8].

Therefore, the global need for clean and drinkable water is increasing due to factors like increase in population, fast urbanization, industrialization, and climate change. United Nations estimates indicate that demand of water globally is projected to increase by 34% by the year 2050, coinciding with a population of 10.2 billion [9]. Water is a vital resource in today's world for supporting life. A significant proportion of the Earth is occupied by various water bodies, predominantly in the form of seas and oceans, as well as underground water and other saline bodies. Just 3% of the entire water supply consists of freshwater, with the rest 97% being saline water [10]. The majority of freshwater exists either in

subterranean reservoirs that are very hard to access or as a form of ice and frozen glaciers. Agriculture utilizes around 70% of the overall water consumption, while 20% is being utilized in the industry, and the residual 10% is allocated to meet residential demands. The world is currently confronting a significant issue of water shortage, as the demand for high-quality water in many locations has increased due to population growth and economic development [11]. Seawater and other saline bodies of water are unsuitable for direct human consumption. Saltwater desalination is widely used, with over 16,000 operating desalination plants in the whole world providing more than 95 million cubic meters of drinking water per day. Approximately three quarters of this water is obtained from saltwater, while one quarter is obtained from brackish water [12].

As per the regulations set by international organizations like the permissible limits of total dissolved solids (TDS) in water is around 500 parts per million (ppm). Nevertheless, these water bodies contain TDS within the range of 10,000-15,000 ppm [13] Table 1 presents the TDS content for different water sources [14].

Table 1: Source water based on the quality of dissolved solids it contains [14].

Water Source	Total dissolved Solids
Potable water	Less than 1000
Average seawater	Around 35000
Mildly brackish water	Between 1000-5000
Moderately brackish waters	Between 5000-15000
Heavily brackish water	Between 15000-35000

Desalination is the procedure of extracting salts from water that has a high salt content (brine) in order to obtain freshwater with a low salt concentration [15]. Desalination, an

ancient method of water treatment, has emerged as a viable and sustainable approach to address water scarcity in both residential and industrial sectors. Water desalination has become a crucial technology, particularly in regions such as the Middle East and African countries where there is insufficient rainfall. Saudi Arabia, a country in the Middle East, is geographically extensive and its population is widely dispersed. Therefore, the nation has turned to the process of seawater desalination and the transfer of fresh water through various methods to fulfill its need for freshwater in the inland areas [16].

1.2 Technologies for desalination

The desalination procedure can eliminate dissolved solids found in saline water sources using either heat evaporation or membrane separation methods. Thermal desalination is a process that requires you to heat seawater to create steam, which is then condensed to produce freshwater while leaving behind dissolved solids to remain in the brine. Whereas for membrane processes it operates in a manner akin to filters, allowing water molecules to pass through a semi-permeable membrane and generate permeate feed with minimal dissolved particles. A basic description of this process is demonstrated in Figure 2. Thermal activities require more energy than membrane processes mostly because of the need for latent heat to evaporate freshwater. Membrane processes rely on electrical energy, which is regarded as a valuable and high-quality form of energy [17].

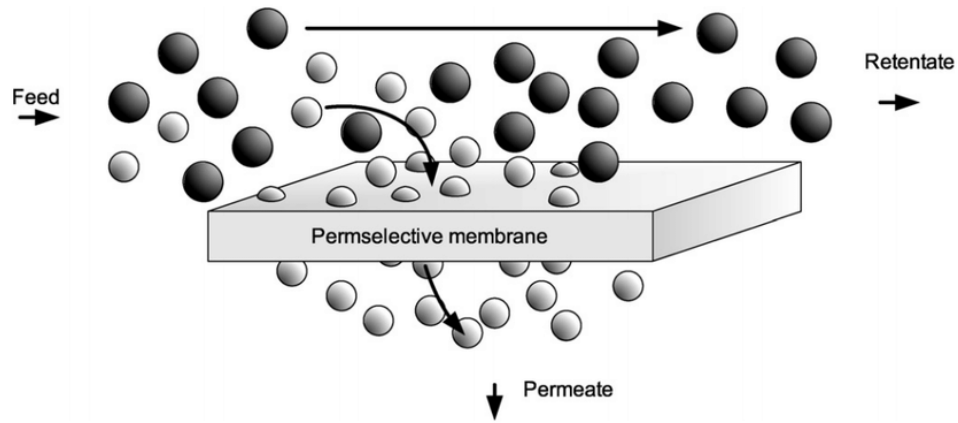


Figure 2: Schematic of Membrane separation [18].

Thermal desalination techniques span a variety of approaches, including technologies like traditional sun stills and multi-effect evaporation/distillation or boiling. On the membrane process side, methods include nanofiltration, and reverse osmosis. Moreover, hybrid methods combine these principles either within a single system or through sequential stages to produce potable water. These innovative combinations include membrane distillation and the integration of reverse osmosis with multi-effect evaporation/distillation technologies, offering versatile solutions for fresh water production. [19]. Figure 3 illustrates the contribution of different desalination technologies.

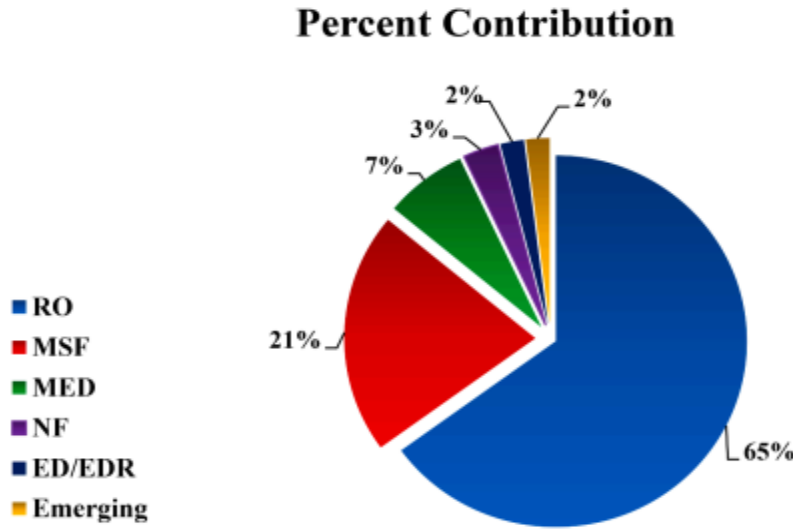


Figure 3: Global distribution of desalination technologies' contribution in terms of percentage

Reverse osmosis (RO) technologies have emerged as the leading technology for desalinating brackish and seawater due to their cost-effectiveness. This is primarily attributed to their significantly lower energy usage and the recent advancements in membrane and energy recovery systems. Hence, the prospect of integrating desalination systems with solar energy holds a significant financial advantage, particularly in the Middle East and regions with abundant sunlight. Table 2 presents data on the efficiency and expenses of several solar desalination facilities.[20].

No table of figures entries found. Table 2: Cost and performance of different solar desalination facilities, as derived from the source mentioned, are presented below [21, 22].

Desalination Method	Source of Water	Efficiency (% Recovery)	Energy Usage (kWh/m³)	Cost of Water Produced (US\$/m³)
Reverse Osmosis	Seawater, Brackish Water	10% to 51%	1.2 to 1.9	3 to 27
Electrodialysis	Brackish Water	25% to 50%	0.6 to 1	3 to 16
Multi-Stage Flash	Seawater, Brackish Water	0.6% to 6%	81 to 144 (thermal)	1 to 5
Multi-Effect Distillation	Seawater, Brackish Water	6% to 38%	50 to 194 (thermal)	2 to 9
Membrane Distillation	Seawater, Brackish Water	3% to 5%	100 to 600 (thermal)	13 to 18

Over the recent years, advancements in technology and ongoing research have led to a notable decrease in the costs associated with water desalination. In gasoline systems, the expense of desalinating seawater is between 2.7 Euro/m³ and 0.35 Euro/m³. In contrast, desalinating brackish water typically costs about half as much. However, when renewable sources are employed, the costs can escalate significantly, sometimes reaching as high as 10.32 Euro/m³, mainly due to the higher costs associated with more sophisticated energy systems. Despite these higher costs, the environmental benefits help balance the financial outlay. Table 3 succinctly summarizes the costs involved in producing fresh water from desalination, considering both conventional and renewable energy-driven processes.

Table 3: Energy source and cost of water production [21]

Water Source	Energy Source	Cost (Euro/m³)
Brackish Water		
	Gasoline	0.20 to 1.06
	Solar Cells	4.5 to 10.33
	Geothermal	2.00
Salt Water		
	Gasoline	0.30 to 2.70
	Wind Power	1.0 to 5.0
	Solar Cells	3.14 to 9.0
	Solar Collectors	3.5 to 8.0

1.3 Reverse Osmosis Plants in Saudi Arabia

The Kingdom of Saudi Arabia has been familiar with water desalination for a considerable period, starting from the early evaluation of the essential requirements for this critical resource. The Kingdom has been diligently doing ongoing research, innovating novel techniques for water generation, and consistently meeting the need. In the mid-1900s, King Abdulaziz bin Abdulrahman Al Saud recognized the difficulties faced by pilgrims and Umrah performers who arrived in Jeddah due to the scarcity of fresh water. To address this issue, he took the initiative to import two large desalination machines. These machines were intended to ensure an adequate water supply for the needs of the pilgrims and Umrah performers, as well as to provide water for the residents of Jeddah.

In 1974, a significant milestone occurred with the issuance of a royal decree to establish The Saline Water Conversion Corporation (SWCC). This decree empowered the Corporation to take on the responsibility of constructing and operating desalination plants

and water transmission systems. In 1978, the Kingdom implemented reverse osmosis desalination technology. In 1978, a major advancement in reverse osmosis desalination took place with the creation of the largest seawater desalination system in Jeddah, Saudi Arabia. A substantial reverse osmosis facility will be established to desalinate extremely saline Red Sea water so as to achieve the target of municipal water requirements in Jeddah, Saudi Arabia. The Saline Water Conversion Corporation (SWCC) of Saudi Arabia has awarded a contract through competitive bidding to the Fluid Systems Division of UOP Inc. The contract encompasses the planning, building, and assembly of the facility, along with two years of operational and maintenance support. The capacity of the first world's largest reverse osmosis (RO) plant was 12,120 cubic meters per day.

This significant accomplishment was a pivotal milestone in the field, emphasizing the feasibility of using reverse osmosis for the large-scale generation of freshwater. The Jeddah plant utilized a recently created membrane that was specifically designed to endure the elevated salinity of seawater. This groundbreaking achievement completely transformed the field of desalination and set the stage for future progress in reverse osmosis technology.

Between 1978 and 2024, a total of forty-two (42) reverse osmosis (RO) plants have been contracted. Table 4 provides details on the current and future seawater reverse osmosis (SWRO) plants in the kingdom, including their production capacity and current state as reported by the Saudi Water Conversion Corporation (SWCC).

Table 4: Desalination using seawater reverse osmosis (SWRO) in Saudi Arabia [23].

Plant name	Process type	Production(m3/day)	Year of operation	Plant name	Process type	Production(m3/day)	Year of operation
Jeddah	RO	12,120	1978	Jubail III B	RO	600,000	Under Design
Albirk	RO	2,270	1983	Rays I	RO	570,000	Under Design
Umluj II	RO	4,400	1986	Shoaiba V	RO	600,000	Under Design
Duba III	RO	4,400	1989	Shuqaiq V	RO	400,000	Under Design
Jeddah RO I	RO	56,800	1989	Jubail II RO Replacement	RO	1,000,000	Under Design

1.4 Thesis Problem statement

Increased production of fresh water from traditional sources, such as seawater, brackish groundwater, and even wastewater, is urgently needed as a result of increased scarcity of high-quality water for human use, industry, and agriculture. Reverse osmosis (RO) membranes are widely used for water desalination due to their high water permeability and excellent salt rejection. However, a significant challenge with these membranes is fouling, which occurs due to the accumulation of contaminants on the surface of the membranes and within their pores. This fouling phenomenon reduces water flux and salt rejection, ultimately compromising the performance and longevity of the membrane. Fouling is mainly characterized by the mechanism through which it happens which can be by 1. pore blockage 2. pore constriction, and 3. cake formation, as indicated in Figure 4, and whether it may be eliminated (i.e., reversible or irreversible) or the substance causing it (i.e., organic or inorganic).

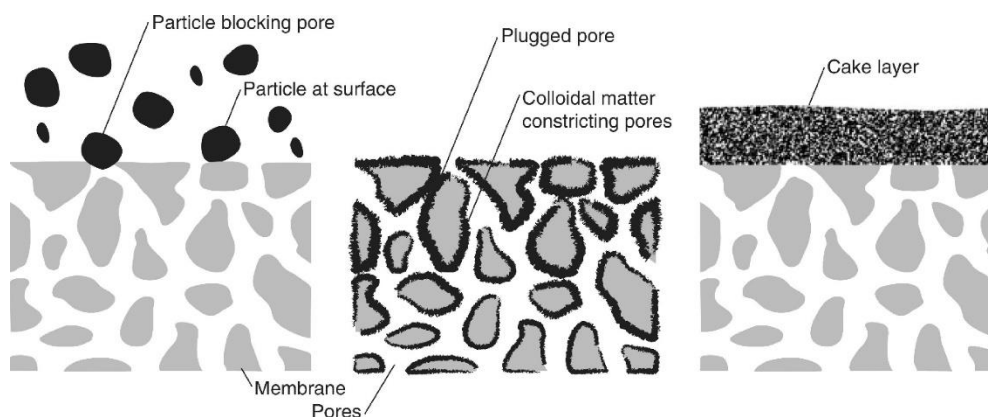


Figure 4: Membrane fouling mechanisms [24]

To address this issue, surface modifications and nanoparticle incorporation have been explored as effective strategies to mitigate fouling while enhancing water permeability. In this context, SA-COFs offer a promising solution due to their high surface area, tunable porosity, and strong hydrophilic functional groups, which can improve antifouling properties and water transport efficiency.

This research aims to fabricate SA-COF-based TFN membranes and evaluate their performance in water desalination, focusing on water flux, salt rejection, and fouling resistance. Additionally, the efficacy of SA-COFs for boron removal will be investigated, as boron contamination is a critical concern in desalination processes.

1.5 Thesis Objectives

The primary goal of this work is to fabricate a thin-film polyamide composite membrane for water desalination and boron removal. This advanced membrane is designed to:

1. Achieve high water flux for improved permeability
2. Enhance ion selectivity control for efficient salt rejection

3. Improve fouling resistance to ensure long-term performance
4. Evaluate the efficacy of using SA-COF for boron removal

To achieve these objectives, the following key steps are undertaken:

1. Synthesis of SA-COF nanoparticles with a high density of sulfonic acid functional groups
2. Integration of SA-COF into a polymeric membrane using interfacial polymerization
3. Performance evaluation of the membrane using a custom-made cross-flow filtration setup to assess water flux, salt rejection, fouling resistance and boron removal efficiency

CHAPTER 2 LITERATURE REVIEW

2.1 Background Osmosis/Reverse Osmosis

Osmosis, illustrated in (Figure 5A), was initially identified by Jean-Antoine Nollet in the 18th century. After him, Wilhelm Pfeffer developed a technique to perform the inaugural experiment quantifying osmotic pressure across a membrane. Van't Hoff utilized these initial osmosis measurements as the basis for formulating the theory of solutions in 1886. This hypothesis posits that solutes act similarly to gas particles, with osmotic pressure being directly proportional to the solution's molarity. Van't Hoff then proposed model that solute molecules unilaterally bombard the membrane, leading to osmotic pressure. He went on to say that the bombardment method was not important because osmotic pressure does not depend on the properties of the membrane. Ferry [25], in his extensive 1934 review of ultrafilter membranes and ultrafiltration, indicated that the initial hypothesized transport mechanisms primarily relied on mechanical sieving, allowing smaller solution components to permeate or flow through the membrane's pores. Nevertheless, regarding semi-permeable membranes solely as mechanical sieves constitutes a gross oversimplification, given the various interactions that occur between the solution and the membrane. A hydrostatic pressure is established at the point of osmotic equilibrium (Figure 5B) in order to prevent the passage of the solvent through the process of osmosis. The osmotic pressure is the name given to this particular pressure. In a process that is referred to as reverse osmosis, the solvent transport is reversed when a pressure that is higher than the osmotic pressure is applied to the side with the high concentration (Figure 5C). In 1953, C. E. Reid was the first person to suggest the utilization of reverse osmosis as a technique for the desalination of saltwater [26].

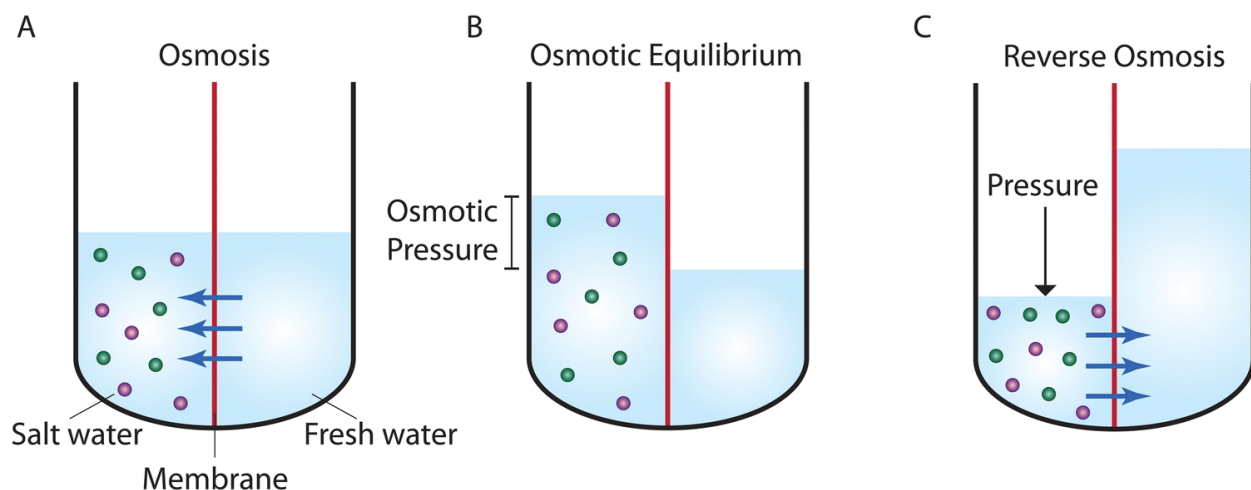


Figure 5: (A) osmosis, (B) osmotic equilibrium (C) RO[26]

Reverse osmosis is the movement of water across a semi-permeable membrane from a high salinity solution to a lower salt concentration solution, counteracting osmotic pressure by a driving force. Consequently, the membrane retains salt. This desalination approach is presently the most significant and is anticipated to maintain this status, owing to ongoing process enhancements that lower prices and foster heightened commercial interest in the technology. These advancements primarily hinge on the creation of novel membrane materials, with innovations in module design, process engineering, pretreatment methods, energy recovery, and the reduction of energy consumption. More so, nanotechnology has allowed for the incorporation of nanoparticles into reverse osmosis procedures, which is in line with ongoing research on conventional polymeric membrane materials [27].

2.2 Interfacial polymerization (IP)

The origin of IP trace back to Alfred Einhorn in the year 1898 when he conducted a reaction between pyrocatechol in water and phosgene in toluene [28]. In 1955, Magat and Strachan provided a detailed account of IP, introducing the term "interphase

polymerization" in a U.S. patent [29]. Later, in 1959, the term "interfacial polycondensation" was coined by Emerson L. Wittbecker and Paul W. Morgan, describing the reaction between acid chlorides and compounds containing active hydrogen (-OH, -NH, -SH) at the interface of two immiscible liquid phases. This development is often mistakenly regarded as the inception of IP. The evolution of IP is closely linked to the progression of polymer science (Figure 6). In 1920, Hermann Staudinger introduced the modern polymer concept, and in 1929, Carothers classified polymers into condensation and addition types [30]. This period marked the rapid advancement of polymer research, eventually leading to the commercial production of high-performance polymers such as nylon 66 in the 1930s. During this time, monolayer polymerization at the air-water interface was observed through the formation of Langmuir film [31]. Early polycondensation reactions, including polyamide (PA) synthesis, required high temperatures and reduced pressure to remove low molecular weight by-products such as water. Consequently, the need for a rapid yet controlled polycondensation process under ambient conditions became evident. This led to the formal establishment of interphase polymerization in 1955, enabling the synthesis of polymeric films and filaments by reacting a dicarboxylic acid halide in an organic phase with a diamine in an aqueous phase at the liquid-liquid interface [29]. By 1959, the introduction of the term "interfacial polycondensation" further accelerated advancements in interfacial polymerization.

Today, the direct fabrication of polymeric membranes via interfacial polymerization remains a subject of significant interest, particularly for membrane separation applications. The method and underlying mechanisms of interfacial polycondensation continue to be explored to optimize polymer membrane performance [32].

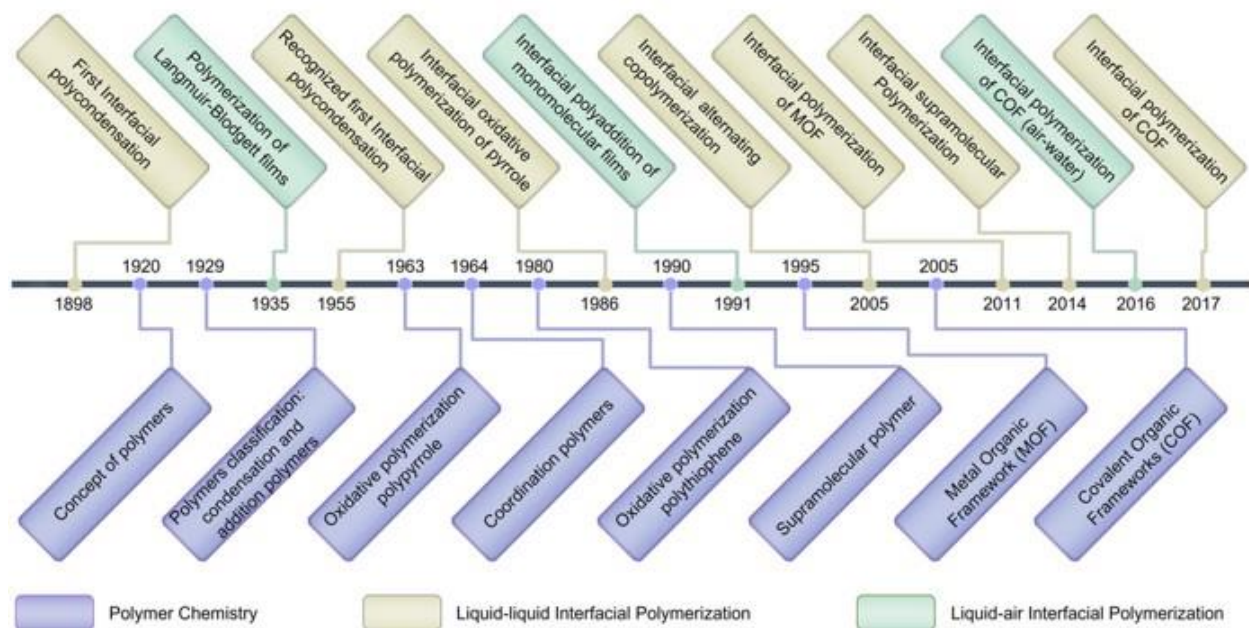


Figure 6: Chronology of major developments in interfacial polymerization.

Interfacial polymerization provides an alternate method for coating a porous substrate with a thin film. Here, at the interface of two insoluble liquids, two monomers that are extremely reactive come together, and a polymerization reaction takes place as shown in Figure 7.

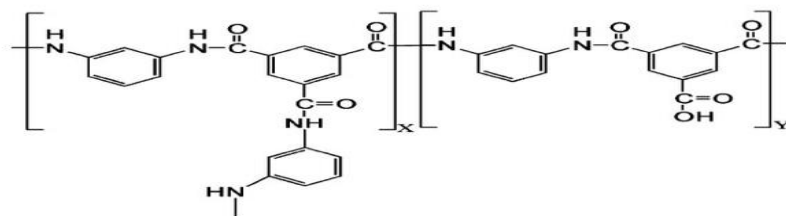


Figure 7: Crosslinked polyamide layer

This is illustrated graphically in Figure 8. The support layer, typically composed of an microfiltration or ultrafiltration membrane (Figure 8A), is submerged in an aqueous solution (Figure 8B) that contains a reactive monomer or a pre-polymer, often of the amine variety. The film or fiber is subsequently submerged in a second solution containing a

water-insoluble solvent (as shown in Figure 8C), in which another reactive monomer, often an acyl chloride, has been dissolved. The amine and acyl chloride monomers undergo a reaction to produce a compact polymeric top layer, as seen in Figure 6D. Heat treatment is frequently used to facilitate the interfacial reaction and promote the crosslinking of the water-soluble monomer or prepolymer. Interfacial polymerization offers the benefit of self-inhibition, where the reaction is hindered by the restricted amount of reactants passing through the existing layer. This leads to the formation of an exceptionally thin film with a thickness of around 50 nm[33].

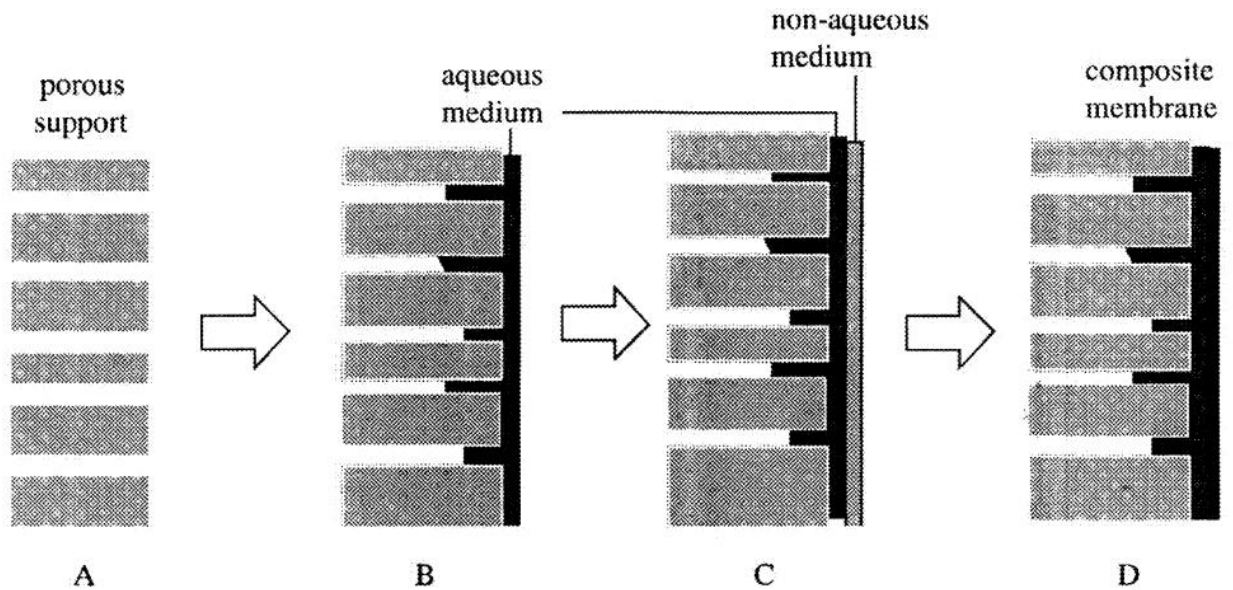


Figure 8: Illustration depicting the creation of a composite membrane using interfacial polymerization [33]

2.3 Reverse osmosis membranes

Polymeric membranes encompass reverse osmosis membranes as a subcategory. Integrally-skinned asymmetric membranes (ISA) and thin-film composite (TFC) membranes have both been utilized in RO applications. Figure 9 depicts a categorical chart of membranes [34].

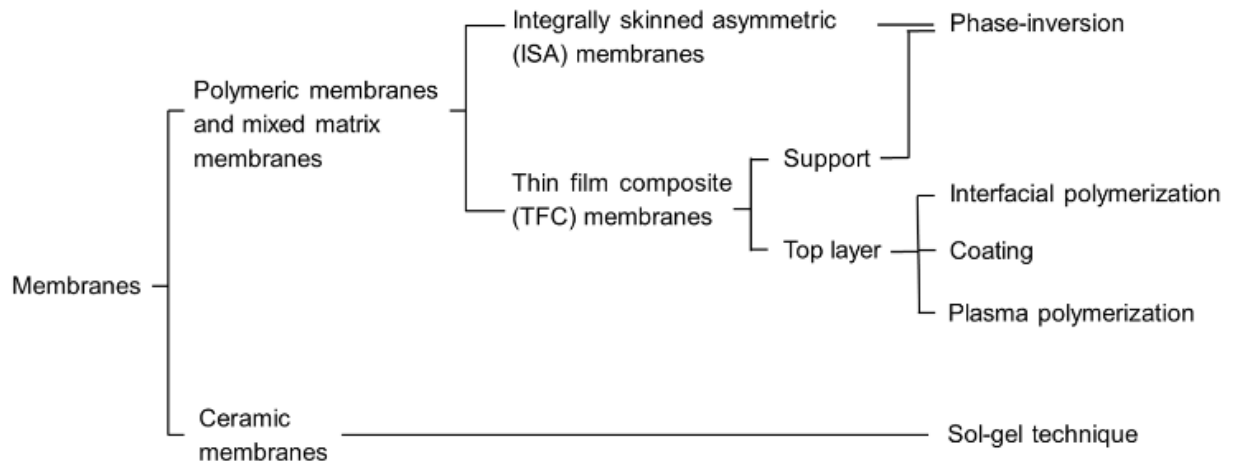


Figure 9: Classification of membranes [34]

2.3.1 ISA Membranes

ISA membranes consist of a skin layer and a sublayer which is highly porous, both made of the same material (Figure 10A). The outermost layer of skin is developed simultaneously with the underlying supportive layer. The thin layer of skin has an impact on how well the membrane performs, namely in terms of permeance and selectivity. They are created using the phase inversion approach, which was invented by Loeb and Sourirajan. This technique entails immersing a casting solution in a bath of a nonsolvent (such as water). The thermodynamic parameters of the system and the kinetics of the solvent and nonsolvent

exchange significantly change the membrane shape, since they determine its permeance and solute rejection.

2.3.2 TFC Membranes

TFC membranes are another significant category of membranes. They are composed of a very thin active layer that is applied on a chemically distinct porous support. Refer to Figure 10B for a visual representation. These membranes exhibit high flexibility and provide the ability to be tailored to suit a particular purpose. The layered structure of the membrane allows for independent optimization of the porous support and the active layer, resulting in maximum overall membrane performance. The selection of the support layer for TFC membranes is crucial, as it needs to offer both high stability and facilitate the creation of an active layer that is free from defects.

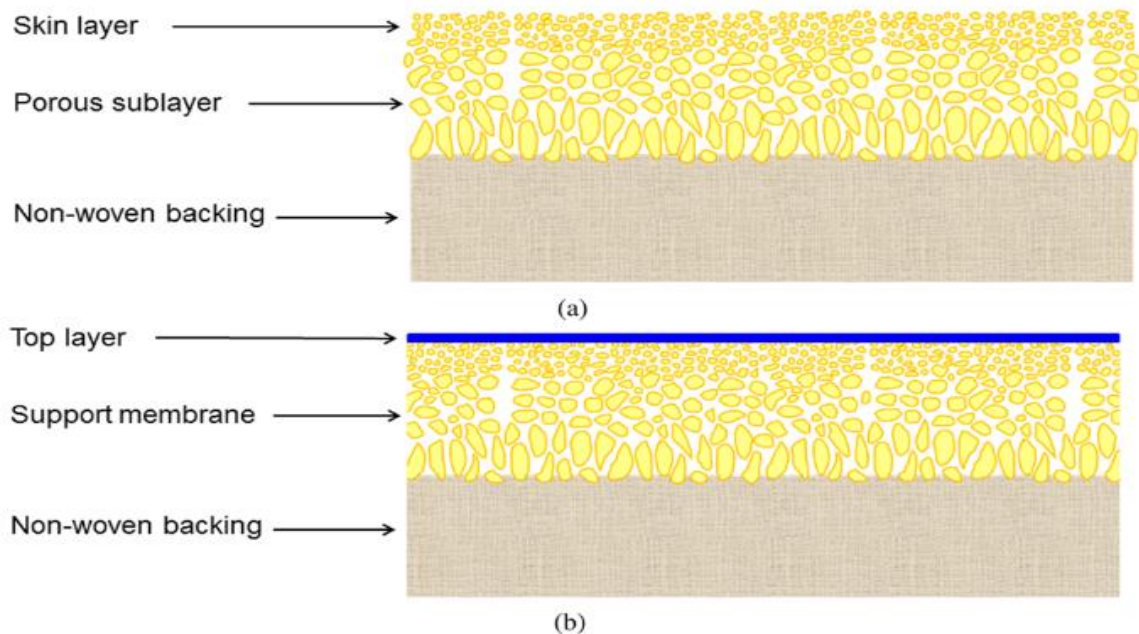


Figure 10: The diagram illustrates (a) ISA membrane and (b) TFC membrane [34]

A key challenge for RO membranes is the trade-off between permeability and salt rejection/selectivity. Achieving a balance between high water permeability and exceptional salt rejection is essential for developing efficient RO membranes. To integrate nanoparticles into the PA layer, nanoparticles can be coated on the support to start a transient layer before interfacial polymerization (IP), or physically blended with MPD or TMC solution before IP. In non-compatible solutions, nanoparticles tend to agglomerate during IP when they physically mix. This causes defects and decreases the membrane separation performance due to uneven nanoparticle dispersion in the polyamide layer. On the other hand, growing nanoparticles on the support with harsh solvents to form an intermediate layer before IP swells the substrate results in a structure change. In addition, membrane fouling remains a significant issue that reduces performance over time. Fouling occurs when organic matter, mineral scaling, colloids, and biofilms build up on the surface or within the pores of the membrane. This process is influenced by factors such as surface hydrophilicity, roughness, charge, feed water quality, and operational conditions. Membranes that are more hydrophilic and smoother are less prone to fouling, as they prevent foulants from adhering. To overcome the challenges faced by RO membranes, researchers have explored various materials and strategies to improve their performance. Among these approaches is the incorporation of nanomaterials such as carbon nanotubes[35] 2D nanosheets[36], zeolites[37], MOFs[38], COFs[39] etc., and non-porous nanofillers like silica[40], graphene oxide (GO)[41], polyvinyl alcohol[42] etc. into RO membranes has shown significant promise. Nanomaterials have demonstrated the ability to boost key membrane properties, including water permeability, chlorine resistance, antifouling capability, and antimicrobial activity. Additionally, they contribute to improved

mechanical strength and thermal stability. These enhancements are primarily attributed to properties like enhanced interfacial interactions and greater structural robustness provided by the embedded nanoparticles[43].

Liu et al.[44] investigated the use of MOF in the PA layer of TFN membranes for RO desalination (Figure 11). Their findings revealed a progressive decline in water contact angle as the loading of the MOF nanosheets in the aqueous phase increased, indicating enhanced surface hydrophilicity. Notably, the optimized TFN membrane, prepared with 0.015 wt% in the aqueous phase, demonstrated a substantial improvement in water permeance approximately 150% greater than the virgin TFC membrane while maintaining NaCl rejection above 99.0% with remarkable stability and anti-fouling properties.

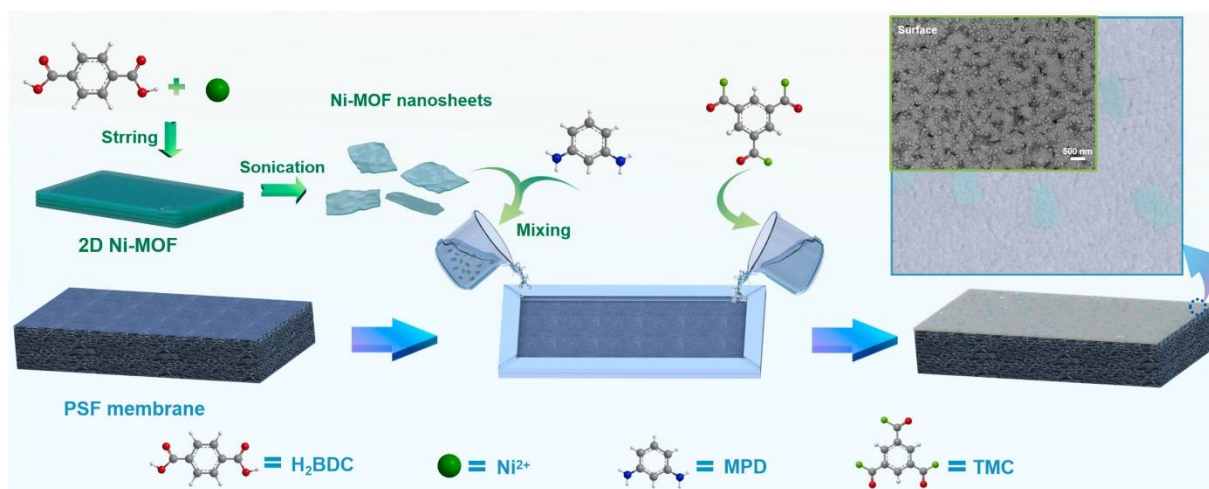


Figure 11: IP reaction schematic for 2D-MOF modified TFN membrane fabrication [44]

Fathizadeh et al.[45] investigated the development of a TFN membrane composed of nano-NaX zeolite in the PA layer via interfacial polymerization as illustrated in Figure 12. Their findings indicate that adding nano-NaX zeolite boosts both the physical and chemical stability of the membrane. As the concentration of MPD and TMC increased, the resulting

TFN membranes exhibited enhanced water permeability but reduced solute rejection. Among the fabricated membranes, the TFN membrane formulated with 0.15% (w/v) TMC, 3% (w/v) MPD, and 0.2% (w/v) nano-NaX zeolite demonstrated the highest water flux but the lowest salt rejection. Conversely, the TFN membrane with 0.10% (w/v) TMC, 2% (w/v) MPD, and 0.2% (w/v) nano-NaX zeolite exhibited a balanced performance, offering efficient separation, high water productivity, and superior thermal stability compared to the conventional TFC membrane.

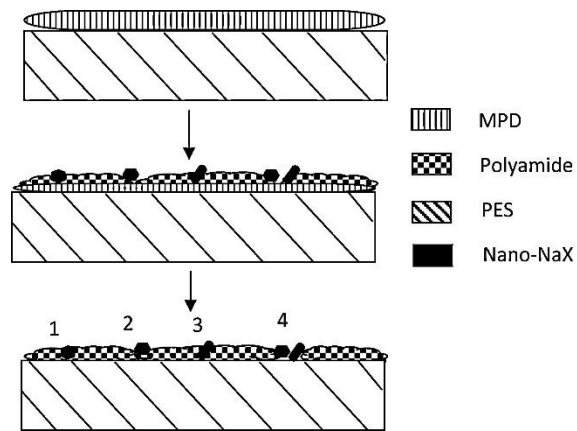


Figure 12: Fabrication of the TFN membrane [45]

Despite the significant advancements in TFN membranes compared to asymmetric membranes for water desalination, the pursuit of novel materials with superior properties for enhancing the PA layer remains a critical area of research. Throughout the years..., this challenge has continued to attract considerable scientific interest. Table 5 provides an overview of various membrane supports integrated with different types of nanoparticles, along with their operating conditions and corresponding performance outcomes.

Table 5: Different nanofillers used for RO membranes

Nanoparticle used	Operating conditions	Flux (LMH)	Salt rejection (%)	Antifouling performance	References
GO (38ppm)	At 25 °C, the cross-flow module flowed 2000-ppm NaCl aqueous solution.	Increased from 9.2 (± 0.1) to 16.6 (± 0.2) which is approximately 80% higher than that of the pristine membrane	99.4	98% anti-biofouling improvement	[46]
N-GOQD (0.02 wt/v%)	A 15 bar, 2000 ppm NaCl solution, stainless-steel dead-end module with 5.1 cm ² effective	Water flux increased linearly from 9.3 to 24.9 which is an increase of almost 3 times	93	-	[47]

	permeation area was employed at ambient temperature.				
SWCNT (20 wt%)		Water flux increased by over 4 times	98.6	-	[48]
r-GO/TiO ₂ (0.02 wt%)	Cross-flow filtration with three parallel filtration cells, 36 cm ² effective membrane area, 15 bar operating pressure, and 2000 mg/L NaCl solution.	Water flux increases with rGO/TiO ₂ nanocomposite concentration, peaking at 51.3(±2.9) at 0.02 wt% rGO/TiO ₂ RO membrane, 21% greater than bare RO membrane 34.3(±2.2)	99.45	Improved fouling resistance	[49]

ZIF-8 (0.4 wt%)	Custom made cross-flow filtration setup with three testing modules, 42 cm ² effective membrane area, 15 bar operating pressure, and 2000 mg/L NaCl solution.	Flux rose from 16.64 to 34.5	99.4	BSA fouling caused the control PA membrane to lose over 50% of its original flow, but PZ4 only lost 13% after 4 hours of continuous operation.	[37]
MWCNTs (0.1 wt%)	Cross-flow arrangement and constant pressure filtration mode were used to assess	Enhanced water flux to 28.05 from 14.86	>90	Better antifouling against BSA and Ca(HCO ₃) ₂	[50]

	membrane permeation at room temperature with an effective membrane area of 18.1 cm ² , NaCl (2000 ppm, pH 7, 25 °C)				
MWCNT (15.5 wt%)	Crossflow filtration system coupled to a fluorescence microscope, NaCl feed concentration of 10 mmol/L at 0.7 MPa,	0.16 m ³ m ⁻² day ⁻¹	99.7	Better antifouling for BSA organic-foulant	[51]

	room temperature				
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Based on what we are aware, an optimized approach combining heat and PTSA has not been employed to significantly expedite the synthesis of SA-COF nanosheets for fabricating TFN membranes for RO. Under conventional conditions, the formation of SA-COF nanosheets typically required 14 days. However, our modified method successfully reduced the synthesis time to just 2 days while maintaining the production of high-quality nanosheets.

COFs are a category of porous crystalline materials characterized by distinct two-dimensional (2D) and three-dimensional (3D) architectures, synthesized via the covalent bonding of multifunctional monomers. COFs are emerging as interesting candidates for membrane fabrication and as effective modifiers for the polyamide layer of TFC membranes. Since Yaghi's initial publication in 2005, its highly ordered and customizable structure, extensive specific surface area, and adjustable photoelectronic characteristics have facilitated their extensive applications in catalysis, photoelectric devices, sensing, energy conversion, and energy storage. Various kinds of COFs, including imine-linked, keto-enol-linked, and hydrazone-linked COFs, have been created, as illustrated in Figure 13.

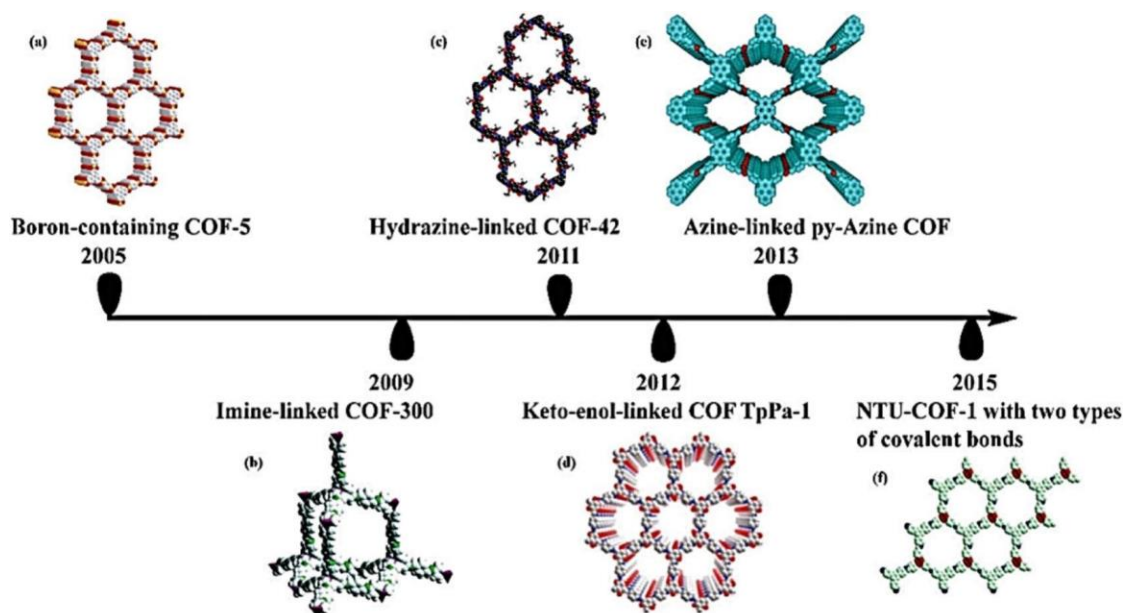


Figure 13: COFs exhibiting different types of covalent linkages[52]

Because of the superior physicochemical qualities that are inherent in COF materials, which precisely fit the requirements of fabricating high-performance separation membranes, a great number of methods have been utilized over the years for the construction of COF-based membranes. This is due to the fact that COF materials have been used for the past few years. In the beginning, because of the restricted technology that was available for creating membranes and due to the poor processing qualities of COF, they were included into polymer matrices in order to make mixed matrix membranes. The objective of this was to provide extra channels that smaller molecules could travel through. In the subsequent steps, in order to make the most of the inherent channels, techniques that were centered on the fabrication of pure COF membranes were also developed. Both the bottom-up strategy (as shown in Figure 14) and the top-down strategy (as shown in Figure 15) are the two most common approaches used to make these membranes.

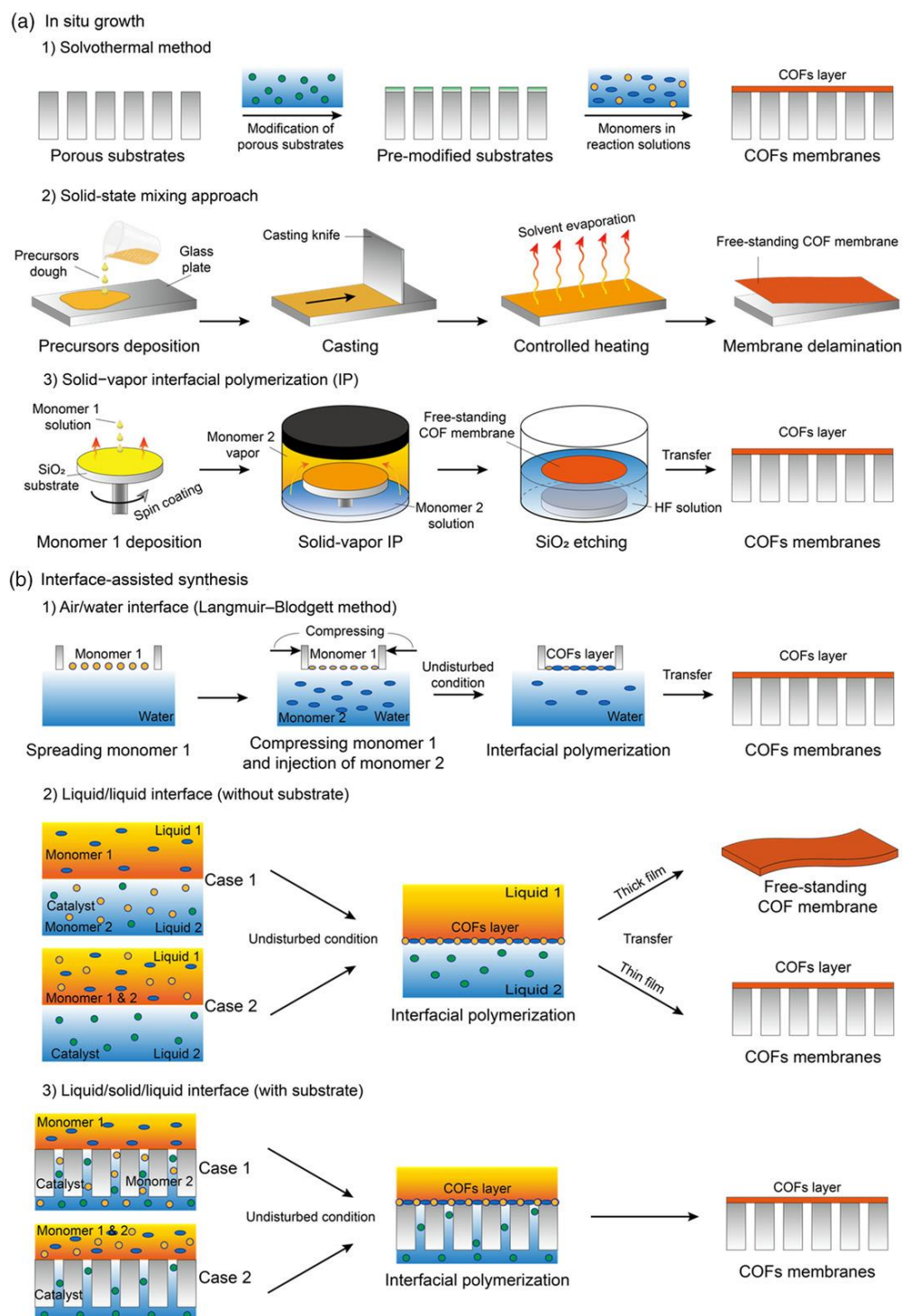


Figure 14: Diagrammatic representations of the bottom-up strategy for the production of COF membranes, which includes a) in situ growth and b) interface-assisted synthesis both of which are shown here

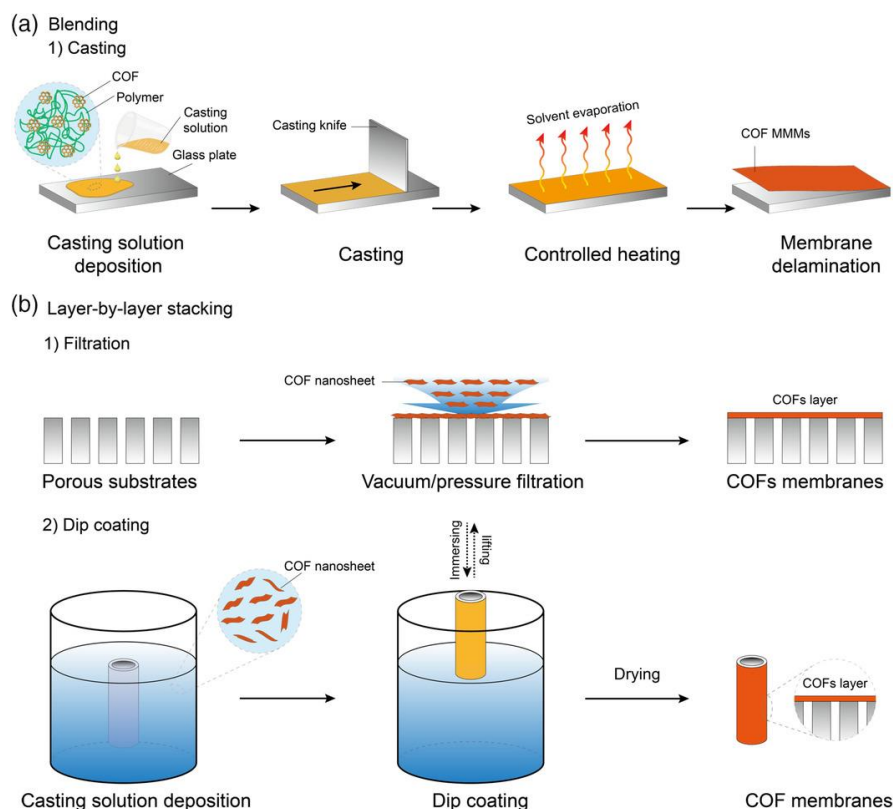


Figure 15: Diagrammatic representations of the top-down technique for the manufacture of COF membranes, which includes a) blending and b) LBL stacking among other components

2.4 Membrane separation mechanism

Porosity, chemical potential, electric potential gradient, and pore size are some of the variables that affect reverse osmosis (RO) membrane separation. Many model theories have been developed to explain the reverse osmosis membrane's separation mechanism, the most popular of which being the solution-diffusion model.

2.4.1 Dissolution-diffusion model

The dissolution-diffusion model, presented by Lonsdale and Podall et al., aims to provide an explanation for reverse osmosis (RO) (Lonsdale H 1972). Assuming a compact and impermeable surface separation layer, the dissolution-diffusion model describes reverse osmosis (RO) membranes. It is predicted that the solvent and the solute can be dissolved in the membrane's separating layer. Subsequently, driven by the disparity in chemical potential resulting from concentration or pressure differences, the solvent primarily permeates through the membrane via molecular diffusion. Both the solubility of the solvent and the solute in the surface separation layer have a direct impact on the permeability rate of reverse osmosis (RO) membranes. Fig. 16 shows the three stages of the solution-diffusion model that explain the movement of water and solute.

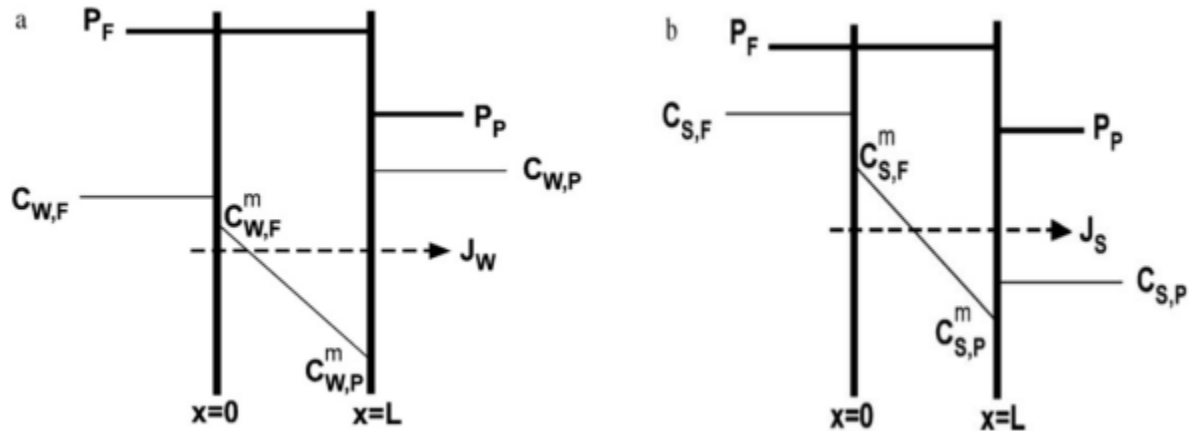


Figure 16: Depicts the concentration profiles of water and salt in a polymeric membrane.

Panel (a) shows the water concentration profile, while panel (b) shows the salt concentration profile.

The fundamental equations governing the movement can be mathematically represented as:

$$J_w = A_w (\Delta P - \Delta \pi) \quad (1)$$

$$J_s = B_s (C_M - C_P) \quad (2)$$

The volumetric water flux, denoted as J_w , is measured in cubic meters per square meter per second ($\text{m}^3\text{m}^{-2}\text{s}^{-1}$). On the other hand, the solute mass flux, represented by J_s , is measured in kilograms per square meter per second ($\text{kgm}^{-2}\text{s}^{-1}$). A_w represents the rate at which pure water passes through a material per unit area under a pressure differential, measured in cubic meters per square meter per second per bar. B_s represents the rate at which solute passes through the material, measured in meters per second. ΔP represents the difference in applied pressure, measured in bars. The symbol $\Delta \pi$ represents the difference in osmotic pressure between the sides of the membrane, measured in bars. C_M and C_P refer to the surface concentration of the solute in the feed and the concentration at the permeate side of the membrane, respectively, measured in kg.m^{-3} . The solute permeance, B_s , is determined by dividing the solute mass flux by the difference in solute concentration (C), which serves as the driving force. Therefore, it results in the subsequent unit: ($\text{kg m}^{-2}\text{s}^{-1} \text{m}^3 \text{kg}^{-1}$), and by simplifying this unit, we obtain (m s^{-1}) [53]

2.5 An overview of the element boron

Boron, a trace element, which predominantly engages in a covalent bonding to form compounds in the natural environment. This tendency is strongly attributed to its small atomic radius and elevated ionization energy. Within aqueous environments, boron is commonly found in various forms, including polyborate anions, neutral boronic acid

molecules, and mono-negative borate ions [54]. In aqueous solutions, particularly within a pH spectrum of 6 to 9, boron predominantly exists as a neutral boric acid molecule alongside minor quantities of singly charged borate anions. The levels of boron found in seawater generally fluctuate from 0.5 to 6.0 ppm, with the typical concentration hovering around 4.6 ppm.[55, 56]. Boric acid exhibits high solubility in water and demonstrates resistance to oxidation and decomposition. Because both boric acid and borate are Lewis acids they can easily form complexes with polyhydroxy compounds in aqueous conditions [57].

2.5.1 Existence of Boron in the Environment

Boron is extensively found in both the water and solid rock layers of the Earth [58]. Boron is never found in its elemental form in nature, but rather exists in numerous complex compounds that combine with oxygen and other elements. It is present in rocks and soils within the lithosphere. The boron content in the earth's crust ranges from 1-500 mg/kg, contingent upon the composition of the rock [59]. According to [60], typical occurs in the earth's crust at approximately 10 milligrams per kilogram, which accounts for a mere 0.001% of the earth's elemental composition. The soil's boron content varies from 2 to 100 milligrams per kilogram, with an average of 30 milligrams per kilogram [61]. The lithosphere has a total of around 1018 kg of boron, which is distributed among continental resources contributing around 1010 kg of boron [62]. Boron is present in saltwater in the hydrosphere at a concentration of around 4.5 mg/L, whereas in ground water its quantities vary between 0.3 and 100 mg/L. The boron contents in the hydrosphere were determined to be distributed across the oceans , groundwater , ice , and surface waters by [63].

2.5.2 Toxicity of Boron

Despite being an essential element, boron can have harmful effects on living organisms. Plants, in particular, exhibit a high level of sensitivity to the concentration of boron. For optimal growth of wheat, it is recommended to maintain the concentration of 0.75 to 1.0 parts per million (ppm) in soil water [64]. Increased levels of boron may gradually lead to the manifestation of poisoning symptoms. Boron toxicity leads to several physiological effects, such as reduced root cell division and leaf chlorophyll levels [65]. Boron toxicity is influenced by both the content of boron in soil water and the length of time of exposure. Conversely, the detrimental impacts of boron have extensively been proven in different experimental works carried out on animals. Prolonged ingestion of food and water polluted with boron is likely to result in the development of syndromes and diseases affecting the cardiovascular, neurological, and digestive systems [66]. Ku et al. [67] discovered that exposure to both borax and boric acid adverse effects on the male reproductive system of rats whether short term or in the long run. Hence, it is crucial to regulate the concentration of boron in water sources and generate water with minimal boron content for diverse applications, such as drinking and irrigation[68].

2.5.3 Chemistry of Boron

Developing deboronation procedures requires a fundamental comprehension of how the chemistry of boron happens. Boron, being the sole metalloid in group 13 of the periodic table, is represented quantum mechanically as $1s^2 2s^2 2p^1$. Three single bonds cannot complete a full valence shell with eight electrons, making it electron scarce. Therefore, all boron exists mostly in the trivalent oxidation state. Boric acid exhibits a high degree of solubility in water, namely 5.5 grams per 100 grams of solution at a temperature of 25 °C.

When dissolved in water, it acts as a Lewis acid. The dissociation occurs by the acceptance of a hydroxyl ion, resulting in the formation of the tetrahydroxyborate ion.



The intrinsic pKa of boric acid is 9.24 at 25 °C in dilute aqueous solutions under typical conditions. The observed pKa value is influenced by extrinsic factors like ionic strength and temperature. Dickson established an empirical equation to establish a relationship between the dissociation of boric acid and the variables of salinity and temperature [69]. Figures 17 (a) and (b) depict the relationship between the apparent pKa and temperature and salinity, respectively, as determined from the given equation. Other publications have demonstrated the presence of negative relationships between temperature and salinity. The formation of different species of boric acid is also influenced by its concentration, as illustrated in Figures 17(c) and (d) [70].

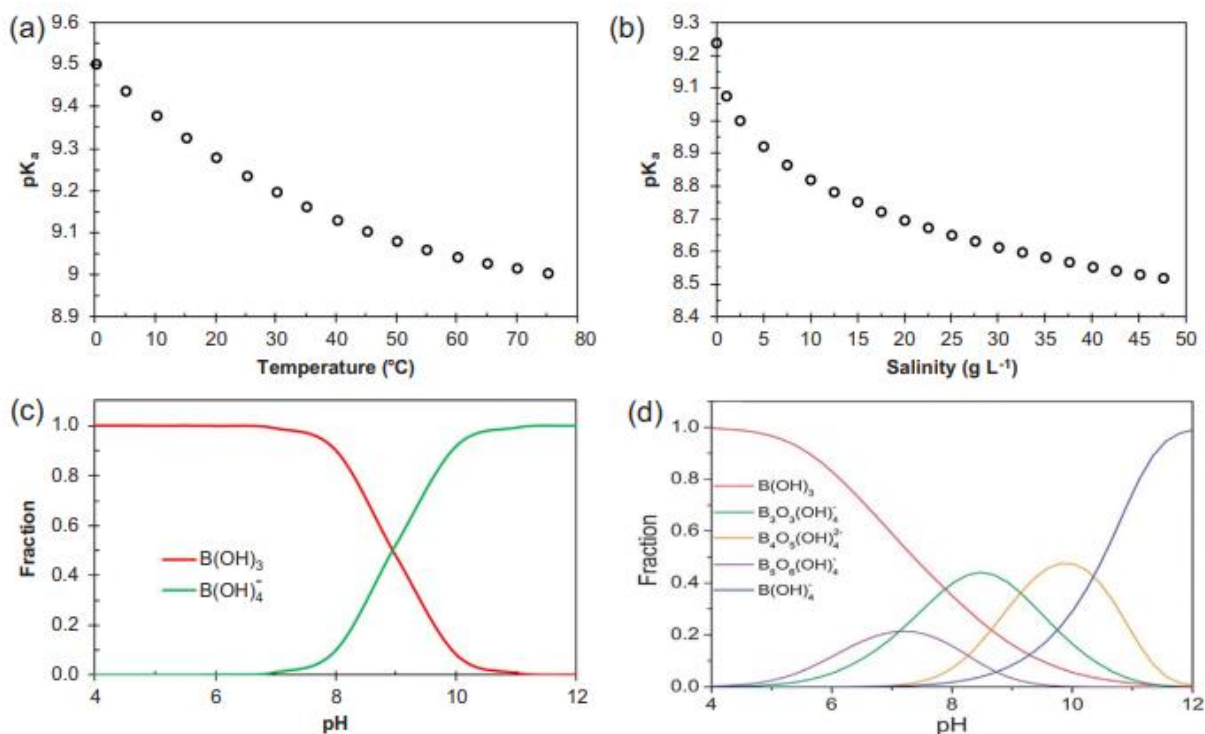


Figure 17: Boric acid dissociation with respect to (a) temperature and (b) salinity; (c) pH at Boron concentration of 0.01 M and (d) pH at Boron concentration of 0.4M [70]

2.6 Design of Boron Removal System

Due to the challenges of complying with boron content regulations in different water sources using a single stage reverse osmosis (RO) process, a lot of multi-stage systems have been developed. These include two-stage Reverse osmosis systems [71, 72], integrated Nanofiltration-Reverse Osmosis systems [73], Reverse Osmosis-Adsorption systems [74, 75], and polyol-assisted RO systems, among others . Figure 18 [63, 76] illustrates the development of two-stage Reverse Osmosis systems by merging the SWRO and BWRO phases. In order to inhibit the production of scale, a higher pH was typically utilized in the second stage of brackish water reverse osmosis (BWRO). [77] employed model called analytical hierarchy process (AHP) to assess the most effective techniques for removing boron. Based on the analysis it was shown that two-stage reverse osmosis (RO) is the optimum method. This method can generate four different permeate streams with varying boron contents by employing permeate split. Additionally, treating low quality permeates in series with ion-exchange can enhance the overall performance of a single stage RO.

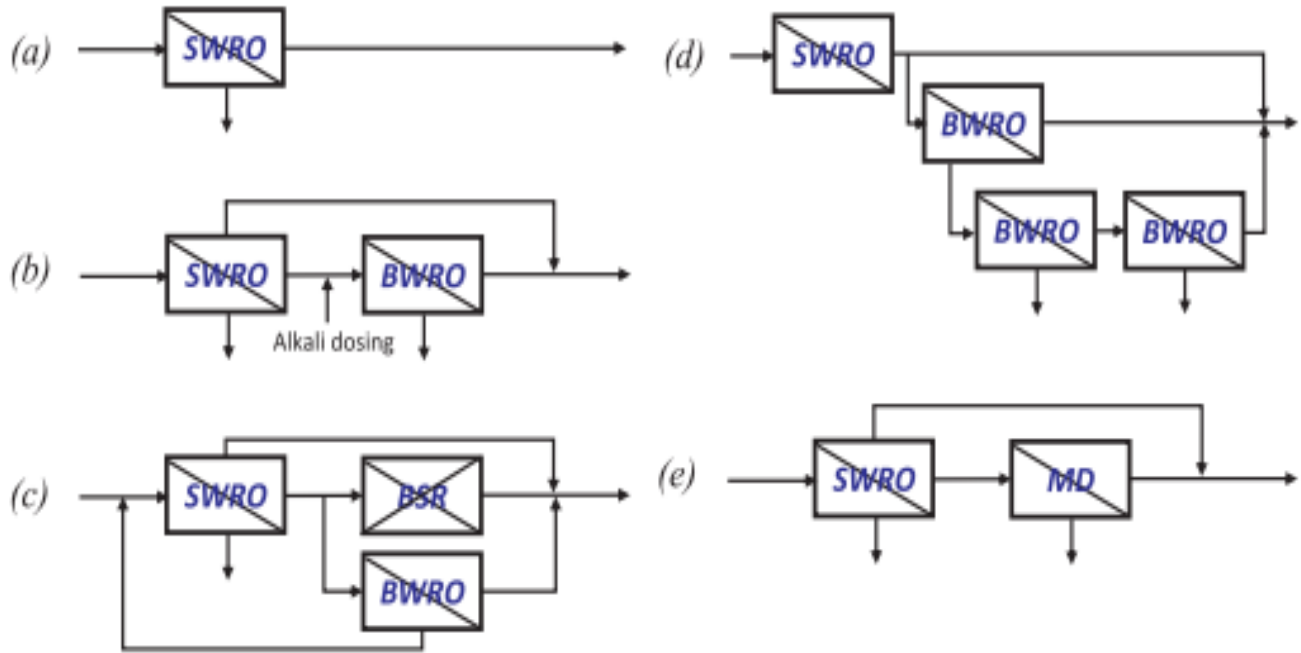


Figure 18: (a) Single-stage RO system for boron removal (b) 2-stage RO system with alkali dosing (c) 2-stage RO system with boron selective resins (BSR). (d) Cascade design (e) 2-stage RO system with membrane distillation [78]

CHAPTER 3 MATERIALS AND METHOD

3.1 Materials

Commercial Polysulfone pellets (PSF) (Mw~35,000), Polyvinylpyrrolidone (PVP), m-Phenylenediamine (MPD), Trimesoyl chloride (TMC), 1,3,5-Triformylphloroglucinol (TFP), 2,5-Diaminobenzenesulfonic acid (DABA), p-toluenesulfonic acid (PTSA) were all purchased from Sigma Aldrich. Dimethylacetamide (DMAC), n-Hexane, and octanoic acid were all purchased from Fisher scientific.

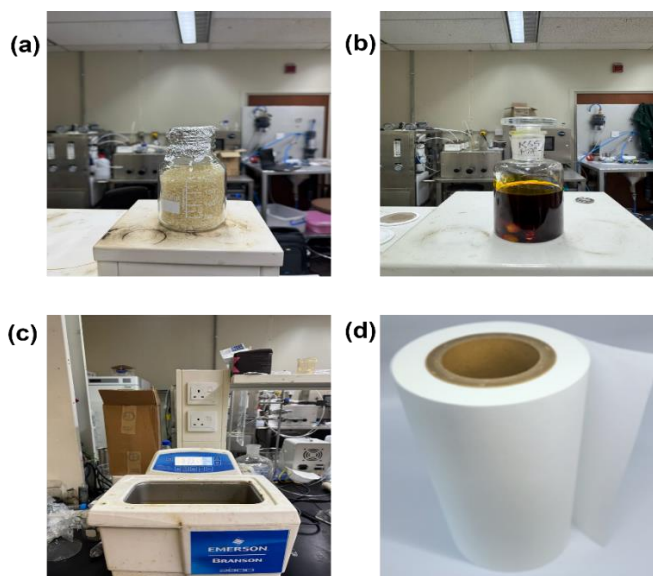


Figure 19: Some materials used for the study (a) PSf pellets (b) Dope solution (c) Sonicator (d) PET non-woven fabric

3.2 Methodology

3.2.1 COF synthesis

Sulphonic acid COF nanosheets were synthesized at the oil-water interface using heat (60 °C) by reacting TFP and DABA in the presence of PTSA. [79] *et al.*, initially introduced a

method akin to ours for the fabrication of COF nanosheets at ambient temperature within approximately 14 days where TFP was dissolved in octanoic acid and DABA was dissolved in water. Very slowly, Tp solution was poured on top of DABA solution and the whole assembly was statically rested. The organic top part was removed through a syringe whereas the aqueous phase was recovered and treated in a dialysis bag. In our investigation, we initially endeavored to expedite nanosheet formation by subjecting the system to elevated temperatures. However, after a two-day heating period, we observed a product comprising a heterogeneous mixture of nanosheets and particles of several hundred nanometers in size. Subsequently, we introduced PTSA into the aqueous phase and subjected the system to a temperature of 60 °C. This modification yielded a product predominantly composed of nanosheets accompanied by smaller particles, which were subsequently separated via dialysis treatment.

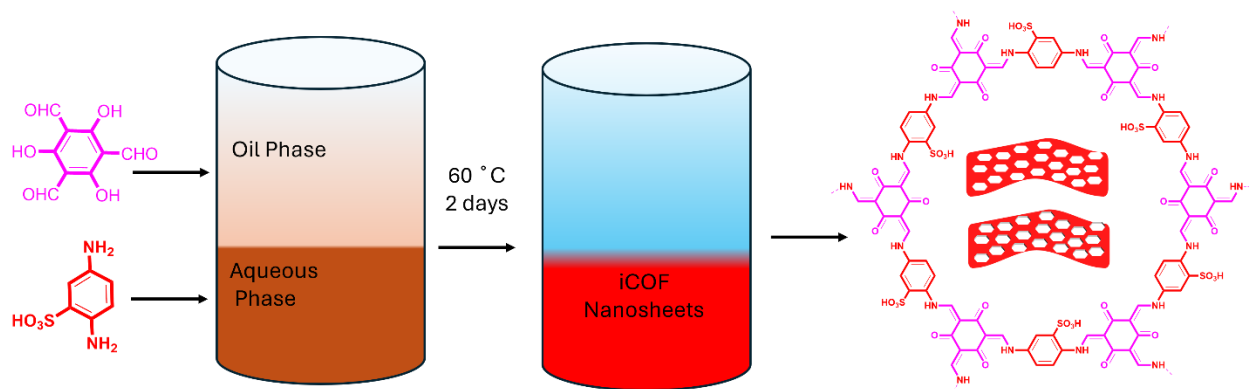


Figure 20: Schematic of the synthesis process

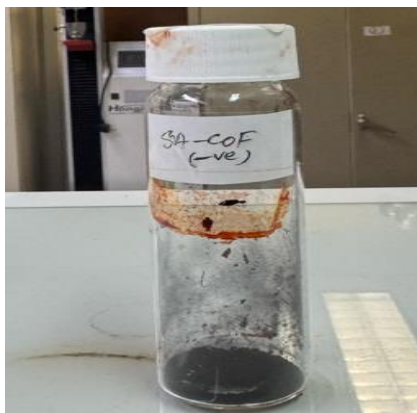


Figure 21: Synthesized COF powder prepared in 2 days

3.3 Membrane preparation

The membrane fabrication was conducted in two phases: 1) Modifying the polyamide layer: We began by using a commercial membrane support and focused on modifying the selective PA layer through interfacial polymerization. By incorporating COF nanosheets, we aimed to enhance the permeability without compromising salt rejection. We prepared two different categories of RO membranes; the first one is the control which is referred to as the pristine membrane in this work and the COF modified RO membranes with different loadings. For the pristine membrane the support was first contained within a Teflon ring that was manufactured in the laboratory. In the following step, 5 mL of the aqueous solution containing 2 wt. % MPD was applied to the support, and it was allowed to stand for ten minutes. Following that, the MPD was removed from the support, and a rubber roller was used to apply the drying process. After exposing the MPD-impregnated support to air for three minutes, 5 mL of TMC solution containing 0.15 wt. % in n-hexane was applied to the surface of the support for one minute. After that, the support was rinsed with n-hexane to remove any remaining TMC as shown in (Figure 22a) . For fabricating the COF modified

RO membranes, the COF was dissolved in water to produce a stock solution that had a concentration of 2 wt. %. After that, a number of different mixed solutions were produced by combining COF and MPD in proportions ranging from 1% to 15%. For reference, a 2 % COF-MPD solution corresponds to 2 wt. % COF relative to MPD. The procedure for the synthesis of membranes followed the same course of action as the procedure for the production of pristine membranes, with the exception that a COF-MPD solution was used instead of an MPD solution. After the membranes were created, they were given labels such as PA-COF₂, PA-COF₄, PA-COF₆, and so on as shown in (Figure 22b).

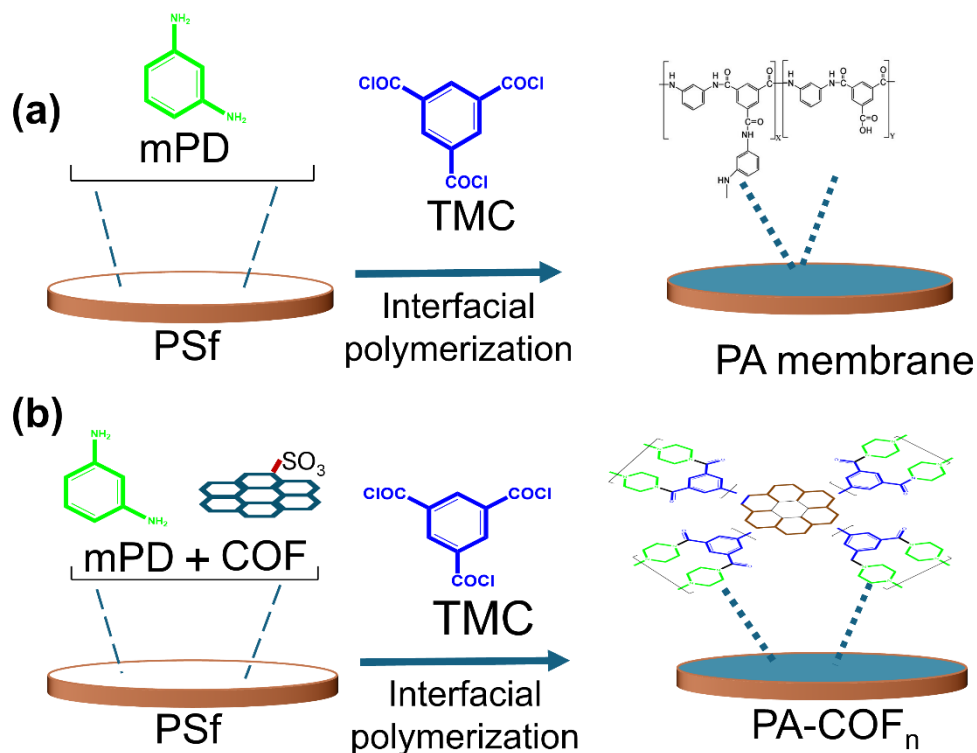


Figure 22: Schematic of the nanomaterial incorporation process

2) Fabricating the membranes from scratch: To gain greater control over membrane structure and properties, we fabricated the membranes entirely from the beginning. This involved preparing the polymer dope solution, casting it onto a non-woven fabric support,

and employing phase inversion to create the porous substrate. The selective polyamide layer was then formed on this substrate using interfacial polymerization, incorporating COFs for improved separation performance. The membrane support was fabricated through solution casting, followed by wet phase inversion to facilitate solvent exchange. The procedure used was described by [37] with little modifications. The PSF pellets were firstly dried in an oven at 80 °C overnight to remove any absorbed moisture. The polymer casting solution for the pristine membrane was prepared by dissolving 18 wt% PSF and 2 wt% PVP in 80 wt% DMAC. The mixture was stirred at 450 rpm for 6 hours to ensure complete dissolution and homogeneity. Subsequently, the solution was left to degas for 24 hours to eliminate entrapped air bubbles, which were relatively abundant due to the high stirring speed. The degassed solution was then cast onto a clean glass plate using a casting knife. The film was quickly bonded onto PET nonwoven fabric after its formation and then submerged in a water bath for 24 hours to allow solvent exchange and phase inversion. On the surface of the prepared membrane samples interfacial polymerization was performed using MPD and TMC followed by crosslinking at 80 °C for 10 minutes.

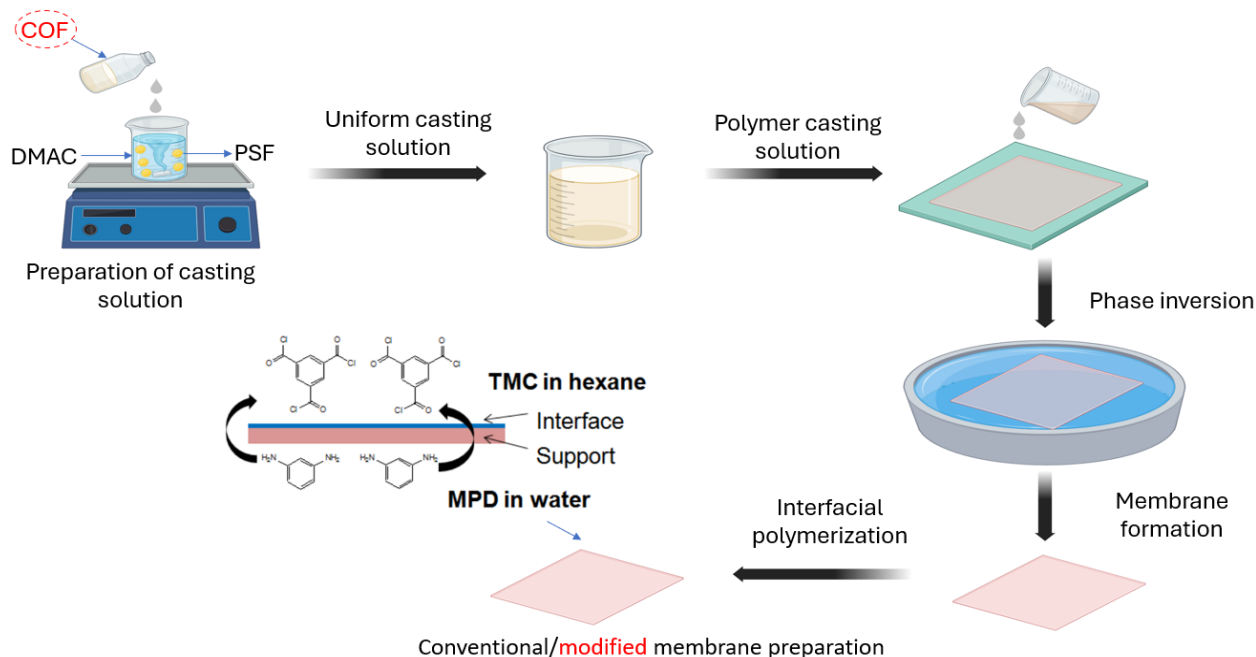


Figure 23: Schematic of the nanomaterial incorporation process in the support

3.4 Membrane separation performance

The membranes' performance was assessed utilizing a custom-made crossflow filtration setup (Shandong Bona Biological Technological Group Co. Ltd) as shown in the schematic and actual system setup as depicted in Figures 19 and 20, respectively under brackish water conditions (Pressure = 20 bar, NaCl (2000 ppm) and Boron (5 ppm) feed solution). The NaCl conductivity was measured using a (LAQUAtwin-EC-33, Japan) conductivity meter and the boron concentration was analyzed by an Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) (Thermo Scientific, Cambridge, UK). The Flux (LMH) was calculated by Eq. (1):

$$F = \left(\frac{V}{A \times \Delta t} \right) \quad (4)$$

where V, A, Δt are the Volume in litres, Area in square metres and Time in hours.

The NaCl rejection was calculated by Eq. (5):

$$R = \left(1 - \frac{C_p}{C_f}\right) * 100 \quad (5)$$

where the permeate solution and feed solution conductivities are C_p and C_f , respectively.

And the boron rejection was calculated in a similar manner as that of NaCl.

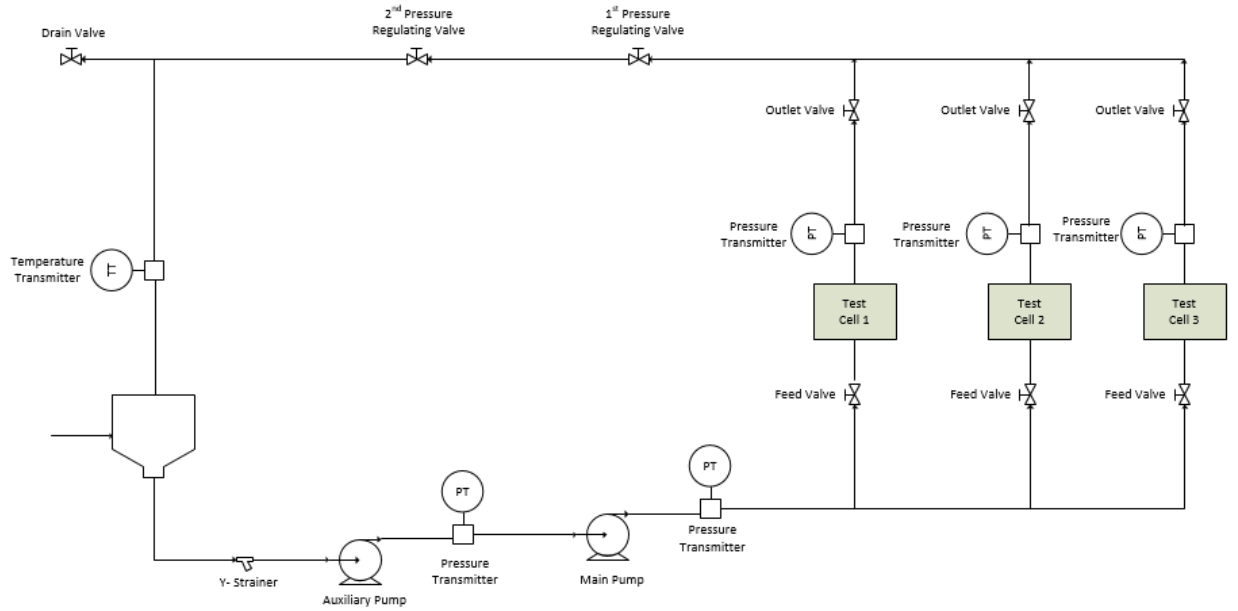


Figure 24: Process flow of the custom-made cross-flow setup



Figure 25: Image of the cross-flow filtration setup

3.5 Characterizations

3.5.1 SEM

SEM is a powerful characterization tool widely used in membrane science to analyze surface and cross-sectional morphology at the micro and nanoscale. SEM operates by focusing a focused beam of high-energy electrons onto the surface of a sample. These signals are detected and translated into high-resolution images that reveal topographical and compositional details of the surface.

In membrane characterization, SEM is essential for assessing the quality and structure of composite membranes. For instance, SEM can clearly show the thickness of the selective polyamide layer in TFC membranes, the porosity of the support layer, or the interfacial adhesion between layers. SEM can also be used to detect defects such as cracks, voids, or uneven coatings, which may compromise membrane performance. Another key advantage of SEM is its ability to perform cross-sectional imaging. By preparing a clean cross section

usually by cryo-fracturing or cutting a clear profile of layered membranes can be observed, allowing for accurate measurement of each layer's thickness and uniformity. This information is vital for correlating membrane structure with its functional performance in separation processes.



Figure 26: Image of SEM machine

3.5.2 AFM

AFM is a nanoscale surface characterization technique that plays a critical role in understanding the surface properties of membranes. Unlike electron-based techniques, AFM uses a probe attached to a cantilever to physically "feel" the surface of a sample. As the probe scans the membrane surface, it interacts with local atomic forces such as van der Waals forces, electrostatic forces, or mechanical contact. The cantilever deflection is monitored using a laser and photodetector system, and the collected data is translated into topographical images with nanometer resolution.

In membrane research, AFM is particularly valuable for evaluating surface roughness and nanostructure. The surface topography of a membrane can significantly influence its

wettability, permeability, and fouling behavior. For instance, rougher surfaces may increase the surface area, which can improve flux but may also promote foulant adhesion. AFM can provide quantitative roughness parameters such as average roughness (R_a), root mean square roughness (R_q), and peak-to-valley height, which are critical for correlating surface features with membrane performance. AFM can also be operated in different modes (contact, tapping, and non-contact), making it suitable for both hard and soft membrane surfaces. Additionally, advanced AFM techniques allow for phase imaging, adhesion mapping, and even mechanical property measurements such as stiffness and elasticity, giving a deeper understanding of the membrane's surface behavior under operational conditions.



Figure 27: Image of AFM machine

3.5.3 CONTACT ANGLE

A contact angle (CA) goniometer is an analytical instrument used to measure the wettability of solid surfaces by determining the contact angle formed between a liquid droplet and the

sample surface. In membrane science, this technique is primarily used to assess the hydrophilicity or hydrophobicity of membrane surfaces, which directly impacts water permeability, fouling behavior, and overall performance.

The CA is defined as the angle between the tangent of the liquid droplet and the solid surface at the point of contact. A lower contact angle (usually $<90^\circ$) indicates a hydrophilic surface where water distributes easily, whereas a larger contact angle ($>90^\circ$) denotes a hydrophobic surface that resists wetting. The measurement is performed by placing a small droplet of deionized water (or another probe liquid) on the membrane surface and capturing the droplet profile using a camera system. Image analysis software then calculates the contact angle with high precision.

In membrane characterization, CA measurements are used to understand the surface chemistry and modifications of the membrane. For example, if a membrane has been functionalized with hydrophilic groups (such as $-\text{OH}$ or $-\text{COOH}$), a noticeable decrease in contact angle is expected. Conversely, hydrophobic modifications (e.g., fluorination or alkylation) would increase the contact angle. This information is crucial in applications such as desalination, wastewater treatment, or gas separation, where surface wettability plays a key role in selectivity and resistance to fouling. Additionally, the contact angle goniometer can be used to monitor changes in surface properties after long-term use, exposure to harsh conditions, or cleaning processes. Repeated measurements allow researchers to track the aging or degradation of membrane surfaces.



Figure 28: Image of contact angle machine

3.5.4 XPS

XPS is a powerful surface-sensitive technique used to study the elemental composition of surfaces approximately within 5–10 nm of the top surface. For membrane characterization, XPS is indispensable in confirming the presence of functional groups, tracking elemental incorporation, and evaluating the success of surface modifications such as the integration of nanomaterials or functional coatings. The principle of XPS is based on the photoelectric effect, where incident X-rays cause the emission of core electrons from the atoms present in a material. This enables not only qualitative but also semi-quantitative analysis of the surface.



Figure 29: Image of XPS machine

3.5.5 Zeta potential

Zeta potential is a fundamental parameter that reflects the surface charge of a material in a particular medium, usually as a function of pH. In membrane science, it provides valuable insight into the electrokinetic behavior of membrane surfaces, especially at the membrane–solution interface. The measurement is based on the principle of electrophoresis, where the mobility of particles in an electric field is converted into potential values using the Smoluchowski or Henry equation. For membranes, zeta potential is a crucial indicator of surface charge density and plays a pivotal role in predicting membrane-solute interactions, including fouling behavior, ion rejection efficiency, and stability. It directly influences the Donnan exclusion mechanism which governs the repulsion or attraction of charged solutes such as salts or organic compounds. A more negatively charged surface typically repels anions, while a positively charged surface favors the retention of cations. Thus, understanding the surface charge helps in optimizing the membrane for specific separation applications such as desalination.



Figure 30: Image of Zeta potential machine

CHAPTER 4 RESULTS AND DISCUSSION

4.1 Characterization of COF

4.1.1 FTIR

The reaction's completion was confirmed via FTIR analysis. Figure 31 illustrates the disappearance of peaks related to amine groups ($3200\text{--}3400\text{ cm}^{-1}$), whereas the peaks relating to -CHO groups changed from 1644 cm^{-1} to 1609 cm^{-1} . Furthermore, the emergence of peaks at 1235 cm^{-1} (C=N) and $1432, 1082, \text{ and } 1085\text{ cm}^{-1}$ (O=S=O) further substantiated the completion of the process.

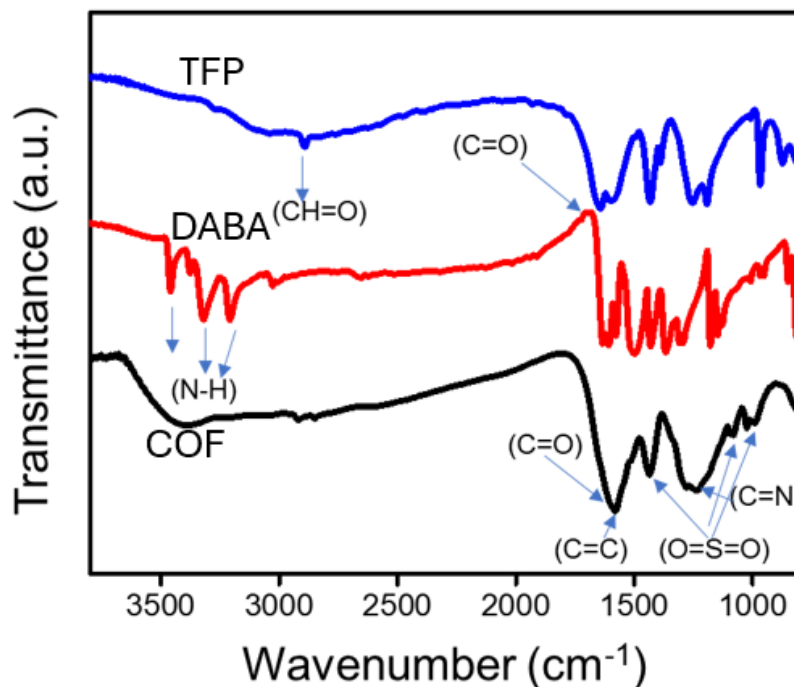


Figure 31: FTIR of (blue) TFP monomer, (red) DABA monomer, and (black) SA-COF

4.1.2 XRD

The XRD characterization of SA-COF revealed that the COF crystal structure had (100) crystallographic peaks at $2\theta = 4.59^\circ$, consistent with the literature on the same COF [80], as illustrated in Figure 32. These findings provide further evidence that the production of

COF nanosheets with great crystallinity was successful. This meticulously arranged structure ensures that there is a high density of sulfonic acid groups within the interlayer, which makes it possible to create perfect conditions for the efficient enrichment of amine monomers and their progressive release [81].

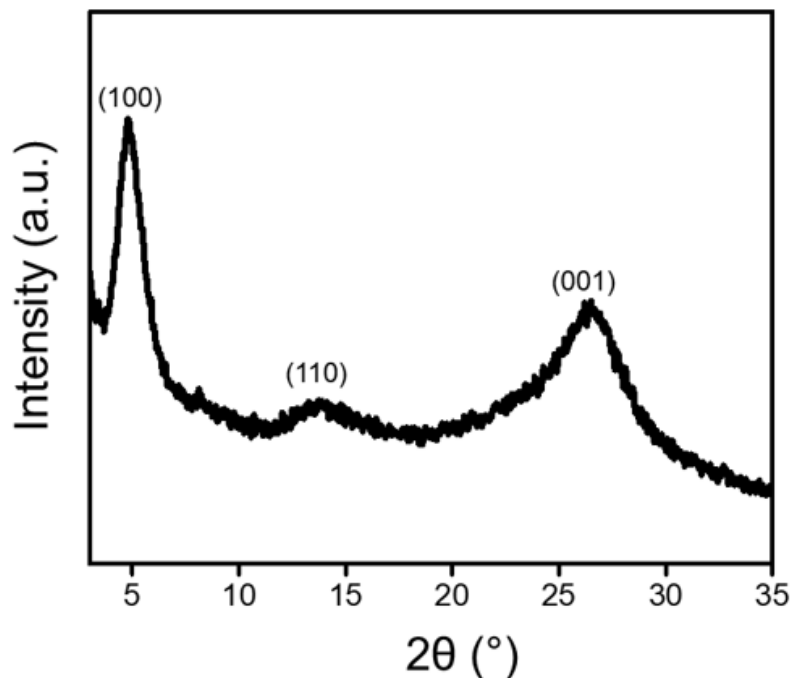


Figure 32: XRD pattern of SA-COF

4.1.3 TEM

Figure 33 (a) illustrates that the SA-COF nanosheets possess an exceptionally thin 2D sheet-like architecture, as evidenced by TEM characterization. The regular and organized crystalline structure that can be seen in the TEM photographs is evidence that the SA-COF nanosheets have a higher level of crystallinity than other nanosheets. Additionally, the selected area electron diffraction (SAED) reveals that the SA-COF nanosheets exhibit superior crystallinity (Figure 33b).

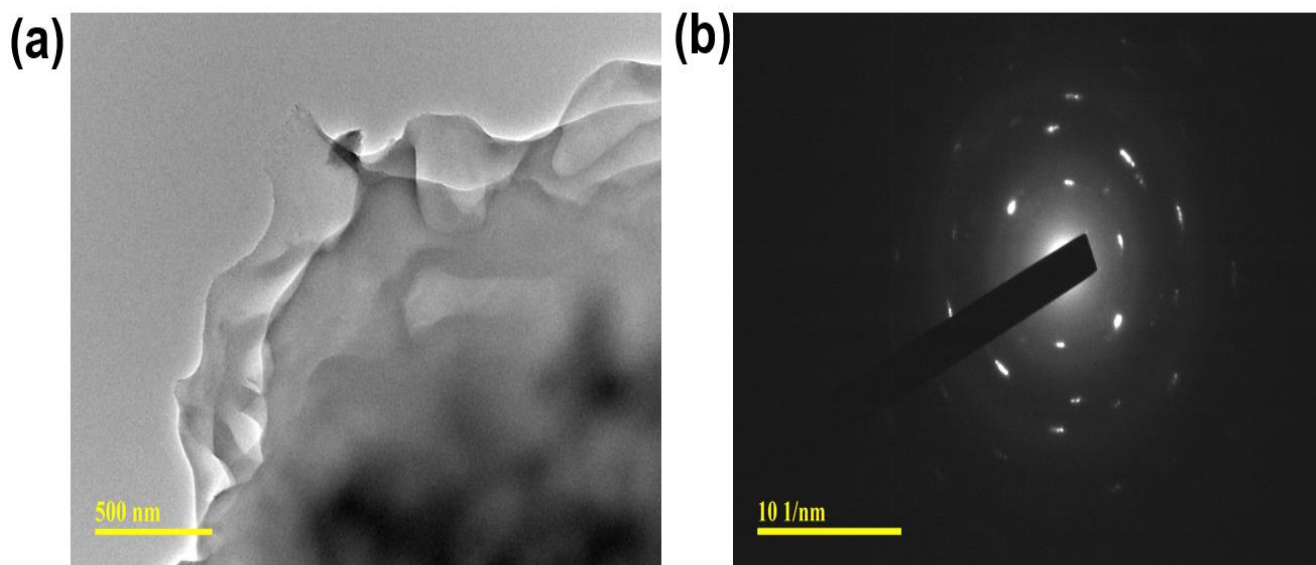


Figure 33: (a) TEM image of SA-COF nanosheets (b) SAED pattern of SA-COF nanosheets

4.1.4 N₂ Adsorption and Desorption

Nitrogen adsorption-desorption measurements were performed at 77 K to evaluate the porous characteristics of the synthesized SA-COF. The resulting isotherm (Figure 34a) shows a Type IV profile with a H4 hysteresis loop, indicating the coexistence of micropores and slit-shaped mesopores. At a relatively low pressure ($P/P_0 < 0.1$) a sharp uptake was observed confirming the presence of micropores, while the hysteresis between $P/P_0 = 0.4$ – 0.9 suggests capillary condensation occurring in mesopores[82]. The BET surface area was calculated to be $380.21 \text{ m}^2/\text{g}$ reflecting a high porosity favorable for filtration and separation applications. The pore size distribution (Figure 34b) showed a dominant peak at

around 1.3 nm supporting the presence of a uniform microporous uniform network.

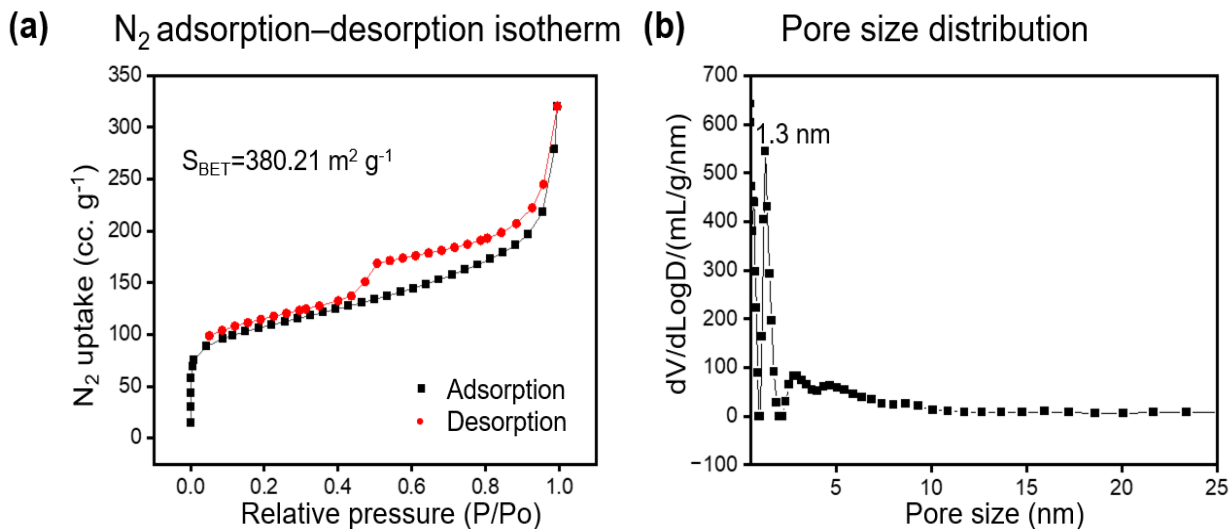


Figure 34: (a) BET of SA-COF (b) PSD of SA-COF

4.2 Characterization COF membranes

4.2.1 SEM

The surface morphology of the fabricated membranes were examined using SEM to evaluate the topological changes associated with the incorporation of SA-COF nanosheets into the PA layer. Figure 35 presents high-magnification images of the pristine PA and the COF-incorporated membranes (denoted as PA-COF_n) where n represents the COF loading in wt%. The pristine membrane displayed a relatively smooth surface with subtle ridge-and-valley morphology, which is typical of interfacially polymerized PA layers. However, with increasing SA-COF content, a pronounced evolution in the surface morphology was observed. The ridges and valleys became more defined, and the membrane surface gradually transitioned into a more textured structure with increased roughness and porosity-like features. This change is attributed to the interaction of COF nanosheets with the polyamide layer during interfacial polymerization, which may alter the diffusion of

monomers and disrupt the growth of the PA layer, leading to the formation of more irregular structures. Particularly at 10 wt% COF loading (PA-COF₁₀), the surface exhibited the most developed ridge-and-valley morphology. This textured topology is advantageous as it potentially increases the effective surface area, thereby improving water flux.

Due to its superior performance in separation tests, PA-COF₁₀ was selected as the optimized membrane formulation and was used as the primary comparison point against the pristine PA membrane in subsequent evaluations. The observed morphological enhancements at this concentration strongly support the functional improvements, affirming that the incorporation of COF nanosheets at an optimal loading plays a critical role in tailoring membrane surface architecture and performance.

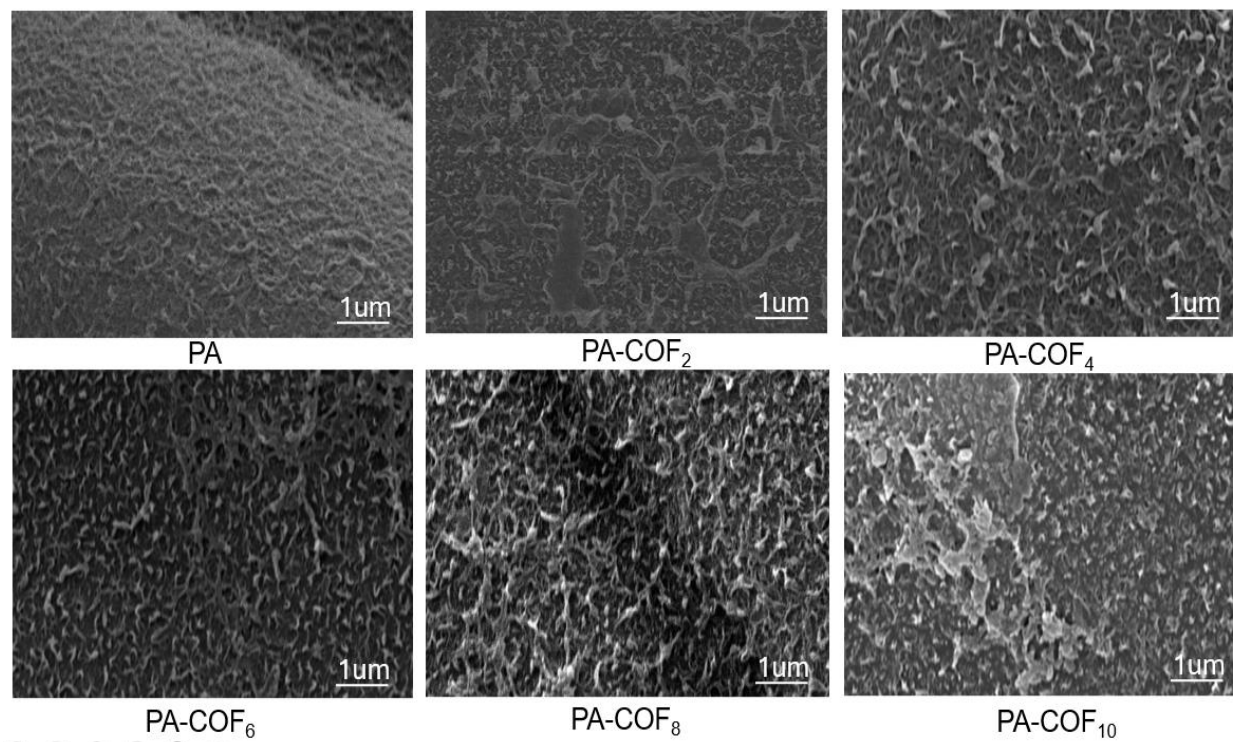


Figure 35: SEM of all PA-COF membranes

The SEM images of the standing PA and PA-COF₁₀ membranes are presented in Figure 36. The surface of the PA membrane displays a typical nodular structure (Figure 36a), while the cross-sectional view reveals a single-layered structure with a smooth bottom surface (Figure 36b). In contrast, the surface of the PA-COF₁₀ membrane exhibits a lamellar, sheet-like morphology characterized by prominent ridges (Figure 36c). Notably, SA-COF nanosheets are clearly visible, distributed on the membrane surface. The cross-sectional SEM of PA-COF₁₀ provides further insight into its morphology (Figure 36d), revealing a bilayered structure with a dense, ultrathin bottom layer (~33 nm) and a seemingly macroporous top layer (~63 nm). We hypothesize that the presence of hydrogen bonding between SA-COF and MPD slows down the diffusion of MPD toward TMC during the interfacial polymerization process. This results in the formation of a denser bottom layer, which further hinders MPD diffusion and leads to the development of a looser, macroporous top layer. This distinct bilayered structure with a thinner separation layer is a direct consequence of the incorporation of SA-COF and its interaction with the polymerization process. The AFM images of PA and top and bottom layer of PA-COF₁₀ membranes are.

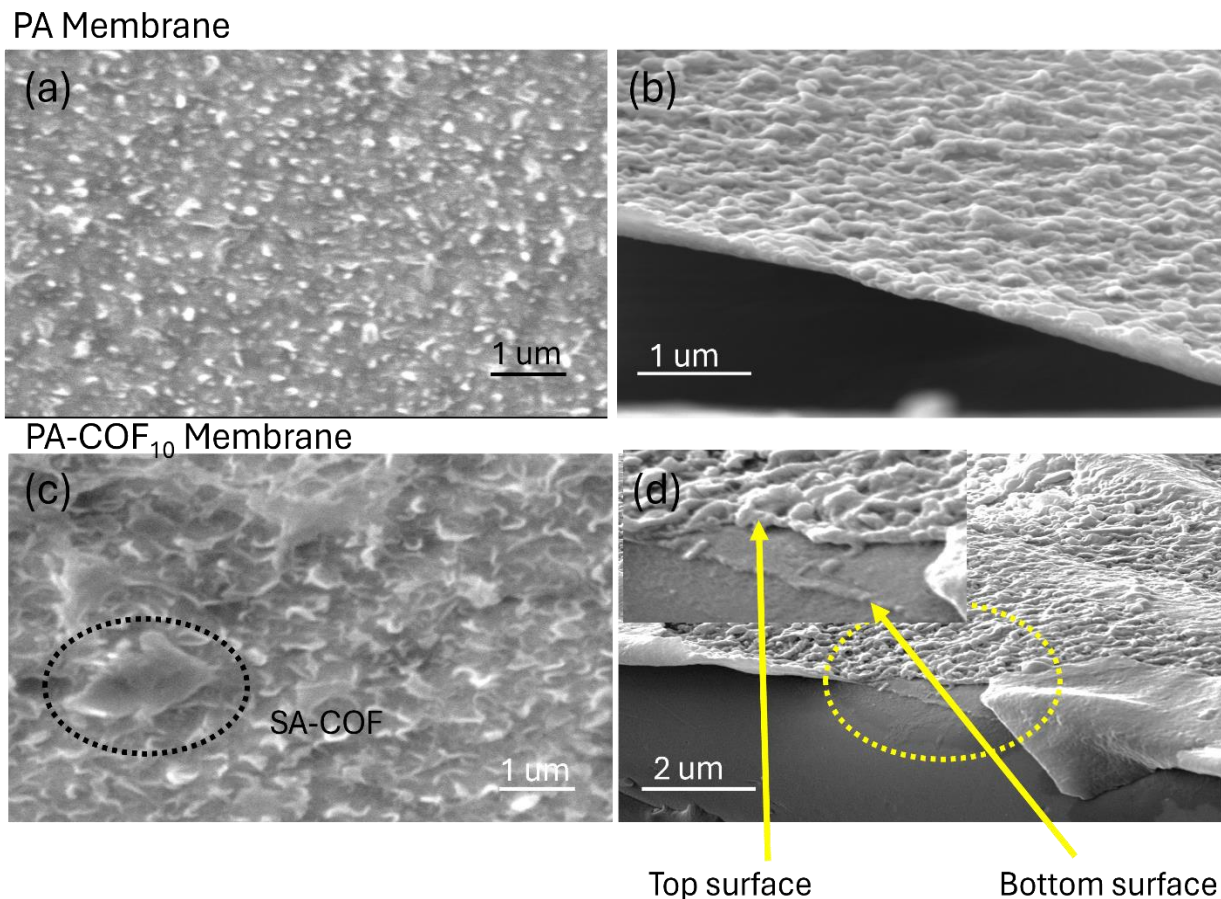


Figure 36: SEM of PA and PA-COF₁₀ membranes. (a) surface, and (b) cross section of PA membranes. (c) surface of PA-COF₁₀ membranes. The encircle area shows SA-COF nanosheets. (d) cross-section of PA-COF₁₀ membranes

4.2.2 AFM

AFM was employed to analyze the surface morphology and roughness of the fabricated PA and PA-COF composite membranes. As shown in Figure 37, the pristine PA membrane exhibited a typical ridge-and-valley structure characteristic of interfacially polymerized polyamide layers, with an average roughness of approximately 421.91 nm. Upon the incorporation of SA-COF, a gradual increase in surface roughness was observed across the series, corresponding to increasing COF loadings from 2 wt% to 10 wt%. The roughness

values notably increased from 457.80 nm for PA-COF₂ to 652.53 nm for PA-COF₁₀, indicating that the COF nanoparticles were well-dispersed and contributed to the formation of more protruded topographical features on the membrane surface.

The increase in surface roughness is attributed to the presence of COF nanosheets embedded within the polyamide matrix, which disrupted the otherwise smooth growth of the PA layer, thereby leading to the formation of more prominent nodular structures. This modification of the surface landscape can play a crucial role in influencing the membrane's hydrophilicity and interfacial interactions with water, which is discussed further in the contact angle analysis section.

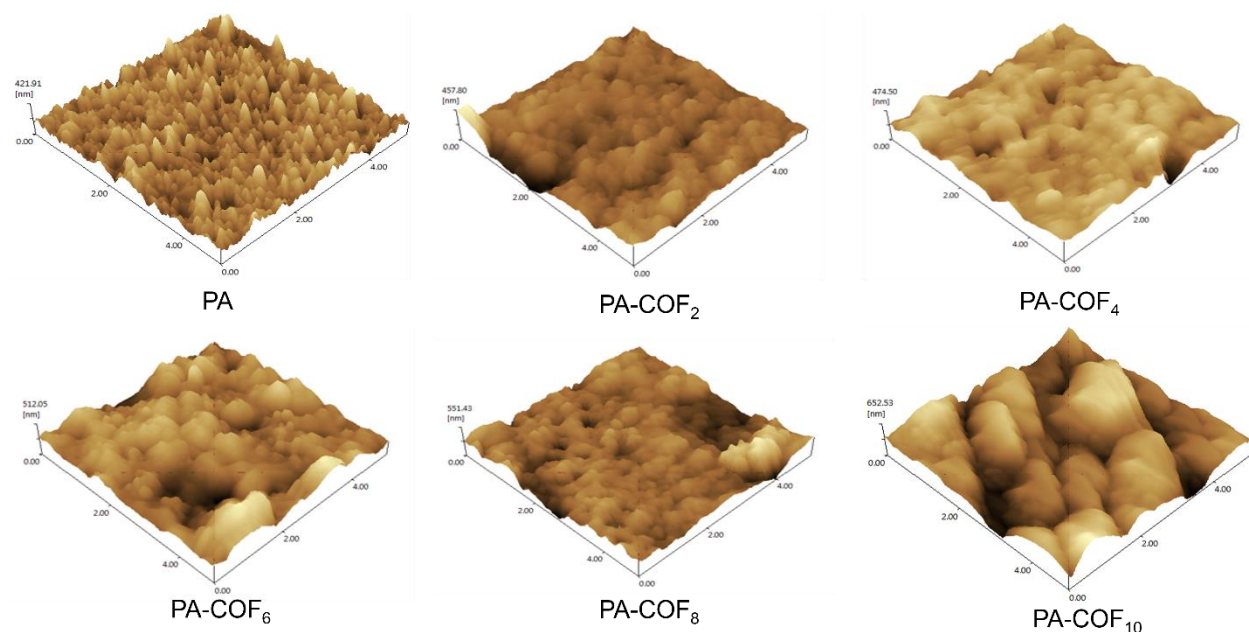


Figure 37: AFM of all PA-COF membranes

4.2.3 FTIR

An FTIR study was performed to reveal details regarding the functional groups and compositional features of the polyamide. Figure 38 displays the FTIR spectra of the TFN

membranes, which show that the IP reaction was successful in forming a PA skin layer on the surface of the membrane support. The three additional peaks seen at 1543, 1610, and 1663 cm^{-1} in the FTIR spectrum of the composite membranes were all ascribed to the PA skin layer covering the support. These peaks correspond to the aromatic amide ring breathing, the N-H bending of amide II in the -CO-NH-group, and the C=O stretching of the amide I bond, respectively.

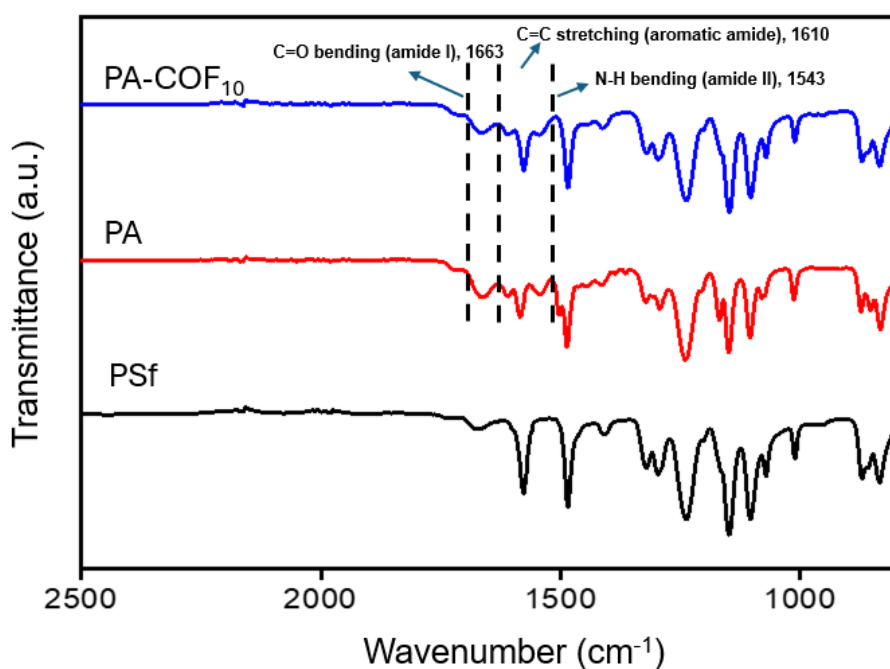


Figure 38: FTIR spectra of PSf (black), PA (red), and PA-COF₁₀ (blue) membranes

4.2.4 XPS

XPS analysis was employed to obtain a more profound understanding of surface chemistry. The XPS full-scan spectrum in Figure 39 indicates that the polyamide active layer of the original membrane, the top side and bottom side of PA-COF₁₀ contains oxygen, nitrogen, and carbon respectively. The elemental composition is presented in Table 6, indicating that

the membranes comprise approximately 74.83–77.58% carbon, 8.2–11.12% nitrogen, and 12.3–16.9% oxygen.

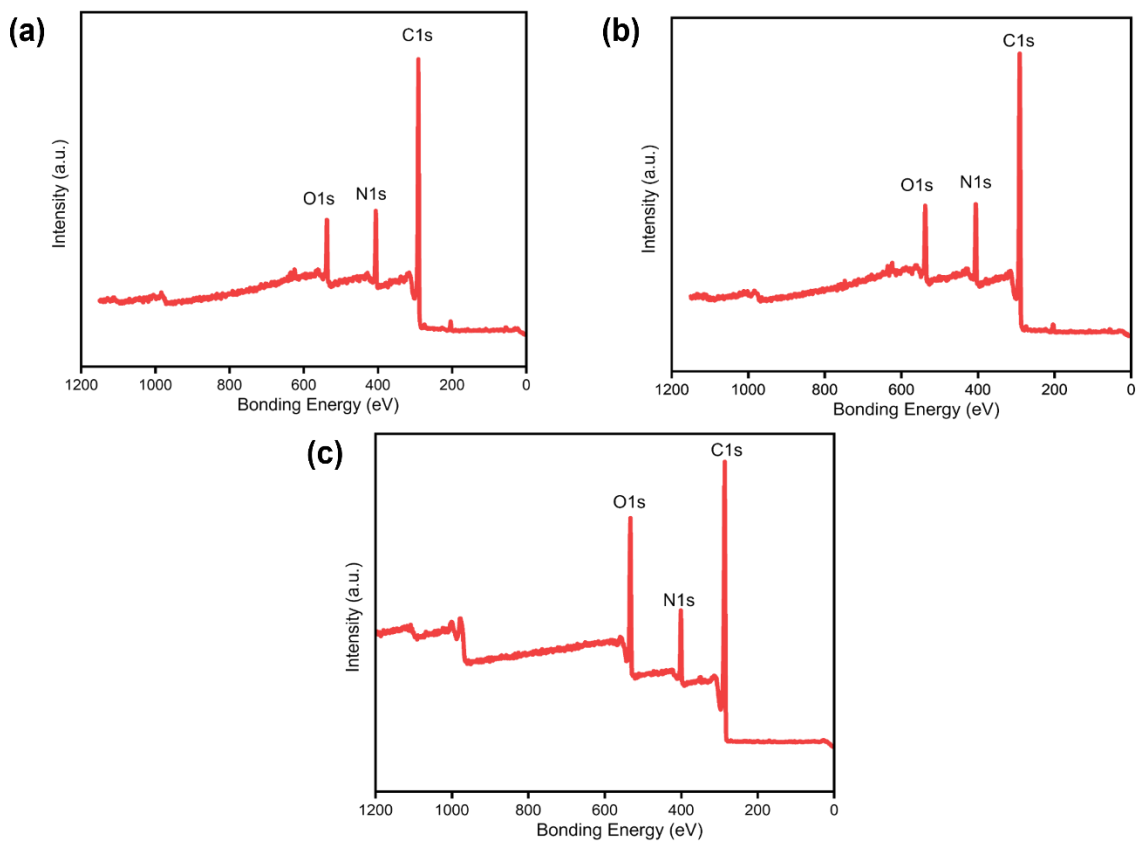


Figure 39: (a) XPS survey of PA membrane (b) XPS survey of PA-COF₁₀ (bottom side)(c) XPS survey of PA-COF₁₀ (top side)

Table 6: XPS elemental composition

Membrane	C (%)	O (%)	N (%)	O/N
PA	76.58	12.3	11.12	1.10
PA-COF ₁₀ (bottom side)	76.11	12.43	11.46	1.08
PA-COF ₁₀ (top side)	74.83	16.97	8.2	2.07

XPS analysis was performed on the PA membrane, PA-COF₁₀ (top layer), and PA-COF₁₀ (bottom layer). The C (1s) spectra for all membranes revealed three distinct peaks corresponding to C–C, C–H, C=C, C–N, and O=C–O bonds, conforming the formation of PA layer, as shown in Figure 40(a–c). Similarly, the O (1s) spectra displayed two peaks which indicated the presence of two oxygen types within the PA layer: N–C=O and O–C=O (Figure 40d–f). The degree of crosslinking (DC) of the PA layer was evaluated using the C=O/C–N ratio, an indicator of crosslink density, which was calculated using Equation (6);

$$DC = \frac{C_{-CONH-}}{C_{-CONH-} + C_{-COO-}} \quad (6)$$

where C-CONH- and C-COO- represent the content of amide and carboxylic groups in the PA layer, respectively.

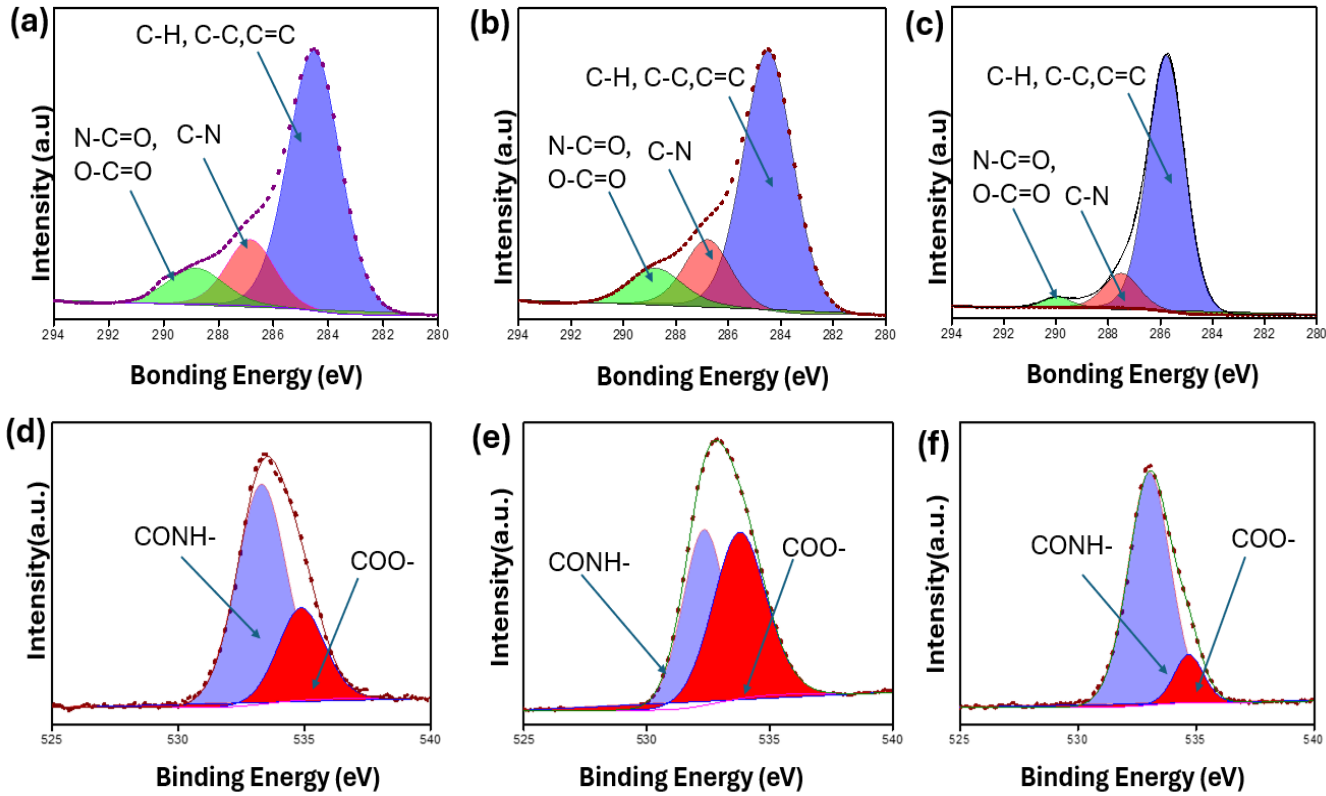


Figure 40: XPS spectra of PA, PA-COF₁₀ (top) and PA-COF₁₀ (bottom) membranes. C (1 s) spectrum of (a) PA, (b) PA-COF₁₀ top, (c) PA-COF₁₀ (bottom). O (1 s) spectrum of (d) PA, (e) PA-COF₁₀ top, (f) PA-COF₁₀ bottom

In a highly crosslinked PA structure, the theoretical ratio of O=C–N/C–N is approximately 1 (or 100%), as the polymer contains fewer carboxylic groups. The XPS analysis revealed variations in the crosslinking degree across the PA structures. For the pristine PA membrane, the DC was calculated to be 81%. In contrast, the bottom dense layer of the PA-COF₁₀ membrane exhibited a higher DC of 92%, while the top loose layer showed a significant reduction to 42%. This decrease in crosslinking for the top layer is consistent with previous findings [83]. The incorporation of SA-COF during interfacial polymerization initially slows down the diffusion of MPD molecules, leading to the formation of a denser, more highly crosslinked bottom layer. However, once this dense layer forms, the restricted diffusion of MPD further inhibits polymerization, resulting in a loose top layer with a lower degree of crosslinking [84, 85]. Additionally, the limited diffusion of MPD molecules leaves unreacted acyl chloride groups, which can self-inhibit the polymerization process, further contributing to the observed crosslinking gradient.

4.2.5 Contact angle

The surface wettability or hydrophilicity of membranes is a vital attribute affecting their permeability. Improving membrane hydrophilicity can be accomplished by integrating functional groups like sulfonic acid and hydroxyl groups, which facilitate hydrogen bonding with water molecules. Multiple researchers [49, 86] have demonstrated that the integration of hydrophilic nanoparticles augments both the total flux and hydrophilicity of membranes, indicating that an enhanced flux is expected based on the contact angles. This

study employed sulfonic acid-containing COF to naturally enhance the hydrophilicity of the membrane. The contact angles of PA-COF membranes with different SA-COF concentrations were measured, as seen in Figure 41a. The results indicate a distinct trend wherein the contact angle diminishes with increasing SA-COF concentration, hence corroborating the role of SA-COF in enhancing membrane hydrophilicity. To validate this enhancement, the water contact angles of the pure PA membranes and the upper and lower layers of PA-COF₁₀ membranes were assessed, as illustrated in Figure 41b. The pure PA membranes displayed a contact angle of 63°, while the lower layer of PA-COF₁₀ demonstrated a reduced contact angle of 46°. The upper surface of PA-COF₁₀ membranes demonstrated a contact angle of 29°, which is significantly lower. The decrease in the contact angle of the bottom layer is ascribed to the integration of hydrophilic SA-COF, enhancing water affinity. The significant reduction in the contact angle of the upper layer can be attributed to multiple variables. The porous and loose structure, along with the hydrophilic characteristics of SA-COF, facilitates the swift dispersion of water droplets. The low cross-linking degree of the top layer indicates the existence of free carboxylic groups, which further improve surface wettability. And also the greater the hydrophilicity of the membrane, the stronger its resistance to fouling [87].

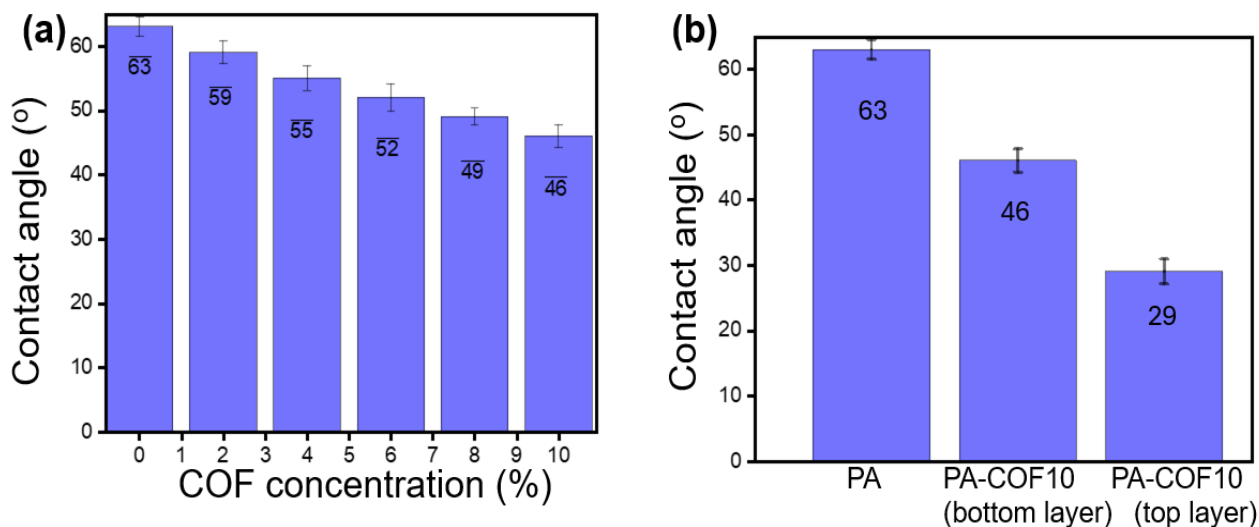


Figure 41: Contact angle of PA membranes

4.2.6 Zeta potential

Figure 42a illustrates the charge on the surface of the membrane using zeta potential highlighting the role of surface charge particularly in fouling resistance. The zeta potential values for membranes with different concentrations of SA-COF were assessed, revealing that the zeta potential becomes progressively more negative with increasing SA-COF concentration, so affirming the contribution of SA-COF to the enhancement of the membrane's electrostatic characteristics. This is especially important in the rejection of solutes owing to electrostatic repulsion and in decreasing the rate of membrane fouling. An increased negative charge augments the membrane's capacity for salt rejection and ion selectivity via electrostatic interactions, hence enhancing the overall efficiency of the membranes [88, 89]. The presence of specific functional groups, such as carboxylic and sulfonic acid groups, in the selective layer results in a substantial proportion of these groups becoming ionized and acquiring a negative charge at neutral pH. The zeta potential of pure PA membranes and the top and bottom layers of PA-COF₁₀ membranes was evaluated. Figure 42b illustrates that the integration of SA-COF into the PA layer led to an enhanced

negative charge. The zeta potential of the bottom layer of PA-COF₁₀ membranes was recorded to be -42.7 mV, markedly more negative than the -33 mV noted for pure PA membranes. The top layer of PA-COF₁₀ membranes displayed a more pronounced negative charge, with a zeta potential of -44.3 mV. The heightened negativity is chiefly ascribed to the negative charge conferred by the SA-COF. The reduced cross-linking in the upper layer presumably results in unreacted acyl chloride groups, which further contribute to the negative surface charge.

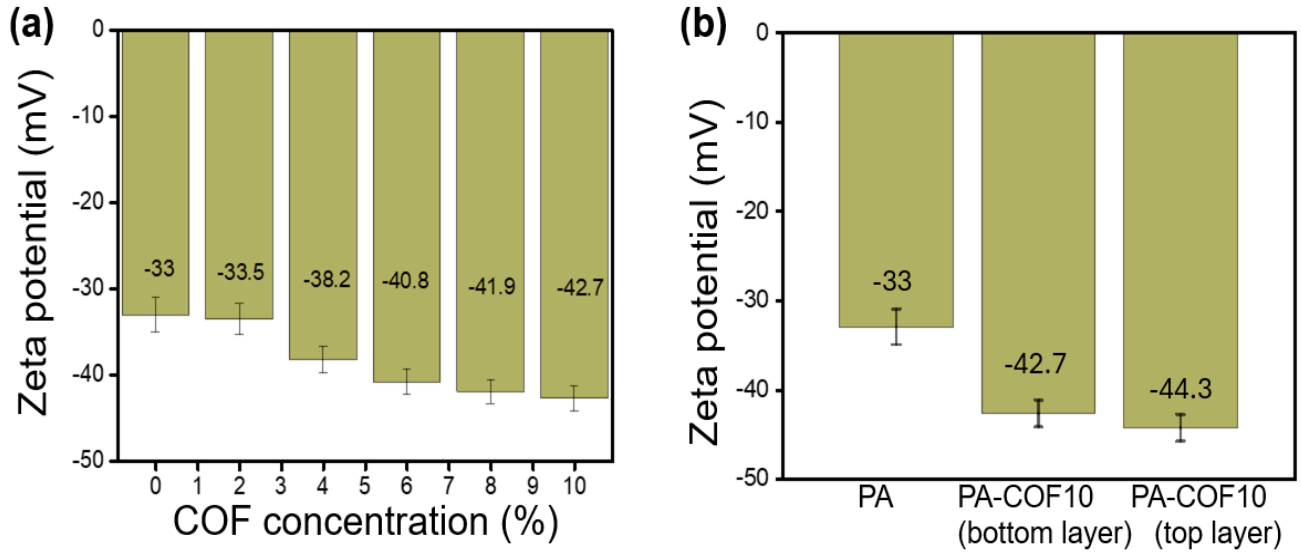


Figure 42: Zeta potential of PA membranes

4.3 Performance Evaluation

4.3.1 Permeability and Selectivity Performance

The performance of pristine PA membranes and PA-COF_n membranes was systematically evaluated in terms of water permeance, salt rejection, and fouling resistance. The PA membrane exhibited a water permeance of 0.39 L/m²·h·bar (flux = 7.8 L/m²·h) and a NaCl rejection rate of 98.6 % for a 2000 ppm NaCl solution. The incorporation of SA-COF into the PA layer significantly enhanced the membrane performance. As shown in Figure 43,

increasing the SA-COF content gradually improved the water permeance without compromising the salt rejection rate at concentrations of SA-COF up to 10 %. This impressive improvement in performance is attributed to the unique properties of SA-COF, including its water processability, ionic nature, and sheet-like morphology, which facilitate uniform integration into the PA matrix. At an optimum SA-COF concentration of 10 %, the PA-COF₁₀ membranes achieved a water permeance of 0.98 L/m²·h·bar (flux = 19.6 L/m²·h), representing more than a 2.5-fold increase over the pristine PA membranes, while maintaining a high salt rejection rate of approximately 98 %. However, when the SA-COF concentration exceeded 10 %, a noticeable decline in salt rejection was observed, dropping to below 90 %, despite a dramatic increase in water permeance of 9.2 L/m²·h·bar (flux = 184 L/m²·h). This loss in performance is likely due to the agglomeration of SA-COF within the PA layer, which may create non-selective interfacial channels that compromise the membrane's salt rejection ability. Additionally, the high concentration of sulfonic acid groups on the SA-COF nanosheets can lead to electrostatic repulsion, causing defects or disruptions in the PA layer structure

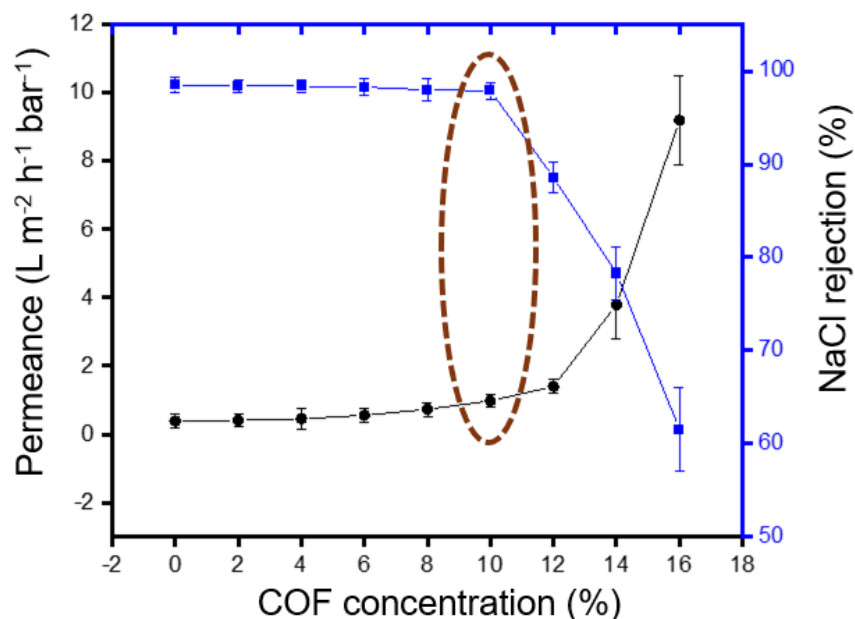


Figure 43: Performance evaluation of PA and PA-COF₁₀ membranes; permeance and salt rejection

4.3.2 Long Term Stability Test

Long-term operational stability is critical for the practical application of RO membranes. To evaluate this, PA-COF₁₀ membranes were tested for 60 h under continuous operation and at various pressures to assess their normalized flux. As shown in Figure 44, the PA-COF₁₀ membranes retained over 90 % of their original flux after 60 h of operation and under gradually increasing pressures. In contrast, pristine PA membranes exhibited a significant decline, losing 23 % of their flux after 60 h and 21 %. These results highlight the superior durability and operational stability imparted by the incorporation of charged SA-COF nanosheets into the PA matrix.

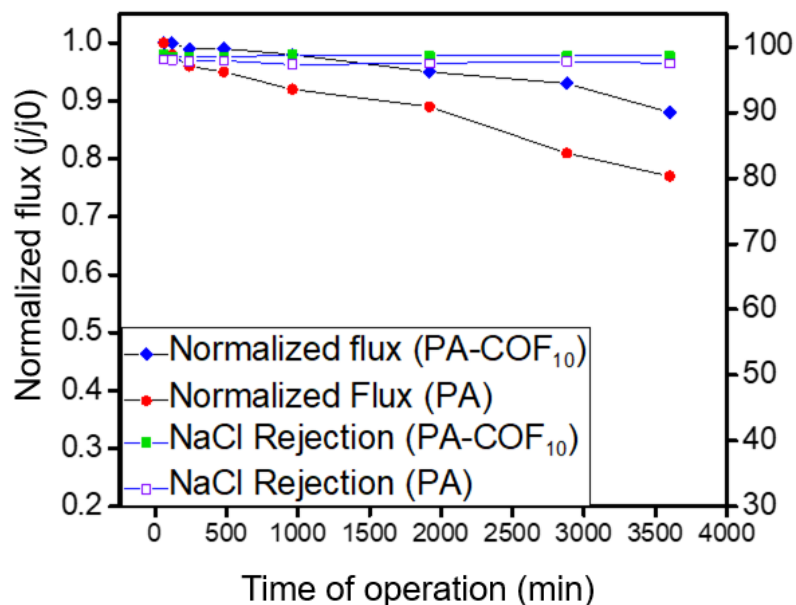


Figure 44: Stability evaluation after long hours of operation

4.3.3 Antifouling Test

Fouling is a significant challenge for RO membranes, as it reduces efficiency, increases operational costs, and shortens membrane lifespan[90]. Proteins like bovine serum albumin (BSA), a common foulant, tend to adhere to membrane surfaces, clogging pores and lowering water permeability. Incorporating SA-COF nanosheets into the PA layer effectively mitigates this issue by enhancing the membrane's negative surface charge. The stronger negative charge induces electrostatic repulsion between the membrane and negatively charged BSA molecules, reducing protein accumulation. This not only helps preserve water flux but also extends the membrane's operational lifespan by minimizing fouling. In addition to the increased negative charge, the PA-COF₁₀ membrane exhibits superior hydrophilicity compared to pristine PA membranes. This enhanced hydrophilicity plays a crucial role in improving antifouling properties by reducing foulant adhesion and facilitating smoother water transport. Together, these attributes significantly enhance the

PA-COF₁₀ membrane's resistance to fouling. As shown in Figure 45, after 35 cycles of BSA exposure, PA-COF₁₀ membranes recovered 93% of their original flux, in stark contrast to the 63% recovery observed for PA membranes. The reduced permeance in PA membranes can be attributed to pore blockage caused by the accumulation of salt and foulant molecules. In contrast, PA-COF₁₀ membranes benefit from the presence of additional negative charges and the formation of supplementary water transport pathways, introduced through the incorporation of pores in SA-COF nanosheets. These pathways enable PA-COF₁₀ membranes to efficiently repel salt ions and foulant molecules via electrostatic interactions while facilitating water flow due to increased hydrophilicity. This combination allows PA-COF₁₀ membranes to maintain consistent permeance over extended periods, showcasing their potential for long-term, efficient performance in desalination applications.

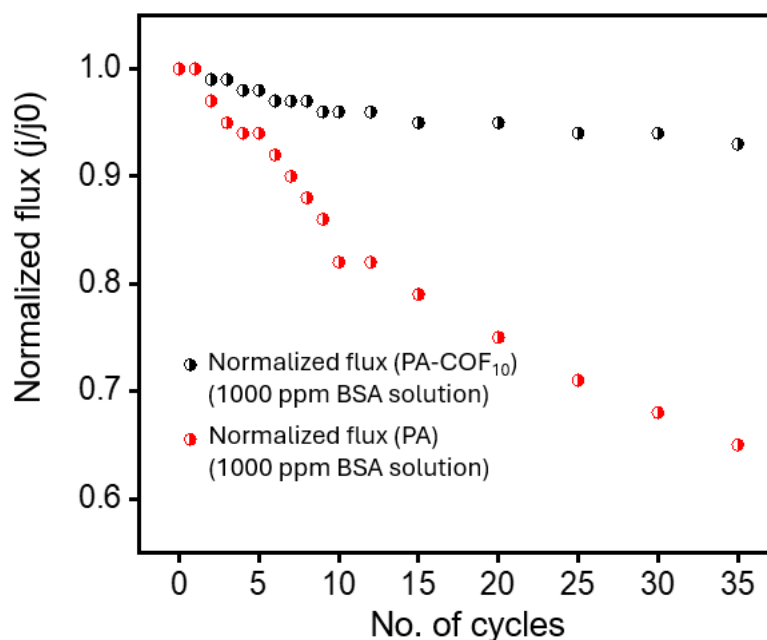


Figure 45: Flux recovery/stability evaluation after various cycles of simulated fouling using BSA as model foulant

4.3.4 Boron Removal Test

By incorporating SA-COF into our membrane support we tested the effectiveness of employing this nanofiller for the removal of boron as it is abundant in sulfonic acid groups. Li et al [56] used an interesting approach called the swelling-embedding-shrinking (SES) strategy to insert $-\text{SO}_3\text{H}$ group from 4-nitrobenzenesulfonyl chloride (NBS) as a molecular plug into the PA structure to effectively reduce the pore size and increase steric hindrance facilitating the removal of boron. Zhang et al [81] incorporated high-density sulfonic groups iCOF nanosheets to form a porous and charged interlayer, thereby creating the PA-iCOF membrane through IP. The PA-iCOF membranes exhibited a water permeance of about three times higher than unmodified polyamide membranes without compromising much of its selectivity. Similarly, an increased salt rejection, improved chlorine resistance, and improved antifouling capabilities were seen in the PA-S-CONs TFC membrane that was fabricated by [91] after they integrated S-CON into the PA matrix.

The incorporation of SA-COF into the membrane support was systematically investigated to evaluate its influence on water flux and boron rejection performance. Membranes with varying SA-COF loadings were fabricated and tested under identical operating conditions. As shown in Figure 46(a,b), both flux and boron rejection improved with increasing SA-COF content up to an optimal loading of 7 wt%. The pristine membrane (with 0% SA-COF) exhibited a flux of approximately $0.31 \text{ L/m}^2\cdot\text{h}\cdot\text{bar}$ and a boron rejection efficiency of around 61%. With incremental addition of SA-COF, the membrane structure likely became more porous and hydrophilic, facilitating enhanced water transport and improved interaction with boron species, thereby increasing both flux and rejection values.

At 7 wt% SA-COF loading, the membrane achieved its highest performance, exhibiting a flux of approximately 0.81 L/m²·h·bar and boron rejection of ~86%, indicating the optimum balance between permeability and selectivity. This enhancement can be attributed to the well-dispersed COF in the support, which provides additional transport pathways while maintaining effective boron exclusion. The sulfonate group (–SO₃[–]) due to its electron-donating oxygen atoms can interact with the boron atom in boric acid, which acts as a Lewis acid. This interaction results in the formation of a stable complex, where the boron is effectively binded by one or more sulfonate groups. This is called the chelation effect, which leads to the initial anchoring of the boric acid to the functionalized surface. The nature of this interaction is primarily ionic or electrostatic in character and it significantly reduces the mobility of the boric acid in solution thereby enabling its separation. Following chelation, a secondary interaction occurs involving hydrogen bonding. Neighboring sulfonate groups, or other functional groups present in proximity, participate in hydrogen bonding with the hydroxyl groups of boric acid. This step further stabilizes the boron-sulfonate complex by enhancing the overall binding strength as described by [92]. However, further increasing the SA-COF content to 9 wt% resulted in a decline in both flux (~11 LMH) and boron rejection (~85%). This reduction is likely due to excessive loading causing COF aggregation or pore blockage, which can hinder water transport and compromise selectivity.

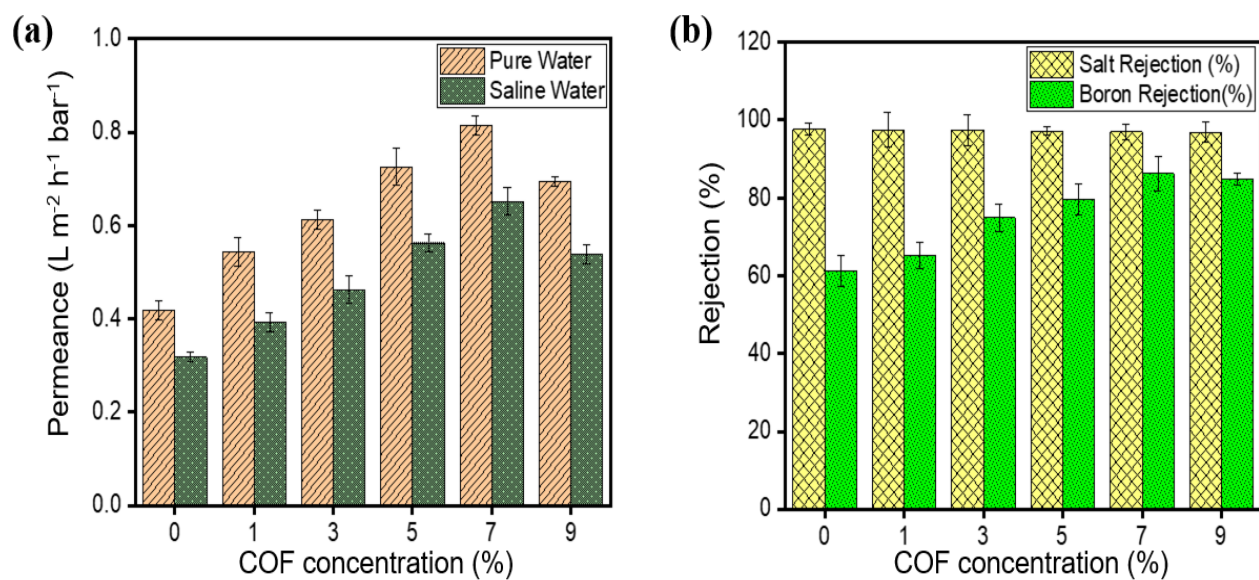


Figure 46: (a) Effect of SA-COF loading on flux and (b) Salt and Boron rejection

CHAPTER 5 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The results of this investigation are as follows:

1. A water-processable SA-COF was successfully incorporated into the PA layer via IP to enhance RO membrane performance
2. The optimized PA-COF₁₀ membrane demonstrated a permeance of 0.98 L/m²·h·bar, which is 2.5 times higher than the pristine PA membrane (0.39 L/m²·h·bar)
3. Despite the increase in water permeability, the PA-COF₁₀ membrane maintained excellent NaCl rejection (>98%), indicating preserved selectivity
4. The addition of SA-COFs significantly enhanced the membrane hydrophilicity, as evidenced by a reduction in water contact angle from 63° (pristine PA) to 29° (PA-COF₁₀)
5. After 35 cycles of fouling with bovine serum albumin (BSA), the PA-COF₁₀ membrane recovered 93% of its initial water flux, compared to only 63% recovery for the pristine PA membrane
6. SA-COF incorporation in the membrane significantly enhanced membrane performance, improving both water flux and boron rejection compared to the pristine membrane, achieving around 86% removal at 7 wt% loading

5.2 Recommendation

1. It is recommended to create an interlayer of COF sandwiched between the support and the PA layer to observe the performance

2. We recommend the exploration of other ionic COFs (positively charged)
3. To conduct an extensive adsorption and computational analysis to further our understanding of the removal mechanism of boron.

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Vitae

Name : [Umar Hussaini Nuhu]
Nationality : [Nigerian]
Date of Birth : [30/01/1998]
Email : [ask4umarhussayn@gmail.com]
Address : [No. 7 Abidjan Crescent Unguwan Rimi Kaduna,
Nigeria]
Academic Background : [M.S Chemical Engineering (2023-2025)
King Fahd University of Petroleum and Minerals, Dhahran,
Saudi Arabia
B. Eng. Chemical Engineering (2015-2022)
Ahmadu Bello University, Zaria, Kaduna, Nigeria]

Journal Publication

1. **Nuhu, U. H.**, Khan, N. A., Hussain, I., Long, M., Salhi, B., Baig, N., Abdulazeez, I., Alam, K., Khan, S., Usman, M., Zahid, U., & Aljundi, I. H. (2025). Rapid synthesis of charged covalent organic framework for sustainable reverse osmosis membranes. Desalination, 607, 118797.
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