

**Sulfate ions (SO_4^{2-}) removal from seawater using
Polyamide thin-film composite Nanofiltration membrane**

BY

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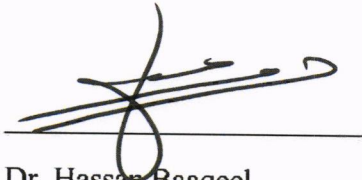
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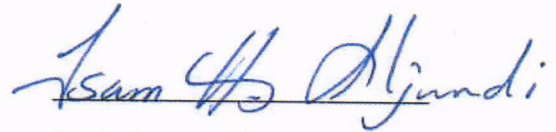
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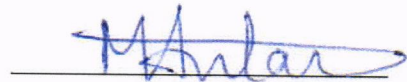
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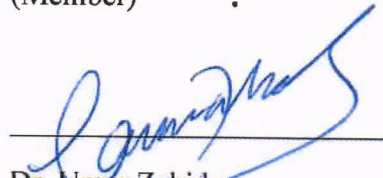
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To a little man in my brain ..

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LIST OF ABBREVIATIONS

CESR: Cost-effective sulfate removal

NF: Nanofiltration

MF: Microfiltration

UF: Ultrafiltration

RO: Reverse Osmosis

TFC: Thin-Film Composite

IP: Interfacial Polymerization

CA: Cellulose-Based Membranes

FTIR: Fourier-transform infrared spectroscopy

EDX or EDS: Energy Dispersive X-Ray Analyzer

FESEM: Field Emission Scanning Electron Microscope

XRD: X-ray powder diffraction

TGA: Thermogravimetric Analysis

CA: Contact Angles

DI: Deionized

LPH: Liter Per Hour

PA: Polyamide

NMP: N-Methyl-2-pyrrolidone

DMAc: N,N-dimethylacetamide

DMF: N,N-dimethylformamide

PES: Poly(ether sulfone)

PEG-400: Polyethylene glycol

PWP: Pure Water Permeability

PSF: Polysulfone

PVP: Polyvinyl pyrrolidone

MAAc: Methacrylic acid

TAc: Tartaric acid

LAc: Lactic acid

PAN: Polyacrylonitrile

TA: Tannic acid

np: Nonporous

DA: Dopamine

PEI: Polyethyleneimine

HPAN: Hydrolyzed PAN

PIP: Piperazine

TMC: Trimesoyl Chloride

PVDF: Polyvinylidene fluoride

P(MMA-co-HEMA): Copolymers of methyl methacrylate and 2-hydroxy ethyl methacrylate

PVC: Polyvinyl chloride

MPD: *m*-phenylenediamine

ABA: 4-aminobenzoic acid

ACA: 6-aminocaproic acid

APA: 3-aminopropanoic acid

DDA: Diaminodipropylamine

CMPI: 2-chloro-1-methyliodopyridine

NaOH: Sodium hydroxide

SBI: 3,3,3',3'-Tetramethyl-1,1'-spirobisindane-6,6'-diol

TB: 6H,12H-5,11-Methanodibenzo[b,f][1,5]diazocine-2,8-diol

RES: resorcinol

DABSA: 2,5-diaminobenzenesulfonic acid

Na₃PO₄: Trisodium phosphate

SDS: Sodium dodecyl sulfonate

CTAB: Hexadecyl trimethyl ammonium bromide

EDA: Ethylenediamine

TEA: Triethylamine

PVA: Poly (vinyl alcohol)

Mel: Melamine

SMF: Sulfonated melamine formaldehyde

SA: Sulfanilamide

GO-TETA: Triethylenetetramine

PS-OW: Commercial polysulfone (PS)

PES-20 kDa: polyethersulfone (PES) with molecular weight cut-off (MWCO) of 20 kDa

PES-150 kDa: polyethersulfone (PES) with molecular weight cut-off (MWCO) of 150 kDa

PSH-100 kDa: hydrophilic modified PS (PSH) with MWCO of 100 kDa

PESH-50 kDa: hydrophilic modified PES (PESH) with MWCO of 50 kDa

PESH: Hydrophilic Polyethersulfone

AEP: 1-(2-aminoethyl) piperazine

PDI: 1,4-phenylene diisocyanate

HDI: Hexamethylene diisocyanate

TDI: Toluene diisocyanate

MDI: Diphenylmethane diisocyanate

DMC: Methacryloxyethyltrimethyl ammonium chloride

BIBB: 2-Bromoisobutyryl bromide

DNPs: Dextran nanoparticles

Dextran10 (MW 10,000)

Dextran40 (MW 40,000)

Dextran70 (MW 70,000)

GAZ: 3,5-Diamino-1,2,4-triazole

DMF: N,N-dimethylformamide

TBAC: Tetrabutylammonium chloride

CCh; Catechol

TMA Trimesic acid

SPEI: Sulfonated Polyethylenimine

DS: Degree of sulfonation

PFBSF: Perfluoro-1-butanesulfonyl fluoride

CDADO: Carboxylated aromatic diamine-diol

CDA: Carboxylated diamine without hydroxyl groups

TAEA: Tris(2-aminoethyl) amine

HTeC: 1,2,4,5-Cyclohexane tetracarboxylic acid/phosphorus pentachloride

BTC: Cyclobutane tetracarboxylic/Anhydride/ PCl_5

DA: Dopamine hydrochloride

NMG: N-methyl-Dglucamine

PMPD: 4-(piperazin-1-yl) benzene-1,3- diamine

3-BPA: 3-bromopropionic acid

DSDA: 4,4'-diaminostilbene-2,2'-disulfonic acid

ABSA: 3-aminobenzenesulfonamide

TPA: Terephthalic acid

BPEI: Branched polyethyleneimine

CC: Cyanuric chloride

SOS: Sodium octyl sulfate

SDBS: Sodium dodecyl benzenesulfonate

BAPA: Bis(3-aminopropyl) amine

1,2-BIS: 1,2-Bis(3-aminopropylamino) ethane

m-XDA: m-Xylylenediamine

DAPP: 1,4-Bis(3-aminopropyl) piperazine

HMDA: Hexamethylenediamine

g: Gram

ATR: attenuated total reflectance

Au: gold

mL: Milliliter

min: Minute

pH: power of hydrogen

EC: electrical conductivity

TDS: total dissolved solids

ppm: Part Per Millions

J: Permeate flux

R: Salt Rejection

ΔV : Permeate Volume

L: liter

Δt : Time Duration

h: Hour

A: Effective Membrane Area

m²: Squared Meter

C_F: Feed Concentration

C_P: Permeate Concentration

F: Feed Input

P: Permeate Flow Rate

C: Concentrate Flow Rate

B: Bypass Flow Rate

N—H bending: Amide II

C=O stretching: Amide I

C₆H₆: Aromatic ring

—NHCO— bond: Acrylamide functional group

C: Carbon

O: Oxygen

S: Sulfur

N: Nitrogen

Cl: Chloride

NaCl: Sodium Chloride

MgSO₄: Magnesium Sulphate

pKa: Dissociation Constant

ABSTRACT

Full Name : Alhomaiddi Mohammad A. Alghurairi Aldossary.
Thesis Title : Sulfate ions (SO_4^{2-}) removal from seawater using Polyamide thin-film composite Nanofiltration membrane.
Major Field : Chemical Engineering.
Date of Degree : April 2022 AD - Ramadhan 1443 AH.

Thin-film composite (TFC) nanofiltration (NF) membranes were fabricated via interfacial polymerization (IP) reaction between different types of amines and 1,3,5-Benzenetricarbonyl trichloride (TMC) on the surface of polysulfone (PSF) support layer, where previously prepared by wet phase inversion method. The different used amine monomers in this research are Bis(3-aminopropyl) amine (BAPA), 1,2-Bis(3-aminopropylamino) ethane (1,2-BIS), m-Xylylenediamine (m-XDA), 1,4-Bis(3-aminopropyl) piperazine (DAPP), and Hexamethylenediamine (HMDA). The chemical structures, and surface properties of each TFC membrane were characterized using Fourier-transform infrared spectroscopy (FTIR), Energy Dispersive X-Ray Analyzer (EDX or EDS), Field Emission Scanning Electron Microscope (FESEM), X-ray powder diffraction (XRD), Thermogravimetric Analysis (TGA), Contact Angles (CA), and Zeta Potential. Nanofiltration performance was evaluated using deionized (DI) water, 1000 ppm NaCl solution, and 1000 ppm MgSO_4 solution separately. The flux of membranes was in the following order: PSF > HMDA TFC > DAPP TFC > MXDA TFC > 1,2-BIS TFC > BAPA TFC, while the salts rejection of membranes as follow: 1,2-BIS TFC > BAPA TFC > MXDA TFC > DAPP TFC > HMDA TFC. 1,2-BIS TFC membrane exhibited the optimum separation performance (R_{MgSO_4} : 92%, R_{NaCl} : 64.9%) with a flux of $4.73 \frac{\text{L}}{\text{m}^2 \text{ h bar}}$. Transmembrane pressure, feed tank temperature, pH, and feed tank cross-flow velocity exhibited a strong influence on 1,2-BIS TFC membrane nanofiltration performance. 1,2-BIS TFC membrane exhibited the highest

salts rejection, and flux when the operating conditions were as follows: Pressure of 30 bar, Temperature of 40 °C, pH of 7, the cross-flow velocity of 1.115 m/s, and cross-flow rate of 360 LPH.

ملخص الرسالة

الإسم الكامل: الحميدي بن محمد الحميدي الغيري الدوسري.

عنوان الرسالة: إزالة أيونات الكبريتات من مياه البحر باستخدام غشاء الترشيح النانوي المركب بغشاء رقيق من مادة متعدد الأמיד.

التخصص: الهندسة الكيميائية.

تاريخ الدرجة العلمية: أبريل 2022 م الموافق رمضان 1443 هـ.

تم تصنيع أغشية الترشيح النانوي ذات الأغشية الرقيقة المركبة بواسطة تفاعل البلمرة البيني بين أنواع مختلفة من الأمينات و 1,3,5- بنزينريكاربونيل ثلاثي كلوريد على سطح طبقة داعمة من لدائن السلفون، الذي تم تحضيره وتصنيعه مسبقاً بإسلوب إنعكاس الطور الرطب. الأنواع المختلفة المستخدمة في هذا البحث من الأمينات هي: Bis(3-aminopropyl) amine (BAPA), 1,2-Bis(3-aminopropylamino) ethane (1,2-BIS), m-Xylylenediamine (m-XDA), 1,4-Bis(3-aminopropyl) piperazine (DAPP), and Hexamethylenediamine (HMDA).

تم التحقق ودراسة التراكيب الكيميائية، والخصائص السطحية لكل من الأغشية الرقيقة المركبة والتي تم تصنيعها لإجراء هذه الدراسة البحثية بواسطة أجهزة مختلفة وهي : مطيافية الأشعة تحت الحمراء باستخدام تحويل فورييه (FTIR) ، تحليل الأشعة السينية المشتتة للطاقة (EDX أو EDS)، مجهر إلكترون لمسح الانبعاثات الميدانية (FESEM) ، حيود مسحوق الأشعة السينية (XRD)، التحليل الحراري الوزني (TGA)، زاوية تلامس (CA)، وإمكانات زيتا.

أيضاً، جميع الأغشية الرقيقة المركبة التي تم تصنيعها لهذه الدراسة البحثية وضعت تحت إختبار أداء الفصل الترشيحي النانوي باستخدام الماء منزوع الأيونات والأملاح، محلول كلوريد الصوديوم بتركيز 1000 جزء في المليون، و محلول كبريتات المغنيسيوم بتركيز 1000 جزء في المليون كلاً على حده. الكميات المتدفقة من السوائل المستخدمة في كل تجربة تتزايد وفقاً للترتيب التالي:

PSF > HMDA TFC > DAPP TFC > MXDA TFC > 1,2-BIS TFC > BAPA TFC

بينما كميات الأملاح التي لا تتجاوز الأغشية الرقيقة المركبة في تزايد وفقاً للترتيب التالي:

$$1,2\text{-BIS TFC} > \text{BAPA TFC} > \text{MXDA TFC} > \text{DAPP TFC} > \text{HMDA TFC}$$

وفقاً لأداء الفصل الترشيحي النانوي في هذا البحث، فإن الغشاء الرقيق المصنع من الأمين 1,2-BIS ، والمحصّر بالنسبة المؤوية

2 $\frac{\text{وزن}}{\text{الحجم}}$ أظهر الأداء الأفضل مقارنةً بالأنواع الأخرى المستخدمة لتحضير الأغشية الرقيقة المركبة الأخرى، حيث تمتع بترشيح

92 % من محلول كبريتات المغنيسيوم، و 64.9 % من محلول كلوريد الصوديوم، و كميات تدفق تقدر بـ $4.73 \frac{\text{لتر}}{\text{بار} \cdot \text{متر}^2 \cdot \text{ساعة}}$.

كما أن العوامل المؤثرة التشغيلية (مثل: الضغط، درجة الحرارة، درجة الحموضة، وسرعة التدفق) لعملية تقييم أداء الفصل

الترشيحي النانوي للغشاء الرقيق المصنع من الأمين 1,2-BIS أظهرت تأثيراً قوياً على الأداء من حيث ترشيح المحاليل الملحية

وكميات التدفق الناتجة أيضاً. أظهرت التجارب المختلفة باختلاف العوامل المؤثرة التشغيلية أن أداء الفصل الترشيحي النانوي

للغشاء الرقيق المصنع من الأمين 1,2-BIS سجل أفضل أداء عند العوامل التشغيلية التالية: الضغط : 30 بار، درجة الحرارة:

40 درجة مئوية، درجة الحموضة: 7، سرعة التدفق : $1.115 \frac{\text{متر}}{\text{ثانية}}$ ، ومعدل التدفق: $360 \frac{\text{لتر}}{\text{ساعة}}$.

CHAPTER 1

Introduction

1.1. Background

Oil and natural gas demand is growing worldwide, where the demand is estimated to increase at the rate of 1.6%/year whereas the volume production loss is estimated to decline between 5-11 %/year. The production facilities' maintenance is estimated to cost approximately 75% of future investments, whilst the major maintenance and repair costs are attributed to the water injection operation, and scale formation issues [1]. Scale formation is a major concern in the field of oil and gas, where it can form in various locations starting from the surface water injection facility to the disposal wells, including the reservoir, and pipelines too. These possible scale formation locations can overwhelm the production with loss, and failure. These will lead to substantial operation costs, and additional capital costs, and it may lead - in some cases - to the well shut down [2 - 6]. The scale formation is mainly caused by the water flooding processes and chemical treatment operations, which are used primarily to enhance the well recovery. The scale formation takes place as a result of exceeding the solubility limits of each element in used water for flooding processes, where temperature and ionic strength of the solution, and pH medium affect scale formation kinetics [7,8]. According to the previous studies and investigations, the result showed that scale samples from the field are composed of organic, inorganic, and crystal water. the result showed that calcium sulfate (CaSO_4), barium sulfate (BaSO_4), and strontium sulfate (SrSO_4) are the main

components in the scale samples from the field in addition to other components and elements [9 - 16]. The higher concentration of sulfate ions (SO_4^{2-}) in seawater, especially Arabian seawater compared to any other seawater streams, can lead to a massive scale formation during the water flooding processes, particularly in offshore and near coast operations. When the water flooding method is used to enhance oil and/or gas recovery, the sulfate ions dissolved in water should be minimized to avoid any substantial sulfate scale formation in the forms of calcium, barium, and strontium, which are hard, adherent, almost insoluble in mineral acids, and difficult to remove mechanically [17,18,19].

The removal or minimization of sulfate ions (SO_4^{2-}) from the injected water to the oil or/and gas reservoir will help maintain the well recovery and save additional cost. Nowadays, various chemical, biological, and physical methods were developed and intensively studied to minimize the scale formation associated with sulfate ions (SO_4^{2-}) in the water flooding processes in all possible scale formation locations. The developed methods to face the growing concern of scale formation can be summarized as follow: lime precipitation, barium precipitation, cost-effective sulfate removal (CESR) process, the SAVMIN™ process, the THIOPAQ™ process, packed bed or fluidized bed reactors, passive treatment, in situ treatment, ion exchange processes, filtration systems, and others [20 - 24]. However, the ultimate threat is to reach a point where these different methods are limited effectiveness. Also, the other factors that can be impacting these methods are non-eco-friendly, costly, and difficult to apply, and manage [25]. With the knowledge of the solubilities of formed compounds in the water at the membrane surface, and recent intensive developments in filtration technology, the Nanofiltration membrane becomes a promising technique to selectively remove divalent ions, such as SO_4^{2-} , from the water [26].

The water separation process, especially filtration systems, is receiving notable attention since 1960, where it has been applied to seawater, brackish water, wastewater treatment, and drinking water separation, and it was commercialized and used in the field of the petroleum industry, chemical processing industry, food industry, pulp and paper industry, and pharmaceuticals and electronic industry [27 - 32]. Membrane technology is one of the separation and treatment processes that showed its efficiency in treating high salinity solutions, with lower cost and pollution compared to other methods. Microfiltration (MF), ultrafiltration (UF), nanofiltration, and reverse osmosis (RO) are the main four types of membrane separation technologies based on the pore size and rejected particle size as shown in Figure 1-1 [33 - 36].

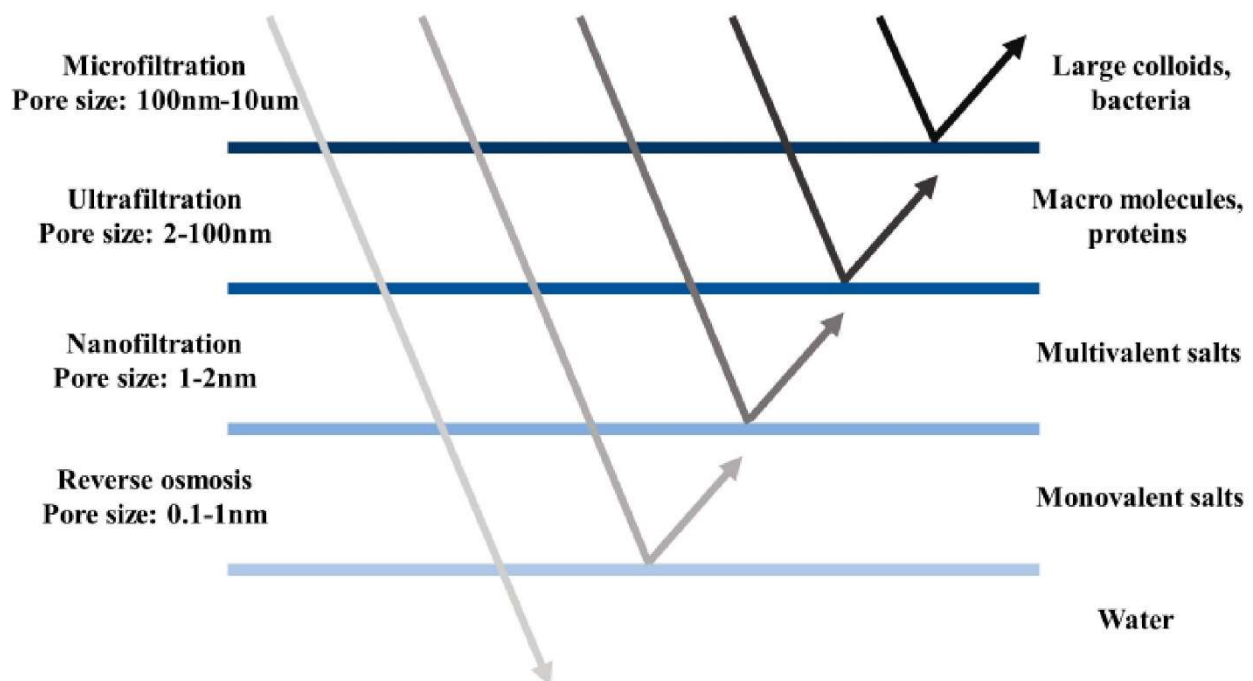


Figure 1-1: The main four classifications of membrane based on their pore size and rejected particle size [37].

Nanofiltration technology has been a hot topic in recent years with intensive developments and studies compared to other membrane categories. The ability to treat high salinity solutions, high

permeation flux at lower operation pressure, lower capital and operational cost (such as chemical inhibitors, membrane cleanup, or replacement), energy-efficient, ecofriendly, and facile operation conditions are the main reasons to be widely explored in the field of membrane compared to other traditional separation processes [38-44]. In addition to these reasons, nanofiltration can be implemented in almost sulfate ions free based on the effect of both the Donnan exclusion, and Steric hindrance [45,46], which mainly contributed to the sulfate rejection. Nowadays, thin-film composite is the most successful polymeric membrane method, which is fabricated in two separated steps: synthesizing a microporous support membrane, followed by interfacial polymerization (IP) between two immiscible solutions of amines and acyl chloride on the microporous support layer surface. Compared to another type of polymeric membrane (Cellulose-Based Membranes, CA), the thin-film composite membrane showed higher chemical and thermal stabilities, an excellent separation performance, and higher permeability flux. Also, a thin-film composite membrane can withstand high pressure due to the mechanical strength provided by the microporous support membrane during the nanofiltration (NF) process [47]. Motivated by the understanding of the main factors attributed to the nanofiltration performance, and the lack of studies on different polyamines other than the common ones in the field of thin-film composite membrane, the objective is devoted to evaluating new different polyamines, and their effectiveness in removing sulfate ions (SO_4^{2-}) from water. Also, pH, temperature, pressure, and cross-flow rate were studied on the effectiveness of the permeability flux, and the salt rejection performance of the fabricated thin-film composite membranes

1.2. The objectives of Thesis work

The main objective of this thesis work is to investigate Sulfate ions (SO_4^{2-}) separation from seawater by using the polyamide thin-film composite nanofiltration membrane, where the specific objectives:

- 1) Synthesizing five different thin-film composite nanofiltration membranes with different types of amines. The amine monomers are Bis(3-aminopropyl) amine (BAPA), 1,2-Bis(3-aminopropylamino) ethane (1,2-BIS), m-Xylylenediamine (m-XDA), 1,4-Bis(3-aminopropyl) piperazine (DAPP), and Hexamethylenediamine (HMDA). These amines are not studied before extensively.
- 2) Characterizing the membranes by using the following techniques: Fourier-transform infrared spectroscopy (FTIR), Energy Dispersive X-Ray Analyzer (EDX or EDS), Field Emission Scanning Electron Microscope (FESEM), X-ray powder diffraction (XRD), Thermogravimetric Analysis (TGA), Contact Angles (CA), and Zeta Potential.
- 3) Evaluating the membranes by using Deionized (DI) water, 1000 ppm MgSO_4 solution, and 1000 ppm NaCl solution separately at the different operation pressures (10 bar, 20 bar, and 30 bar), feed tank temperature of $22^\circ\text{C} \pm 1^\circ\text{C}$, pH of 7 ± 0.5 , and cross-flow rate of 360 liters per hour (LPH).

- 4) Investigating the effect of operation conditions, such as pH, feed tank temperature, transmembrane pressure, and feed tank cross-flow velocity, on the permeation properties of the best membrane.

CHAPTER 2

Literature Review

2.1. Background

This chapter gives an overview of the thin-film composite nanofiltration membrane. It covers well-known different substrates, additives, and solvents that were used to synthesize the porous support layer. The monomers used to synthesize Polyamide (PA) layer are covered with their significance on the permeability flux and salt rejection performance. The effect of surfactant and additive is summarized from recent previous research.

2.2. Porous support layer substrates

The effect of thin-film composite support layer substrate on the membrane performance and morphology was studied since the TFC membrane was found. Several studies attempted to evaluate the support layer substrate by changing the composition, different solvents, and introducing new additive types on the support layer. Wang, Qian, et al. [55] studied the effect of different solvents on the support layer. N-Methyl-2-pyrrolidone (NMP), N,N-dimethylacetamide (DMAc), and N,N-dimethylformamide (DMF) were used to dissolve 17 % (w/v) Poly(ether sulfone) (PES) and 40 % (w/v) Polyethylene glycol (PEG-400). The support layer performance evaluation exhibited the highest MgSO_4 rejection in DMAc and NMP, while the pure water

permeability (PWP) follows the following order: DMF ($810 \frac{\text{L}}{\text{m}^2 \text{ h bar}}$) > DMAc ($600 \frac{\text{L}}{\text{m}^2 \text{ h bar}}$) > NMP ($310 \frac{\text{L}}{\text{m}^2 \text{ h bar}}$). Another study was conducted by Ali, Mohamed E.A., et al. [48], where N,N-dimethylacetamide (DMAc) was used as a solvent to dissolve 16 % (w/v) Polysulfone (PSF) and 0.3% (w/v) Polyvinyl pyrrolidone (PVP) to enhance the support layer performance with adding different organic acids in the support layer. Methacrylic acid (MAAc), Tartaric acid (TAc), and Lactic acid (LAc) are three organic acids additive were used separately to prepare the support layer in addition to Polysulfone (PSF), Polyvinyl pyrrolidone (PVP), and N,N-dimethylacetamide (DMAc). The pure water permeability (PWP) of PSF, PSF/MAAc, PSF/Tac, and PSF/Lac are $1.12 \frac{\text{L}}{\text{m}^2 \text{ h bar}}$, $2.4 \frac{\text{L}}{\text{m}^2 \text{ h bar}}$, $2.64 \frac{\text{L}}{\text{m}^2 \text{ h bar}}$, and $2.89 \frac{\text{L}}{\text{m}^2 \text{ h bar}}$, respectively, while the PSF/Tac exhibits the highest MgSO_4 rejection. Jiang, Chi, et al. [49] introduced aqueous template-induced surface nanostructures on the pristine Polysulfone (PSF) and Polyacrylonitrile (PAN) substrates to enhance nanofiltration performance, where he modified PSF support with 1) loose Tannic acid (TA)/Fe networks (PSF-TA/Fe), 2) dense TA/Fe coating (PSF-Ta/Fe^{np}, where superscript “np” represents a nonporous surface), and 3) dopamine/polyethyleneimine (PSF-DA/PEI), and hydrolyzed PAN support (HPAN). The effect of aqueous template-induced surface nanostructures on the pristine support layer was not too significant, where the pure water permeability (PWP) of PSF, PSF-TA/Fe, PSF-Ta/Fe^{np}, PSF-DA/PEI, PAN, and HPAN is $310 \pm 28 \frac{\text{L}}{\text{m}^2 \text{ h bar}}$, $236 \pm 12 \frac{\text{L}}{\text{m}^2 \text{ h bar}}$, $208 \pm 14 \frac{\text{L}}{\text{m}^2 \text{ h bar}}$, $261 \pm 16 \frac{\text{L}}{\text{m}^2 \text{ h bar}}$, $167 \pm 13 \frac{\text{L}}{\text{m}^2 \text{ h bar}}$, and $186 \pm 17 \frac{\text{L}}{\text{m}^2 \text{ h bar}}$, respectively, with exhibiting highest Na_2SO_4 rejections (99.4 %) in TFC membrane that interfacial polymerized on the substrate of pristine PSF, and PSF-TA/Fe between Piperazine (PIP) (1 % w/v) and Trimesoyl chloride (TMC) (0.1 % w/v). After interfacial polymerization between Piperazine hexahydrate ($\text{C}_4\text{H}_{10}\text{N}_2 \cdot 6\text{H}_2\text{O}$) (1 % w/v), and Trimesoyl chloride (TMC) (0.1 % w/v) on

Polyvinylidene fluoride (PVDF) substrates with pore sizes ranging from 25-450 nm, Wu, Junhui, et al. [50] studied the effect of PVDF pore sizes on the nanofiltration performance. The results concluded that Polyvinylidene fluoride (PVDF) substrate with a pore size of 100 nm exhibits the highest pure water permeability (PWP) ($19.3 \frac{\text{L}}{\text{m}^2 \text{ h bar}}$), and Na₂SO₄ rejection (98 %). In another study by Yao, Zhikan, et al [51], two amphiphilic copolymers with different ratios of methyl methacrylate and 2-hydroxy ethyl methacrylate P(MMA-co-HEMA) were dissolved in N,N-dimethylacetamide (DMAc) with Polyvinyl chloride (PVC), Polyethylene glycol 400 (PEG400), and LiCl for each. The support layer contains P(MMA-co-HEMA) with HEMA content (wt.%) of 54.9 exhibited the highest pure water permeability (PWP) with $321.7 \pm 21.8 \frac{\text{L}}{\text{m}^2 \text{ h bar}}$, while the pure water permeability (PWP) of the support layer without amphiphilic copolymers exhibited the lowest with a value of $248.4 \pm 49 \frac{\text{L}}{\text{m}^2 \text{ h bar}}$.

These studies were based on the long-term developments in the field of Thin-film composite (TFC) membrane, especially the membrane support layer, where it showed how different solvents, and additives can enhance the separation performance. As it can be taken from these studies, N,N-dimethylacetamide (DMAc) and Polyvinyl pyrrolidone (PVP) are two excellent choices as solvent, and additive in the preparation of the support layer of Polysulfone (PSF).

2.3. Previous study of Thin-film composite (TFC) membranes

Various studies were conducted over years on the development of thin-film composite (TFC) membranes. In these different studies, different amine monomers, different organic solvents, monomers optimization, substrate modification, additive addition, surfactant introduction, porous addition, post functionalization, and post-treatment with acid were used to enhance the performance of synthesized Thin-film composite (TFC) [67]. In these following subsections, the effect of different amine monomers, and organic solvents on Thin-film composite (TFC) membrane is going to summarize with monomers optimization. Also, the effect of different types of surfactants and additives, and their compositions based on previous studies is going to present in the followed subsection too.

2.3.1. Thin-film composite (TFC) active layer monomers

Tables 2-1, 2-2, 2-3, 2-4 summarized different studies of different amine monomers, and organic solvents were used to synthesize thin-film composite (TFC) membrane. Table 2-1 summarized the different studies of synthesized thin-film composite (TFC) membrane with Piperazine (PIP) monomer. Table 2-2 summarized studies associated with thin-film composite (TFC) membrane that was synthesized based on *m*-phenylenediamine (MPD) monomer. Table 2-3 summarized thin-film composite (TFC) membranes based on Polyethyleneimine (PEI) monomer. The rest of the amine monomers were used to synthesize thin-film composite (TFC) membrane in the last five years with an implication of sulfate ions (SO_4^{2-}) rejection were summarized in Table 2-4. These studies were varied by different factors, including substrate

modification, different organic solvents, monomers optimization, and the introduction of diamine or triamine monomers, additives, and surfactants.

Table 2-1: The studies summary of thin-film composite membrane based on Piperazine (PIP) monomer.

Substrate	Monomer A	Monomer B	Testing conditions	Permeability Flux [$\frac{L}{m^2 \text{ h bar}}$]	Salt rejection [%]	Reference
Polysulfone (PSF) (16)- polyethylene glycol (PEG) (50)-N-Methyl-2-pyrrolidone (NMP).	0.35 % (w/v) PIP 0.35 % (w/v) PIP/ 4-aminobenzoic acid (ABA) 0.35 % (w/v) PIP/6-aminocaproic acid (ACA) 0.35 % (w/v) PIP/3-aminopropanoic acid (APA)	0.2 % (w/v) TMC/n-hexane	Filtration mode: Cross-flow. Pressure: 6 bar. Temperature: 25 °C. pH: 7. Salt concentration: 1000 ppm.	PIP TFC: 11.9 PIP-ABA TFC: 70	Na ₂ SO ₄ (95 %, 93.2 %) > MgSO ₄ (91.4 %, 62.5 %) > MgCl ₂ (61.5 %, 21 %) > NaCl (29.9 %, 15.5 %) for PIP, and PIP-ABA, respectively.	[52]
PSF - Pore size 12 nm	TFC: Diaminodipropylamine (DDA)/1% (w/v) Piperazine (PIP) DP-TFC: Diaminodipropylamine (DDA)/1% (w/v) Piperazine (PIP)/Polyethylenimine (PEI) (1 g/L) DPC-TFC: Diaminodipropylamine (DDA)/1% (w/v) Piperazine (PIP)/ 0.01–0.05% (w/v) 2-chloro-1-methylodopyridine (CMPI)/ 0.01–0.05% (w/v) NaOH	0.1% (w/v) Trimesoyl chloride (TMC)	Filtration mode: Cross-flow. Pressure: 10 bar. Temperature: 25 °C. Salt concentration: 1000 ppm.		Na ₂ SO ₄ (94 %, 983%,82%) > MgSO ₄ (96%, 87 %, 89%) > MgCl ₂ (83%) for TFC, DP-TFC, and DPC-TF, respectively.	[53]
PES	PPA: 1 % (w/v) PIP SBI ₅ -PIP ₅ : SBI/PIP (5/5 w/w) TB ₇ -PIP ₃ : TB/PIP (7/3 w/w) RES ₃ -PIP ₇ : RES/PIP (3/7 w/w)	0.1% (w/v) Trimesoyl Chloride (TMC)/cyclohexane	Filtration mode: Cross-flow. Pressure: 1 bar. Temperature: 25 °C. Salt concentration: 2000 ppm.	SBI ₅ -PIP ₅ = 18.11	SBI ₅ -PIP ₅ exhibited highest salt rejection, where follows: Na ₂ SO ₄ (99.2 %) > MgSO ₄ (98.8 %) > NaCl (39%)	[54]
PES (17)-PEG-400(40)-DMAc	2 % (w/v) PIP	0.1 % (w/v) TMC/n-hexane	Filtration mode: Cross-flow. Pressure: 6 bar. Temperature: 25 °C. Salt concentration: 1000 ppm.	13	Na ₂ SO ₄ (99%) > MgSO ₄ (98%) > MgCl ₂ (92%) > NaCl (55%).	[46]
PES	NF-PD: 3 % (w/v) 2,5-diaminobenzenesulfonic acid (DABSA)/0.05 % (w/v) Piperazine (PIP) NF-P: 0.1 % (w/v) Trisodium phosphate (Na ₃ PO ₄)/0.2 % (w/v) PIP	0.15 % (w/v) TMC 0.08 % (w/v) TMC	Filtration mode: Dead-end Pressure: 4 bar. Temperature: 25 °C Salt concentration: 10 mM.	11.8 ± 0.5 11.2 ± 0.5	Na ₂ SO ₄ (98%, 99%) > MgSO ₄ (70%, 86%) > NaCl (40%, 22%) > MgCl ₂ (8%, 5%) for NF-PD, and NF-P respectively.	[58]
PSF PFS-TA/Fe PSF-Ta/Fenp	1% (w/v) PIP 1% (w/v) PIP/0.1% (w/v) Sodium dodecyl sulfonate (SDS) 1% (w/v) PIP/0.3% (w/v) hexadecyl trimethyl ammonium bromide (CTAB)	0.1% (w/v) TMC/n-hexane	Filtration mode: Cross-flow. Pressure: 6 bar. Temperature: 25 °C. Salt concentration: 2000 ppm.	TFC-T (PSF-1% (w/v) PIP): 5.7 TFC-R (PSF-TA/Fe-1% (w/v) PIP): 21.3	TFC-T = Na ₂ SO ₄ : 99.4 TFC-R = Na ₂ SO ₄ : 99.4	[49]

PSF-DA/PEI	1% (w/v) m-phenylenediamine (MPD)					
PAN	1% (w/v) ethylenediamine (EDA)					
HPAN	1% (w/v) resorcinol (RES)/3% (w/v) TEA					
PAN	1 % (w/v) PIP/0.6 % (w/v) Na ₃ PO ₄	0.05% (w/v) TMC/n-hexane	Filtration mode: Cross-flow. Pressure: 3 bar. Temperature: 25 °C. Salt concentration: 10 mmol/L.	NF-FO: 8.33 RO-FO: 2.08	NF-FO: Na ₂ SO ₄ (95%) > NaCl (22%) RO-FO: Na ₂ SO ₄ (95%) > NaCl (90%)	[57]
Polyethersulfone (PES) – Pore size 13 nm	PA-TFC-C: 1% (w/v) PIP/0.5% (w/v) Sodium hydroxide (NaOH) PA-TFC-I: 1.0% (w/v) Poly (vinyl alcohol) (PVA)-1 % (w/v) PIP/0.5 % (w/v) Sodium hydroxide (NaOH) PA-TFC-P: 1% (w/v) PIP/0.5 % (w/v) Sodium hydroxide (NaOH)- 1.0 % (w/v) Poly (vinyl alcohol) (PVA)	0.1% (w/v) TMC/n-hexane	Filtration mode: Cross-flow. Pressure: 4 bar. Temperature: 25 ± 0.1 °C. Salt concentration: 2000 ppm.	PA-TFC-C: 9.4 ± 0.5 PA-TFC-I: 28.2 ± 0.3 PA-TFC-P: 8.8 ± 0.4	Na ₂ SO ₄ (98.8 ± 0.2, 99.8 ± 0.1, 99.4 ± 0.3) > MgSO ₄ (95, 98, 96) > NaCl (33.3 ± 1.6, 46.2 ± 2.3, 38.5 ± 1.4) for TFC-C, TFC-I, and TFC-P respectively.	[58]
Polysulfone (PSF)	PIP1: 1 % (w/v) PIP PIP1-Mel0.3: 1 % (w/v) PIP/0.3 % (w/v) melamine (Mel) PIP1-SMF0.3-SA0.05: 1 % (w/v) PIP/0.3 % (w/v) Sulfonated melamine formaldehyde (SMF) /0.05 % (w/v) sulfanilamide (SA)	0.1% (w/v) Trimesoyl chloride (TMC)	Filtration mode: Cross-flow. Pressure: 5 bar. Temperature: 25 °C. Salt concentration: 2000 ppm.	PIP1: 4.624 PIP1-Mel0.3: 5.678 PIP1-SMF0.3-SA0.05: 6.97	PIP1: MgSO ₄ (92.5%) PIP1-Mel0.3: MgSO ₄ (95.5%) PIP1-SMF0.3-SA0.05: MgSO ₄ (96%)	[59]
PES (16)-PVP (2)-DMF	0.15 % (w/v) Piperazine (PIP)/0.15 % (w/v) Sodium dodecyl sulfate (SDS)/0.4 % (w/v) Triethylamine (TEA)/0.005, 0.01, and 0.03 % (w/v) Triethylenetetramine (GO-TETA)	0.5 % (w/v) TMC/n-hexane	Filtration mode: Cross-flow. Pressure: 6 bar. Temperature: ambient. Salt concentration: 1000 ppm.	M0 _{TETA=0%} : 8.3 M1 _{TETA=0.005%} : 10.63 M2 _{TETA=0.01%} : 11.5 M3 _{TETA=0.03%} : 12.2	Na ₂ SO ₄ (46.3%, 48.2%, 53.1%, 65.3%) > NaCl (35.8%, 18.4%, 22.2%, 32.2%) for M0, M1, M2, and M3 respectively.	[60]
PS-OW PES-20 kDa PES-150 kDa PSH-100 kDa PESH-50 kDa	1.0, 0.6, 0.3, 0.1, 0.05 % (w/v) PIP on PSH-100 kDa substrate.	0.03, 0.06, 0.1 % (w/v) TMC/n-hexane:	Filtration mode: Cross-flow. Pressure: 2 bar. Temperature: 25 ± 0.2 °C. Salt concentration: 1000 ppm.	PS-OW: Nah PES-20 kDa: <u>30.4</u> PES-150 kDa: <u>67.5</u> PSH-100 kDa: 55.1 PESH-50 kDa: 46.6	PS-OW: Nah PES-20 kDa: Na ₂ SO ₄ ~90%. PES-150 kDa: Na ₂ SO ₄ ~90%. PSH-100 kDa: Na ₂ SO ₄ ~92%, MgSO ₄ ~55%. PESH-50 kDa: Na ₂ SO ₄ ~98.1%, MgSO ₄ ~78.3%.	[61]
Hydrophilic Polyethersulfone (PESH)	(60 mmol/L) 1-(2-aminoethyl) piperazine (AEP)	(16 mmol/L to 0.0625 mmol/L) TMC/n-hexane.	Filtration mode: Cross-flow. Pressure: 6 bar. Temperature: 25 °C.	AEP/TMC ratio = 15: 7.78	AEP/TMC ratio = 15: Na ₂ SO ₄ , and MgSO ₄ = 92%, and 88%	[62]

	(60 mmol/L) 1-(2-aminoethyl) piperazine (AEP)/Piperazine (PIP) Polyethyleneimine (PEI)		Salt concentration: 1000 ppm.	PIP/TMC ratio = 60: 7.50 PEI/TMC ratio = 3.75: 7	PIP/TMC ratio = 60: Na ₂ SO ₄ , and MgSO ₄ = 91%, and 80% PEI/TMC ratio = 3.75: Na ₂ SO ₄ , and MgSO ₄ = 75%, and 70%	
PES (18)-DMF	0.5% (w/v) PIP/PEI-xx/PDI-yy 0.5% (w/v) PIP/PEI-xx/HDI-yy 0.5% (w/v) PIP/PEI-xx/TDI-yy 0.5% (w/v) PIP/PEI-xx/MDI-yy Polyethyleneimine (PEI)	(1,4-phenylene diisocyanate) PDI-yy (Hexamethylene diisocyanate) HDI-yy (Toluene diisocyanate) TDI-yy (Diphenylmethane diisocyanate) MDI-yy	Filtration mode: Dead-End. Pressure: 2 bar. Temperature: ambient. pH: 6. Salt concentration: 2000 ppm.	PEI-0.1/PDI-0.2: 0.65	PEI-0.1/PDI-0.2: Both Na ₂ SO ₄ , and MgSO ₄ = 97.1%	[63]
PSF	PA-Br1 : 0.35% (w/v) Piperazine (PIP)/0.01 mol/L NaOH PA-PDMC : PA-Br/Methacryloxyethyltrimethyl ammonium chloride (DMC) with ATRP time (0.2, 0.5, 1.0, 3.0, and 8.0 h).	0.20% (w/v) 1,3,5-benzenetricarboxylic chloride (TMC)/1% (w/v) 2-Bromoisobutyl bromide (BIBB)/n-hexane	Filtration mode: Cross-flow Pressure: 6 bar Temperature: 25 °C Salt concentration: 1000 ppm.	PA-Br1 : 5.5 PA-PDMC _{0.5h} : 17	PA-Br : Na ₂ SO ₄ (98.1) > MgSO ₄ (89) > NaCl (54.2) > MgCl ₂ (35) PA-PDMC : Reduced significantly	[64]
PVDF – 100 nm From [25-450 nm]	0.1 - 1.5% (w/v) Piperazine hexahydrate (C ₄ H ₁₀ N ₂ ·6H ₂ O, 98%)	0.1% (w/v) TMC/n-hexane	Filtration mode: Cross-flow. Pressure: 5 bar. Salt concentration: 1000 ppm.	PIP _{1%} (w/v): 19.3	PIP _{1%} (w/v): Na ₂ SO ₄ = 98.0%	[50]
Polysulfone (PSF) (Pore size: 0–50 nm)	0.5 % (w/v) PIP/0-0.9% (w/v) dextran nanoparticles (DNPs) [Dextran10 (MW 10,000), dextran40 (MW 40,000), dextran70 (MW 70,000)]	0.1% (w/v) TMC/n-hexane	Filtration mode: Cross-flow. Pressure: 6 bar. Temperature: 25 °C. Salt concentration: 2000 ppm.	0.5% (w/v) DNPs 40T: 21.12 (2.2 x the pristine)	0.5% (w/v) DNPs 40T: Na ₂ SO ₄ = 98.4%.	[65]
PSF	0.5 % (w/v) Piperazine (PIP)/ 0,0.2, 0.6 ,1.0 and 2.0 % (w/v) 3,5-Diamino-1,2,4-triazole (GAZ)	0.1% (w/v) TMC/hexane	Filtration mode: Cross-flow Pressure: 6 bar. Temperature: 25 °C. pH: 7. Salt concentration: 1000 ppm.	0.6 % (w/v) GAZ: 30.5	Na ₂ SO ₄ (93.5) > MgSO ₄ (74%) Low monovalent ions rejection.	[66]
Polyacrylonitrile (PAN) (13)- P84 polymer (22)- Dimethylformamide (DMF)	1 % (w/v) PIP 1 % (w/v) Piperazine (PIP)/0.01 to 0.2% (w/v) m-phenylenediamine (MPD) with DMF activation	0.15% (w/v) TMC/hexane	Filtration mode: Cross-flow Pressure: 5 bar. Temperature: 25 ± 1 °C. Salt concentration: 2000 ppm.	PIP _{1%} -MPD _{0.1%} : 7.48 ± 1.1	Na ₂ SO ₄ : 99.27 % to 99.53%.	[67]

Table 2-2: The studies summary of thin-film composite membrane based on *m*-phenylenediamine (MPD) monomer.

Substrate	Monomer A	Monomer B	Testing conditions	Permeability Flux [$\frac{L}{m^2 \cdot h \cdot bar}$]	Salt rejection [%]	Reference
M0: PVC/PEG400/LiCl/ DMAc M1: M0/ HEMA (content wt.% 36.1) M2: M0/ HEMA (content wt.% 54.9)	1% (w/v) MPD/0.6% (w/v) Na ₃ PO ₄	0.05% (w/v) TMC/n-hexane	Filtration mode: Cross-flow. Pressure: 3 bar. Temperature: 25 °C. Salt concentration: 5 mmol/L.	TFC-0: 1.1 TFC-1: 0.63 TFC-2: 0.3	TFC-0: (Na ₂ SO ₄ : 90%). TFC-1: (Na ₂ SO ₄ : 95%) TFC-2: (Na ₂ SO ₄ : 99%)	[51]
PSF(16)-PVP(0.3)- DMAc PSF/MAAc PSF/Tac PSF/LAc	2% (w/v) <i>m</i> -phenylenediamine (MPD)	0.1% (w/v) TMC/n-hexane	Filtration mode: Cross-flow. Pressure: 7 bar. Temperature: 25 °C. pH: 7. Salt concentration: 2000 ppm.	1.12 2.4 2.64 2.89	PSF/Tac-TFC: MgSO ₄ , Na ₂ SO ₄ : 94.1% and 97%.	[48]
PVDF (18)- acetone/DMF (1:3 v:v)- Tetrabutylammoniu m chloride (TBAC)	2% (w/v) <i>m</i> -phenylenediamine (MPD)/2% (v/v) Triethylamine (TEA)/0.15% (w/v) Sodium dodecyl sulfate (SDS)	0.15% (w/v) TMC/acetone	Filtration mode: Dead-End. Pressure: 3.5 bar. Salt concentration: 2000ppm.	PA-TBAC-0.025: 2.69	Highest rejection in PA-TBAC-0.025, and PA-TBAC-0.03, where are approximately identical as follow: MgSO ₄ (>97%), NaCl (>75%)	[68]

Table 2-3: The studies summary of thin-film composite membrane based on Polyethyleneimine (PEI) monomer.

Substrate	Monomer A	Monomer B	Testing conditions	Permeability Flux [$\frac{L}{m^2 h bar}$]	Salt rejection [%]	Reference
PSF	(1 mg/mL) Polyethyleneimine (PEI)/(1 mg/mL) Catechol (CCh)/tris(hydroxymethyl) aminomethane buffer solution (pH:8.5, 10mM)	0.15% (w/v) TMC/n-hexane [Time Contact: 5-10-20-30 min]	Filtration mode: Cross-flow. Pressure: 7 bar. Temperature: 25 °C. pH: 5.8 ± 0.1. Salt concentration: 1000 ppm.	4.43	10 mins of CCh/PEI-TMC: MgCl ₂ (93.5 ± 0.9%) > MgSO ₄ (92.7 ± 0.9%) > Na ₂ SO ₄ (90.9 ± 1.0%) > CaCl ₂ (90.2 ± 0.7%) > NaCl (38.2 ± 1.0%).	[69]
PES	0.2–2.5% (w/v) Polyethyleneimine (PEI)	0.05–0.30% (w/v) Trimesic acid (TMA)/0.15% (w/v) Sodium dodecyl sulfate (SDS)/Equal volume of ethanol and deionized water	Filtration mode: Cross-flow. Pressure: 3 bar. Temperature: 25 ± 0.2 °C. Salt concentration: 1000 ppm.	PEI _{0.6} -TMA _{0.1} NF: 19.1	PEI _{0.6} -TMA _{0.1} NF: MgCl ₂ (93%) > NaCl (38.2%) > MgSO ₄ (20.4%) > Na ₂ SO ₄ (8.8%).	[70]
PSF	0.05–0.3% (w/v) Sulfonated Polyethyleneimine (SPEI) Degree of sulfonation (DS) = 0, 15.8 and 32.7% of PEI	TMC/cyclohexane	Filtration mode: Cross-flow. Pressure: 6 bar. Temperature: 25 °C. Salt concentration: 1000 ppm.	SPEI _{0.3} TFC: 20.9 TFC0: 5.78 TFC15: TFC 32.7: 46.1	SPEI _{0.3} TFC: Na ₂ SO ₄ (29.4%) > NaCl (5.5%) TFC0: Na ₂ SO ₄ (8.4%) > NaCl (3.2%) TFC15: Low rejection TFC 32.7: low rejection	[71]
PES-Pore size=20nm.	0.1% (w/v) Polyethyleneimine (PEI)/N, N-dimethylformamide (DMF). 0.1% (w/v) Polyethyleneimine (PEI)/0.1% (w/v) Perfluoro-1-butanefluoride (PFBSF)/N, N-dimethylformamide (DMF).	0.1% (w/v) TMC/n-hexane	Filtration mode: Cross-flow. Pressure: 6 bar. Salt concentration: 1000 ppm.	PA/PES NF: Nah FPA/PES NF: 1.8	PA/PES NF: Na ₂ SO ₄ (53%) > MgSO ₄ (81%) FPA/PES NF: Na ₂ SO ₄ (92.6%) > MgSO ₄ (71.6%)	[72]
PAN (15)-PEG 400 (2)-DMF	1% (w/v) PEI 1% (w/v) PEI/[0.25%,0.5%,1% (w/v)] of Zr-MOF (in nano-gel UiO-66-NH ₂)	0.15% (w/v) TMC/n-hexane	Filtration mode: Cross-flow. Pressure: 4 bar. Temperature: 25 ± 2 °C. Salt concentration: 2000 ppm.	TFC/PEI: 6 TFN/PEI-1: 21 TFN/PEI-2: 38 TFN/PEI-3: 40	TFC/PEI: Na ₂ SO ₄ (88%) < MgSO ₄ (92%) TFN/PEI-1: Na ₂ SO ₄ (80%) < MgSO ₄ (92%) TFN/PEI-2: Na ₂ SO ₄ (62.1%) < MgSO ₄ (88.1%) TFN/PEI-3: Na ₂ SO ₄ (48%) < MgSO ₄ (84%)	[73]

Table 2-4: The studies summary of thin-film composite membrane based on other monomer types.

Substrate	Monomer A	Monomer B	Testing conditions	Permeability Flux [$\frac{L}{m^2 \text{ h bar}}$]	Salt rejection [%]	Reference
PSF (19)-DMF	0.5,1,2,3% (w/v) Carboxylated aromatic diamine-diol (CDADO)/0.1% (w/v) Dodecyl sulfonic acid sodium (SDS) 2.5% (w/v) PIP/0.1% (w/v) Dodecyl sulfonic acid sodium (SDS) 0.2% (w/v) carboxylated diamine without hydroxyl groups (CDA) /0.1% (w/v) Dodecyl sulfonic acid sodium (SDS)	0.3% (w/v) TMC/n-hexane	Filtration mode: Cross-flow. Pressure: 10 bar. Salt concentration: 2000 ppm.	CDADO- 2% (w/v): 5.3	CDADO- 2% (w/v): Na ₂ SO ₄ (91%) > NaCl (70%) > CaCl ₂ (17%)	[74]
PES	1% (w/v) Tris(2-aminoethyl) amine (TAEA) 1.5% (w/v) TAEA 1.5% (w/v) TAEA	1% (w/v) HTeC (1,2,4,5-Cyclohexane tetracarboxylic acid/phosphorus pentachloride) 0.1% (w/v) BTC (cyclobutane tetracarboxylic/anhydride/PCl ₅) 0.1% (w/v) TMC	Filtration mode: Cross-flow. Pressure: 10 bar. Temperature: 25 °C. Salt concentration: 2000 ppm.	HTeC–TAEA: 7.67 BTC–TAEA: 6.82 TMC–TAEA: 7.73	HTeC–TAEA: MgCl ₂ (98.4%) > CaCl ₂ (98.0%) = MgSO ₄ (98.0%) > NaCl (78.8%) > Na ₂ SO ₄ (75.1%). BTC–TAEA: MgSO ₄ (99.0%) > MgCl ₂ (98.3%) > CaCl ₂ (98.0%) > Na ₂ SO ₄ (97.4%) > NaCl (52.1%). TMC–TAEA: MgSO ₄ (88.7%) > Na ₂ SO ₄ (85.2%) > MgCl ₂ (81%) > CaCl ₂ (79.2%) > NaCl (53.4%).	[75]
PES	Dopamine hydrochloride (DA)/N-methyl-Dglucamine (NMG)/Buffer solution (pH=8.5, 20mM Tris) DA/NMG/0.01, 0.1, 0.2 and 0.1% (w/v) Silica (SiO ₂)	0.3% (w/v) TMC/hexane	Filtration mode: Cross-flow. Pressure: 6 bar. Temperature: 25 ± 2 °C. Salt concentration: 1000 ppm.	M-0: 2.1 M-0.1: 4.72	M-0: Na ₂ SO ₄ (90%) > MgSO ₄ (80%) > NaCl (52%) > MgCl ₂ (19%) M-0.1: Na ₂ SO ₄ (92.1%) > MgSO ₄ (82%) > NaCl (49%) > MgCl ₂ (14%)	[76]
PES- carbon nanotube (CNT) interlayer	PMPD: 0.10-1.0% (w/v) 4-(piperazin-1-yl) benzene-1,3- diamine (PMPD) PMPD-PA: PMPD-1% (w/v) 3-bromopropionic acid (3-BPA) for 2 h	0.1% (w/v) TMC/hexane	Filtration mode: Cross-flow. Pressure: 5 bar. Temperature: 25 ± 0.5 °C. Salt concentration: 1000 ppm.	0.8% (w/v) PMPD: ~20.2 PMPD-PA: ~19	0.8% (w/v) PMPD: Na ₂ SO ₄ (97.2%) > MgSO ₄ (93%) > NaCl (21%) PMPD-PA: Na ₂ SO ₄ (98.4%) > MgSO ₄ (96%) > NaCl (24.1%)	[77]

Poly (<i>m</i> -phenylene isophthalamide) (PMIA) (17)-lithium chloride (LiCl) (5)-DMAc	0.5–3.0% (w/v) lysine	0.05–0.30% (w/v) TMC/n-hexane	Filtration mode: Cross-flow. Pressure: 2 bar. Temperature: 25 °C. Salt concentration: 1000 ppm.	18.4-58.8	15.15-54.91% (Na ₂ SO ₄) 12.8-19.20% (MgSO ₄) 3.96-10.20 % (MgCl ₂) 16.4-4.4% (NaCl)	[78]
PES	1,3,5,7% (w/v) 4,4'-diaminostilbene-2,2'-disulfonic acid (DSDA)/ 0, 0.05 , 0.1, 0.2, 0.3% (w/v) SDS	0.02, 0.04, 0.06, 0.08 % (w/v) TMC/n-hexane	Filtration mode: Dead-End. Pressure: 4 bar. Salt concentration: 10 mM.	DSDA ₅ /SDS _{0.1} -TMC _{0.04} : 10.0 ± 0.5	DSDA ₅ /SDS _{0.1} -TMC _{0.04} : Na ₂ SO ₄ (~97%), MgSO ₄ (90%)	[79]
PES	1% (w/v) 3-aminobenzenesulfonamide (ABSA)/0.2% (w/v) Sodium dodecyl sulfate (SDS)/0.2% (w/v) Triethylamine (TEA)	0.5% (w/v) TMC/n-hexane	Filtration mode: Dead-End. Pressure: 15 bar. Temperature: 25 ± 1 °C. Salt concentration: 1000 ppm.	12.4	Na ₂ SO ₄ rejection: 95%	[80]
PSf (16.5)-DI water (0.3)-SLS (0.3)- 1-Methyl-2-pyrrolidinone (NMP) (82.9)	1) 0.15% (w/v) Sodium dodecyl sulfate (SDS). 2) 0.05–0.25 (g/L) Terephthalic acid (TPA)/0.50, 1, 1.5% (w/v) Branched polyethyleneimine (BPEI)	0.10% (w/v) Cyanuric chloride (CC)/n-hexane	Filtration mode: Cross-flow. Pressure: 7 bar. Temperature: 25 °C. Salt concentration: 1000 ppm.	TPA _{0.15} -BPEI ₁ : 12.8	TPA _{0.15} -BPEI ₁ : Na ₂ SO ₄ rejection: 85.6%	[81]

2.3.2. Previous study of additives/surfactants on thin-film composite (TFC) membrane

The role of additives and surfactants was not studied extensively by researchers. Although limited studies suggested that including additives and surfactants in the PA TFC membrane formation would have a positive impact on the membrane performance. The presence of surfactant in the aqueous solution of amine would improve the membrane surface wettability, and polymerization efficiency between aqueous solution and organic solution in interfacial polymerization reaction [82]. Ang, Micah Belle, et al. [83] investigated different structures of surfactants on the thin-film composite membrane. Sodium dodecyl sulfate (SDS), Sodium octyl sulfate (SOS), and Sodium dodecyl benzenesulfonate (SDBS) are three surfactants that introduced separately in the aqueous solution of 0.8% (w/v) Polyethyleneimine (PEI). The investigation results concluded that Sodium dodecyl sulfate (SDS) exhibited highest the permeability flux, and salt rejection. On the other hand, Yu, Wen-Han, et al. [79] optimized the Sodium dodecyl sulfate (SDS) composition by preparing the aqueous solution of 4,4'-diaminostilbene-2,2'-disulfonic acid (DSDA) with varying the composition of Sodium dodecyl sulfate (SDS) from 0,0.05,0.1,0.2,0.3% (w/v). Also, the optimization was applied on 4,4'-diaminostilbene-2,2'-disulfonic acid (DSDA) (1,3,5,7% (w/v)), and Trimesoyl Chloride (TMC) (0.02,0.04,0.06,0.08 % (w/v)). The membrane performance was optimized at the interfacial polymerization reaction between aqueous solution of 5% (w/v) DSDA and 0.1% (w/v) SDS and organic solution of 0.04% (w/v) TMC. Other studies were reported in Tables 2-1, 2-2, 2-3, 2-4.

On the other side, an additive such as Triethylamine (TEA) plays a major role in neutralizing HCl produced during amide formation, promoting cross-linking to form polyamide (PA) layer

formation, and adjusting solution pH which impacts thin-film composite (TFC) membrane performance [83]. According to different studies conducted by different researchers with synthesizing thin-film composite (TFC) membrane by using different amine monomers (Piperazine (PIP), *m*-phenylenediamine (MPD), and 3-aminobenzenesulfonamide (ABSA)), equimolar between Triethylamine (TEA) and amine monomer resulted in acceptable permeability flux and higher salt rejection performance. These studies indicated that the amount of Sodium dodecyl sulfate (SDS) in an aqueous solution beside Triethylamine (TEA) is too critical on the thin-film composite membrane performance. So, the amount of each surfactant and additive should be appropriate [60, 72, 80]. These different studies suggested that an aqueous solution of amine concentration should be equimolar between used the amine monomer and additive such as Triethylamine (TEA), while the concentration of Sodium dodecyl sulfate (SDS) suggested to be low compared to the concentration of amine monomer such as 0.1% (w/v).

CHAPTER 3

Materials and Methods

3.1. Background

This chapter summarizes the list of chemical materials, solutions preparation, and thin-film composite fabrication procedures used in this research study. Also, surface membrane characterization tests (such as FTIR, FESEM, XRD, TGA, Contact Angles, and Zeta Potential), and membrane nanofiltration performance were summarized, and explained in this section.

3.2. Materials

Polysulfone (PSF, average Mw ~35,000 by LS, average Mn ~16,000 by MO, pellets (Transparent)), Polyvinylpyrrolidone (PVP, Average Molecule Weight of 10,000 g/mole) and N,N-dimethylacetamide (DMAc, puriss. p.a., ≥99.5% (GC), Molecular Weight = 87.12 g/mole) were purchased and provided by Sigma-Aldrich Company, Schnelldorf, Germany. Deionized (DI) water was produced by a lab-scale desalination unit at chemical department of King Fahad University of Petroleum and Minerals (KFUPM). n-Hexane (Molecular Weight = 86.18 g/mole) was purchased and delivered by Supelco, Inc Company, Bellefonte, Pennsylvania, United States.

Five different polyamines [Bis(3-aminopropyl) amine (BAPA, 98%, Molecular Weight = 131.22 g/mole), 1,2-Bis(3-aminopropylamino) ethane (1,2-BIS, technical grade, 94%, Molecular

Weight = 174.29 g/mole), m-Xylylenediamine (m-XDA, 99%, Molecular Weight = 136.19 g/mole), 1,4-Bis(3-aminopropyl) piperazine (DAPP, $\geq 99\%$, Molecular Weight = 200.32 g/mole), and Hexamethylenediamine (HMDA, 98%, Molecular Weight = 116.20 g/mole)] were purchased from Sigma-Aldrich Company, Schnelldorf, Germany. Other related chemicals [Triethylamine (TEA, $\geq 99\%$, Molecular Weight = 101.19), 1,3,5-Benzenetricarbonyl trichloride (Trimesoyl Chloride, TMC ,98%, Molecular Weight = 265.48 g/mole)] were also purchased from Sigma-Aldrich Company, Schnelldorf, Germany. Sodium dodecyl Sulfate (SDS (USP-NF, BP, Ph. Eur.) Pure, pharma grade, MW = 288.38 g/mol) was provided by PanReac Applichem ITw reagents, Darmstadt, Germany

3.3. Fabrication of thin-film composite (TFC) nanofiltration membranes

3.3.1. Preparation of PSF Porous Support

A PSF Porous Support membrane was used to manufacture the membrane. A microporous interlayer was made of polysulfone (PSF) polymers, and polyvinylpyrrolidone (PVP). The PSF membrane was prepared by the wet phase inversion method [55, 48, 84]. The polysulfone (PSF) polymer was dried in the vacuum oven (manufactured and supplied by MTI Corporation, Richmond, CA, USA) overnight. N,N-Dimethylacetamide (DMAc) was used as a solvent. 15% wt. of polysulfone (PSF) polymer solution was prepared by transferring 3 grams into 250 ml Erlenmeyer Flask. 16.2 grams of N,N-Dimethylacetamide (DMAc), and 0.8 g of polyvinylpyrrolidone (PVP) were added to the PSF polymer. 15 wt. % PSF, 4 wt. % PVP, and 81 wt. % DMAc were the result of the casting solution composition.

The casting solution was prepared inside a fume hood using a hot plate at 40 °C with continuous stirring for 24 hours. The solution was left for another 24 hours to release all bubbles. The glass was rinsed with the solvent (N,N-Dimethylacetamide, DMAc, $\geq 99.5\%$) to avoid blocking pores during casting. The membrane casting machine was washed and dried from deionized water. The polysulfone (PSF) polymer solution was cast with 100 μm thickness on the glass by using a micrometer adjustable film applicator (manufactured and supplied by MTI Corporation, Richmond, CA, USA). The glass with casting film was immersed in the deionized water bath for 10 minutes under ambient conditions. After the membrane was formed, it was placed into a beaker of deionized water overnight. The obtained PSF support was washed with deionized water several times and then stored in deionized water at ambient conditions.

3.3.2. Preparation of the aqueous and the organic solutions

Both an aqueous solution and the organic solution were prepared separately. In an aqueous solution, five different polyamines were used to do the preparation separately. Figure 3-1 showed the used five different polyamines in this research, which are Bis(3-aminopropyl) amine (BAPA), 1,2-Bis(3-aminopropylamino) ethane (1,2-BIS), m-Xylylenediamine (m-XDA), 1,4-Bis(3-aminopropyl) piperazine (DAPP), and Hexamethylenediamine (HMDA). In addition to the main polyamine, Triethylamine (TEA), Sodium dodecyl sulfate (SDS), and Deionized (DI) water were used to have the aqueous solution. 2 grams of the main Polyamine, 2 grams of Triethylamine (TEA), 0.1 grams of Sodium dodecyl sulfate (SDS), and 96 grams of deionized (DI) water. The resulting weight fraction compositions of aqueous solution were 2 wt. %, 2 wt. %, 0.1 wt. %, and 95.9 wt. % respectively. The aqueous solution was mixed by using Analog Magnetic Hotplate Stirrer (manufactured by SCILOGEX Company, Rocky Hill, CT, United States). The pH value of

each aqueous solution was suggested to be basic where which would be beneficial for neutralizing produced HCl during interfacial polymerization (IP) reaction [82], where each aqueous solution pH value is recorded in Table 3-1.

Table 3-1: pH values of each aqueous solution of polyamine, along with its component weight percentage.

Aqueous Solution	Polyamine Name	Polyamine wt. %	Triethylamine (TEA) wt. %	Sodium dodecyl Sulfate (SDS) wt. %	Deionized (DI) water wt. %	pH
1	BAPA	2	2	0.1	95.9	12.153
2	1,2-BIS	2	2	0.1	95.9	12.107
3	m-XDA	2	2	0.1	95.9	11.906
4	DAPP	2	2	0.1	95.9	12.018
5	HMDA	2	2	0.1	95.9	12.217

The organic solution was prepared by using 0.2 wt. % 1,3,5-Benzenetricarbonyl trichloride (TMC) in an n-Hexane solvent. The preparation duration was 6 hours using Analog Magnetic Hotplate Stirrer (manufactured by SCIOLOGEX Company, Rocky Hill, CT, United States).

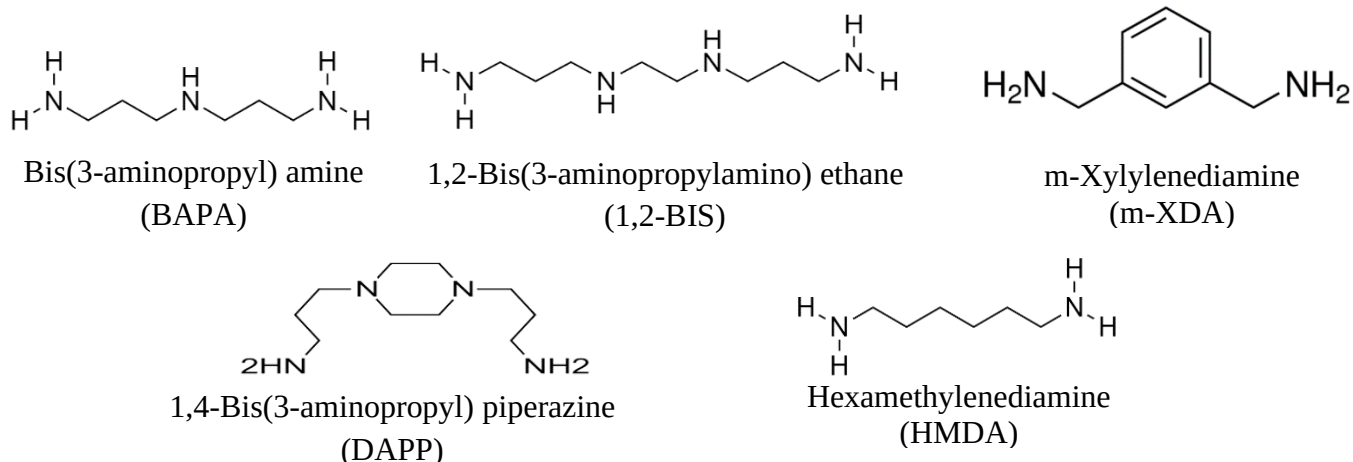


Figure 3-1: Chemical structure of used polyamines in this research study.

3.3.3. Synthesizing thin-film composite nanofiltration membranes

Thin-film composite nanofiltration membrane was synthesized by using the interfacial polymerization (IP) method. The interfacial polymerization (IP) method is one of the famous

fabrication methods in polymer membranes. TFC membranes were fabricated similarly to many previous literatures [85,86]. Figure 3-2 showed the schematic diagram of TFC membrane synthesis.

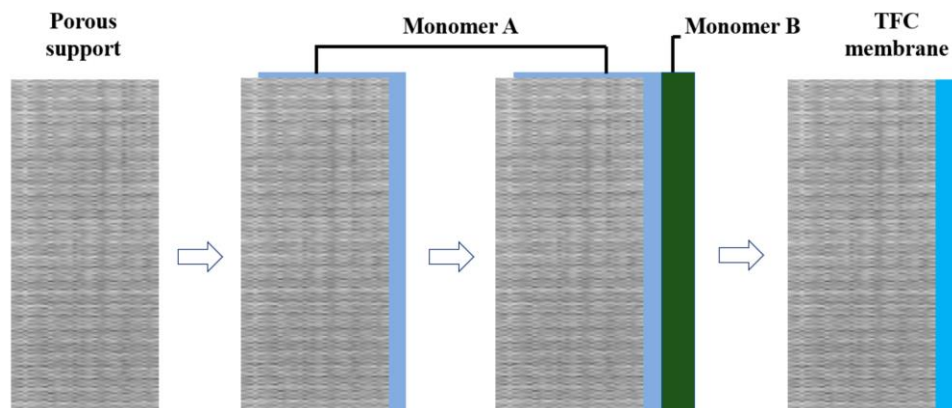


Figure 3-2: The schematic diagram of TFC membrane synthesis [37].

A PSF microporous membrane was soaked in it for 5 minutes. The treated PSF membrane was transferred to a cleaned glass surface to remove the excess aqueous solution by using a rubber roller. A treated microporous membrane was interfacially polymerized by using the organic solution (0.2 wt. % TMC), and soaked for 2 minutes. After completing the reaction, the membrane was rinsed by using hexane solvent to remove any residual reagents. The membrane was cured in an oven at 65 °C for 5 minutes. Then, the membrane was stored in deionized (DI) water for further use and tests.

Five different TFC membranes were synthesized with the same procedure, weight fractions, time duration, and same organic solution (TMC solution was used in this study). The used polyamines were Bis(3-aminopropyl) amine (BAPA), 1,2-Bis(3-aminopropylamino) ethane (1,2-BIS), m-Xylylenediamine (m-XDA), 1,4-Bis(3-aminopropyl) piperazine (DAPP), and Hexamethylenediamine (HMDA). Figure 3-3 showed the interfacial polymerization reaction

between 1,2-Bis(3-aminopropylamino) ethane (1,2-BIS) and 1,3,5-Benzenetricarbonyl trichloride (TMC), where n and m are the polymerization chain number, and x is the stoichiometry number. Also, Figure 3-4 showed the reaction mechanism between 1,2-Bis(3-aminopropylamino) ethane (1,2-BIS) and 1,3,5-Benzenetricarbonyl trichloride (TMC) with the presence of triethylamine (TEA). The rest of the polyamide followed both reaction mechanisms in Figure 3-2 and 3-3 with changing amine monomer, where Table 3-2 summarized them.

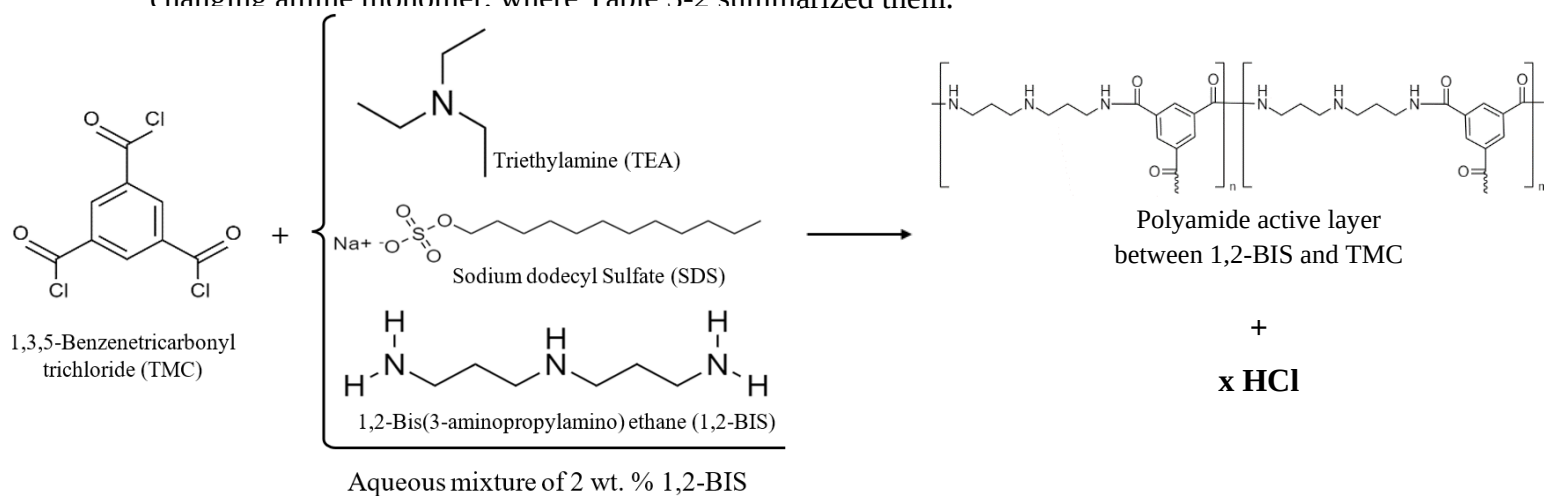


Figure 3-3: Interfacial polymerization (IP) reaction between 1,2-Bis(3-aminopropylamino) ethane (1,2-BIS) and 1,3,5-Benzenetricarbonyl trichloride (TMC) in the presences of SDS and TEA [87].

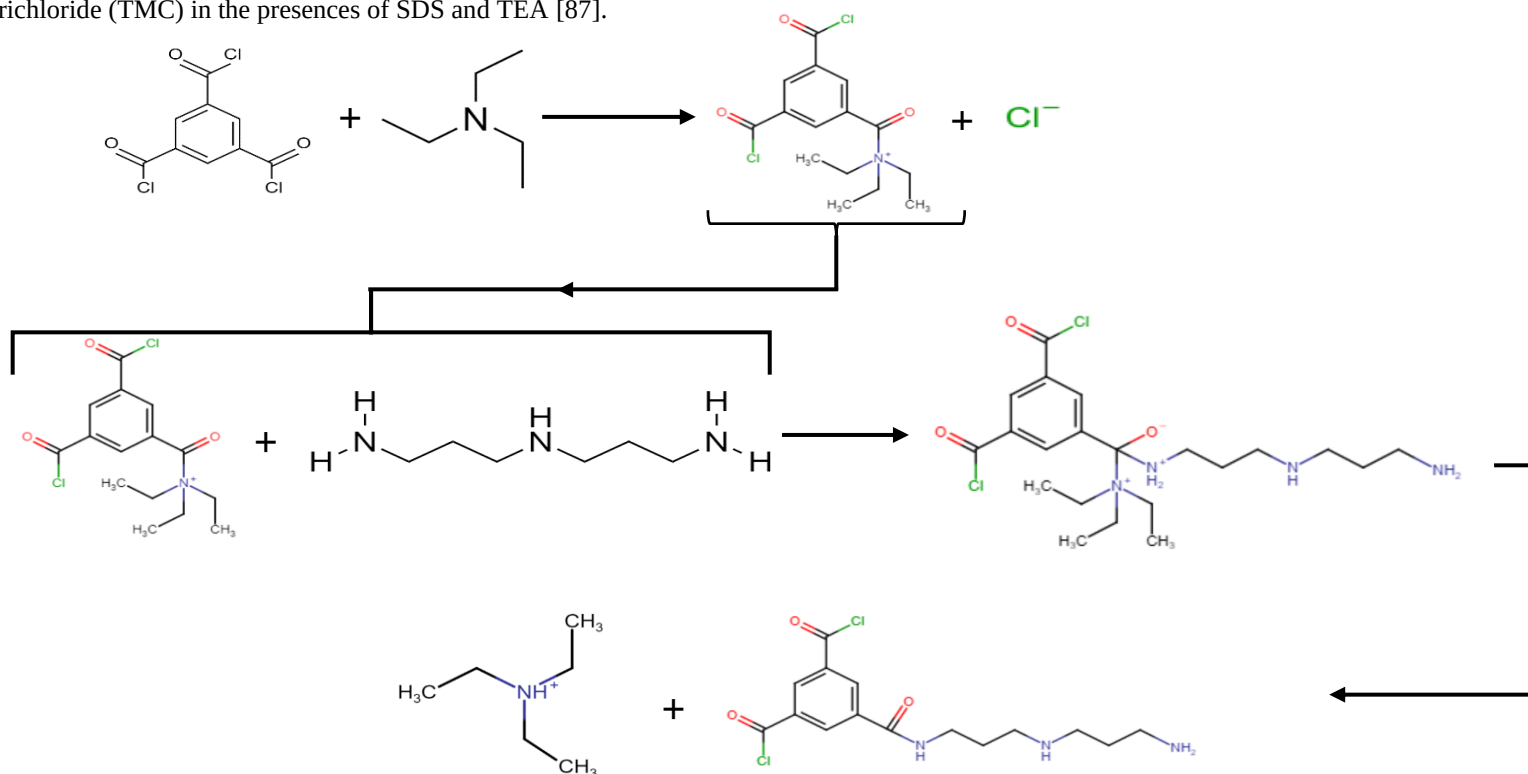


Figure 3-4: The reaction mechanism between an acyl chloride (TMC), and amine (1,2-BIS) and with the presence of triethylamine (TEA) [88].

Table 3-2: The structure of resulted polyamines (PA) based on the interfacial polymerization (IP) reaction between an acyl chloride monomer and amine monomer [87].

TFC Membrane Name	Amine monomer	Acyl chloride monomer	Polyamines (PA) Active layer
BAPA TFC	Bis(3-aminopropyl) amine	1,3,5-Benzenetricarbonyl trichloride (TMC)	
1,2-BIS TFC	1,2-Bis(3-aminopropylamino) ethane		
m-XDA TFC	m-Xylylenediamine		
DAPP TFC	1,4-Bis(3-aminopropyl) piperazine		
HMDA TFC	Hexamethylenediamine		

3.4. Characterization of membranes

3.4.1. Fourier-transform infrared spectroscopy (FTIR)

The membrane - coated and non-coated - functional groups were investigated by using Fourier-transform infrared spectroscopy (FTIR) with smart iTR™ attenuated total reflectance (ATR) sampling mode (NICOLET iS10, Thermo Fisher Scientific Company, Waltham, Massachusetts, United States). The spectra were measured in the 4000–400 cm^{-1} region with a resolution of 32 cm^{-1} for 64 scans. Prior FTIR analysis, the membrane samples were dried by putting them in the

vacuum oven (manufactured and supplied by MTI Corporation, Richmond, CA, USA) for 24 hours at 55° C.

3.4.2. Energy Dispersive X-Ray Analyzer (EDX or EDS)

An elemental and quantitative compositional of membranes - coated and non-coated - were identified by using an energy dispersive X-Ray analyzer (EDX or EDS), which is part of a field emission scanning electron microscope (FESEM, TESCAN LYRA3, Brno – Kohoutovice, Czech Republic) instrument. The same samples used in a field emission scanning electron microscope characterization are the same ones that were used in these characterization tests with the same drying and sputtering pre-testing process.

3.4.3. Field Emission Scanning Electron Microscope (FESEM)

The surface morphology of the membrane was observed using a field emission scanning electron microscope (FESEM, TESCAN LYRA3, Brno – Kohoutovice, Czech Republic) with electron-beam energy of 20 kV. The coated and non-coated membrane samples were dried, and sputtered under vacuum with an ultrathin layer made of gold (Au) as conducting material.

3.4.4. X-ray powder diffraction (XRD)

XRD patterns of coated and non-coated membranes were examined by using a benchtop powder x-ray diffraction (XRD) instrument (MiniFlex 600, Rigaku). Crystalline impurities, amorphous materials, and other things that might be affecting the structure can be identified in the respective spectrum by using this characterization test. X-ray diffraction test was performed with

a diffraction angle (θ) of 5° to 90° with 0.02° as a step angle and a speed of $2^\circ/\text{min}$ under a voltage of 40 kV and a 15 mA amperage.

3.4.5. Thermogravimetric Analysis (TGA)

The thermal resistance and stability of coated and non-coated membranes were examined by using thermogravimetric analysis (TGA) (SDT Q600 TA-Instruments, New Castle, DE, USA). The analysis was conducted in the temperature range of $22\text{--}800^\circ\text{C}$ with heating rate, and nitrogen flow rate conditions as follow $10 \frac{^\circ\text{C}}{\text{min}}$, and $100 \frac{\text{ml}}{\text{min}}$ respectively. The analyzed membranes were dried in the vacuum oven (manufactured and supplied by MTI Corporation, Richmond, CA, USA) overnight at 55°C .

3.4.6. Contact Angles (CA)

Membrane Wettability was observed using a Water Contact Angle Measurement System (Biolin Scientific Attension, Gothenburg, Sweden). Deionized water was used in a motor-driven micro-syringe to evaluate the hydrophilicity of a dry membrane surface at ambient conditions. The measurement of contact angles was taken shortly after drop formation on the surface at different locations in each type of membrane either coated or not. Then, the average values were reported.

3.4.7. Zeta Potential

The surface charge measurements of 1,2-BIS TFC membrane were determined by using the Malvern Zetasizer Nano ZS, Zen3600, where the surface characterization was performed by using an electrokinetic analyzer at the temperature of 25°C . An electrolyte solution, containing the tracer

particles (recommended negatively charged polystyrene beads in the Malvern transfer standard **DTS1235 or SDS solution**), with a pH range of 2-11 was contacted with the membrane surface during the analyzing process. Prior to sample analysis, a membrane sample is soaked in Deionized (DI) Water for a day to remove unreacted monomer. The surface zeta potential was calculated using the extrapolation approach, applying the following formula:

$$\text{Surface zeta potential} = - \text{intercept} + \text{tracer zeta potential}$$

where the tracer zeta potential is recorded far from the wall.

3.5. Performance Evaluation of the TFC Membranes

3.5.1. Laboratory Experimental set-up

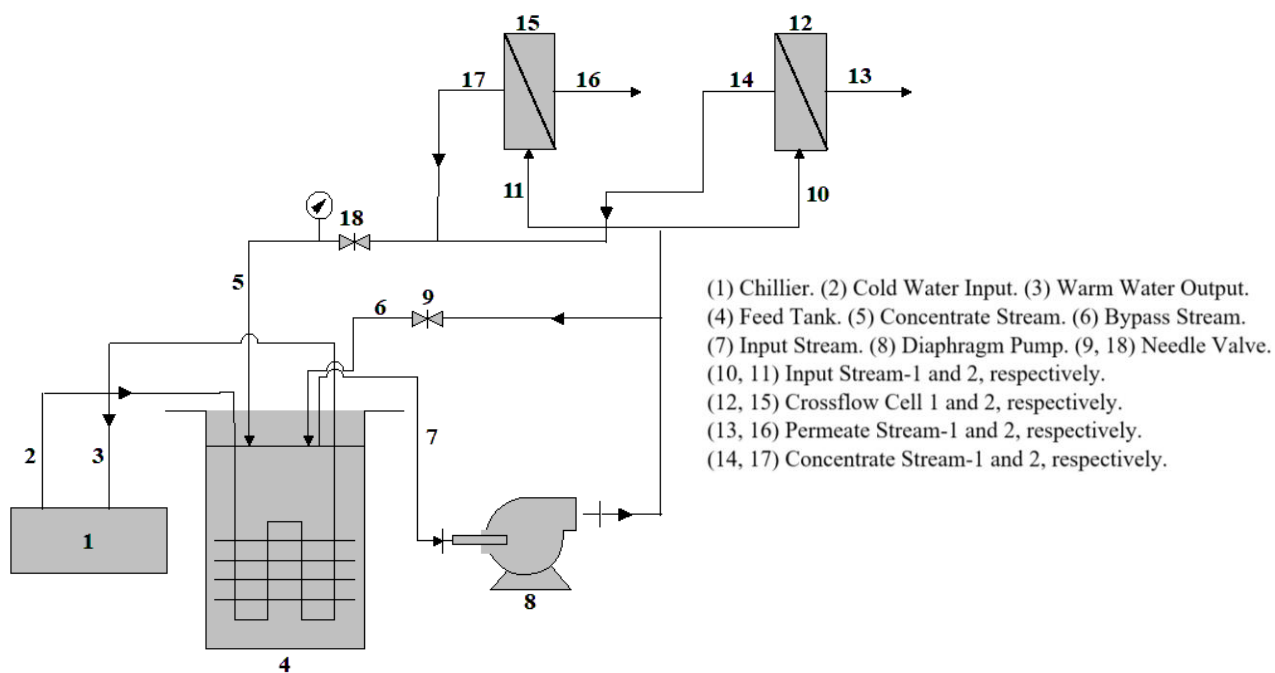


Figure 3-5: Schematic diagram of the laboratory experimental set-up.

The laboratory experimental set-up consisted of a diaphragm pump (Serial Number of M03SAGSNSCA, hydra-cell pump, Minneapolis, MN, USA), and two parallel crossflow membrane cells (CF016, Sterlitech Corporation Company, Kent, WA, USA). Each membrane cell

had an effective area of 16 cm². A chillier (refrigerating Circulator Water Bath) (Proline RP-1845 PL1 PCA, Lauda Dr. R. Wobser GmbH & Co. KG, Lauda-Königshofen, Germany) was used to manage the feed tank temperature. The pH and temperature of the feed tank were observed and recorded by the portable pH/EC/TDS/Temperature Meter (HI9811-5, Hanna Instruments, Woonsocket, RI, USA). The input stream was connected to both cross-cell modules via a diaphragm pump. Two needle valves were used to manage the Bypass and Concentrate streams, which resulted in transmembrane pressure. The permeate sample was collected through Permeate streams 1 and 2 over a recorded time duration. Also, the permeate conductivity of both streams was measured by the edge® Dedicated Conductivity/TDS/Salinity Meter (HI2003-01, Hanna Instruments, Woonsocket, RI, USA). A schematic diagram of the laboratory experimental set-up is shown in Figure 3-5.

3.5.2. Membrane Compaction

Prior to sampling, the membranes were compacted with deionized (DI) water for one hour at a transmembrane pressure of 30 bar, which is the same as the maximum operating pressure in this study. The compaction process was observed by the visual comparison between the initial deionized (DI) water flux and deionized (DI) water flux after time. The Compaction process was completed after reaching a steady flow rate.

3.5.3. Experimental Procedure

Permeate flux and salts rejection were measured using the laboratory experimental set-up of the crossflow filtration system as described previously (See Figure 3-5). Coated and non-coated

membranes were characterized at different operating pressure (10 bar, 20 bar, and 30 bar). The feed tank was maintained at a temperature of $22^{\circ}\text{C} \pm 1^{\circ}\text{C}$, and a pH of 7 ± 0.5 with a fully closed bypass stream. Deionized (DI) water, 1000 ppm MgSO_4 solution, and 1000 ppm NaCl solution were used as feed aqueous solutions respectively to create the standard curve of permeate flux, and salts rejection at different operating pressure. Deionized (DI) water was used for system rinsing and cleaning before and after using salt solution.

Five different coated membranes (BAPA TFC, 1,2-BIS TFC, m-XDA TFC, DAPP TFC, and HMDA TFC) were characterized with Deionized (DI) water, 1000 ppm MgSO_4 solution, and 1000 ppm NaCl solution once. Then the best experiment performance of one of the coated membranes was replicated twice in addition to the non-coated membrane (PSF membrane). All flux and rejection measurements were collected after 15 minutes of running the crossflow experiment to ensure stability and steady-state status. Permeate flux, and salt rejection were measured three times at each operating pressure by using a timer at every 10 ml of collected permeate sample, results of which have been averaged. The permeate flux (J), and salt rejection (R) were calculated by using the following equations:

$$J \left(\frac{\text{L}}{\text{m}^2\text{h}}, \text{LMH} \right) = \frac{\Delta V}{A \Delta t} \quad \text{Eq (1)}$$

where ΔV is the permeate volume (L), Δt is the time duration (h), and A is the effective membrane area (m^2). C_F , and C_P are the concentration of feed tank and permeate sample, respectively.

$$R (\%) = \frac{C_F - C_P}{C_F} \times 100 \quad \text{Eq (2)}$$

The best performance of coated membranes at feed tank temperature of 22°C, and pH of 7 with a fully closed bypass stream was further investigated with changing different operating conditions. The permeate flux and rejection of coated membrane were analyzed at different feed tank temperatures (22°C, 30°C, 35°C, and 40°C) at each pH value of the feed tank (3, 7, and 10) by using 1000 ppm NaCl solution, and 1000 ppm MgSO₄ solution separately. Different operating pressures (10 bar, 15 bar, 20 bar, 25 bar, and 30 bars) at each pH value of the feed tank (3, 7, and 10) of both saline solutions separately were performed experimentally at the best feed tank temperature performance (based on the previous experiments) to study the effects on the permeate flux and rejection. The effect of cross-flow velocity ($\frac{m}{s}$) on the permeate flux and rejection was studied at the best system conditions of transmembrane pressure, feed tank temperature, and feed tank pH. The needle valve controlling the bypass stream was used to reduce the cross-flow rate going to membrane cell modules. The bypass flow rate was calculated by collecting the sample of bypass over time duration, and the cross-flow rate was determined by material balance as follows:

$$F = P + C + B \quad \text{Eq (3)}$$

Where F is the feed input (L/h), P is the permeate flow rate (L/h), C is the concentrate flow rate (L/h), and B is the bypass flow rate (L/h). Then, the cross-flow velocity was calculated by dividing the cross-flow rate over the flow cross-sectional area ($0.23 \times 3.9 \text{ cm}^2$) by taking into consideration the appropriate unit conversion.

CHAPTER 4

Results and Discussion

4.1. Background

This chapter discusses different results were affected by using five different amine monomers [Bis(3-aminopropyl) amine (BAPA), 1,2-Bis(3-aminopropylamino) ethane (1,2-BIS), m-Xylylenediamine (m-XDA), 1,4-Bis(3-aminopropyl) piperazine (DAPP), and Hexamethylenediamine (HMDA)] in this research study. These results were produced and generated by using different characterization tests, such as Fourier-transform infrared spectroscopy (FTIR), Energy Dispersive X-Ray Analyzer (EDX or EDS), Field Emission Scanning Electron Microscope (FESEM), X-ray powder diffraction (XRD), Thermogravimetric Analysis (TGA), Contact Angles (CA), Zeta Potential, and Nanofiltration performance Evaluation.

4.2. Characterization of chemical structure and composition of membranes

The chemical structure and quantitative compositional of membranes were verified by using Fourier-transform infrared spectroscopy (FTIR), and an energy dispersive X-Ray analyzer (EDX or EDS). Figure 4-1 (See Figure A-2 in the appendix for more detailed figures) shows the comparison between FTIR spectra for the PSF support layer, and PA composite layers (BAPA, 1,2-BIS, M-XDA, DAPP, and HMDA), while Table 4-2 summarizes the individual atomic percentage that appears on each membrane surface.

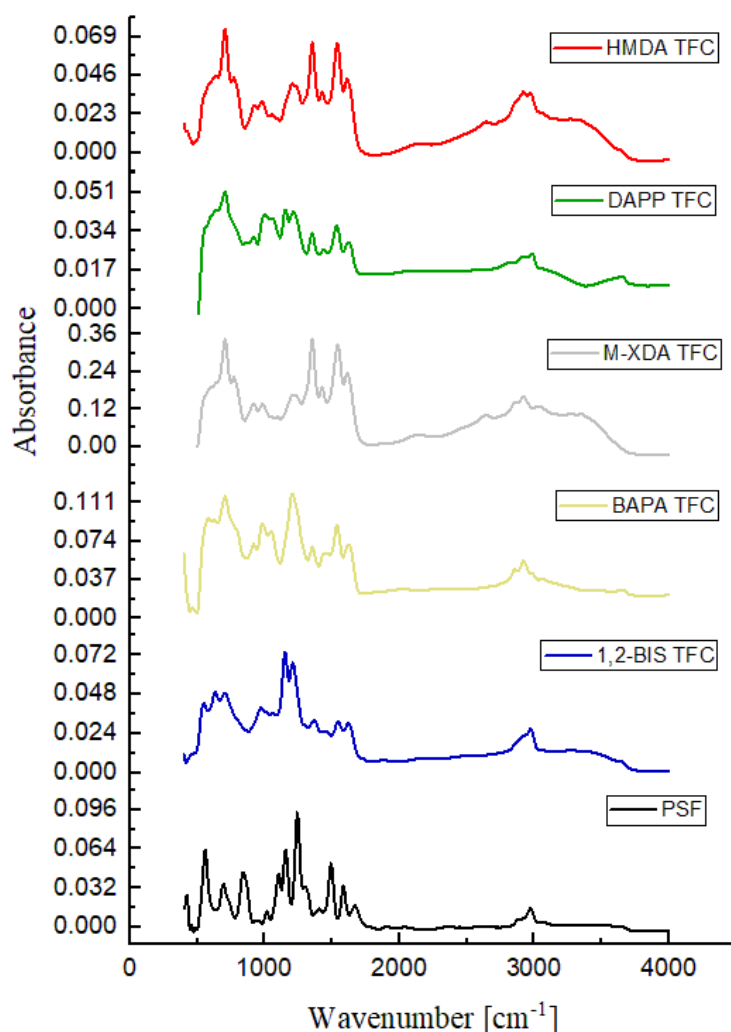


Figure 4-1: FTIR spectra of PSF support layer, and five different active layers of polyamide (PA) that interfacial polymerized with 0.2% (w/v) TMC with the presence 2% (w/v) TEA, and 0.1% (w/v) SDS in an aqueous solution.

The PSF support layer exhibited typical absorption peaks of aromatic rings stretching at 1585 cm^{-1} , while the $\text{CH}_3\text{—C—CH}_3$ stretching was found at 1493 cm^{-1} [89-91]. Also, C-O-C was identified at the wavenumber of 1242 cm^{-1} with high intensity compared to other peaks [92,93]. Symmetric and asymmetric O=S=O stretching of the support layer was located at 1153 cm^{-1} , and 1300, respectively [94]. In addition, the primary Amide group was observed in spectra at 1670 cm^{-1} due to the presence of polyvinylpyrrolidone (PVP) in the support layer preparation [95].

On the other five different PA composite layers, Nitro functional groups were observed in different wavenumber locations due to different used polyamines in this study. The common behavior found in their spectra was overlapping between N—H bending and C—N stretching due to the similar wavenumber range, where literature suggests that they are located between 1540-1554 cm^{-1} , and 1537-1590 cm^{-1} , respectively [95-97]. Also, Aromatic ring breathing C_6H_6 and C=O stretching share a close wavenumber range of 1600-1610 cm^{-1} , and 1620-1662 cm^{-1} , respectively which makes each of these peaks hard to distinguish [95,98]. The Band Signal of Carboxylic acid, O—H stretching was found in the five different PA composite layers with different intensities in the range of 3200-3600 cm^{-1} , while O-H bending was observed in approximately close to 1450 cm^{-1} [95,97,99-102]. The strong peak before O-H bending was exhibited due to the presence of S=O in the used surfactant (SDS, Sodium dodecyl Sulfate) in an aqueous mixture of polyamide. Its peak was observed approximately close to 1365 cm^{-1} [96].

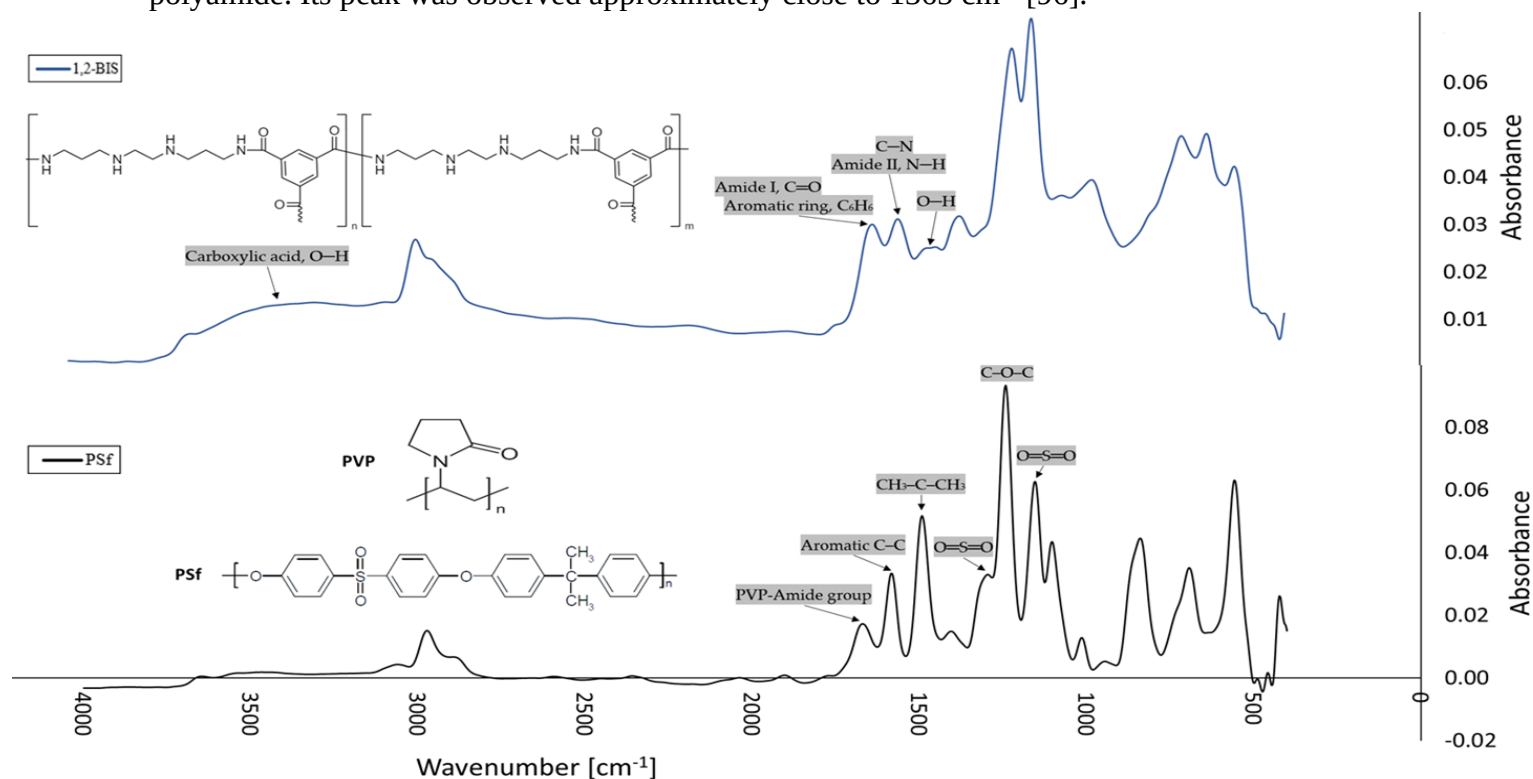


Figure 4-2: FTIR spectra comparison between PSf support layer, and 1,2-BIS PA layer, where the presented functional groups in both indicated. The PSf support layer was prepared with 81% (w/v) DMAC, and 4% (w/v) PVP, and 1,2-BIS PA was prepared by interfacial polymerization between aqueous solution of 2% (w/v) 1,2-BIS, 2% (w/v) TEA, and 0.1% (w/v) SDS and organic solution of 0.2% (w/v) TMC.

In the PA layer of 1,2-BIS, the strong band peak at 1547 cm^{-1} shown in Figure 4-2 is ascribed to either or both amide II (N—H bending), and C—N stretching. Also, amide I (C=O stretching), and aromatic ring breathing (C_6H_6) have a possibility to share the same peak shown at a wavenumber of 1620 cm^{-1} . Carboxylic acid, O—H stretching, O—H bending, and S=O of surfactant were observed at 3360 cm^{-1} , 1439 cm^{-1} , 1369 cm^{-1} respectively. Table 4-1 summarizes the major peaks of five different PA composite layers, which share the same explained pattern of 1,2-BIS PA layer with roughly different wavenumber locations.

The presence of amide I, and II with the aromatic ring in 1,2-BIS PA composite layer are strong evidence of successful interfacial polymerization (IP) between the aqueous mixture of 1,2-BIS and organic solution of TMC, where the acrylamide functional group (—NHCO— bond) formed as result. Also, the C—N—H group was suggested to form due to the coupling of in-plane N—H bending and C—N stretching. In addition to these results, the absence of acyl chloride peak at $1760\text{--}1770\text{ cm}^{-1}$ (See Figure A-1 in the appendix for FTIR spectra of TMC) confirms the formation of the PA layer as a result of the IP reaction.

Table 4-1: Major Peak Characteristics of PA composite Layers.

Peak Assignment	PA composite layers				
	BAPA	1,2-BIS	M-XDA	DAPP	HMDA
amide II (N—H bending), and C—N stretching	1539 cm^{-1}	1547 cm^{-1}	1547 cm^{-1}	1535 cm^{-1}	1543 cm^{-1}
amide I (C=O stretching), and aromatic ring breathing (C_6H_6)	1632 cm^{-1}	1620 cm^{-1}	1612 cm^{-1}	1628 cm^{-1}	1616 cm^{-1}
Carboxylic acid, O—H stretching	3336 cm^{-1}	3360 cm^{-1}	3360 cm^{-1}	3309 cm^{-1}	3360 cm^{-1}
O—H bending	1466 cm^{-1}	1439 cm^{-1}	1427 cm^{-1}	1439 cm^{-1}	1431 cm^{-1}
S=O of surfactant	1346 cm^{-1}	1369 cm^{-1}	1350 cm^{-1}	1346 cm^{-1}	1350 cm^{-1}

Table 4-2: Elements detected by EDX of PSF support layer, and five different active layers of polyamide (PA).

Atomic [%]	C [%]	O [%]	S [%]	Cl [%]	Total [%]
PSF	76.95	21.87	1.19		100
BAPA	84.07	13.15	2.72	0.06	100
1,2-BIS	81.43	16.74	1.77	0.06	100
M-XDA	85.65	11.75	2.61		100
DAPP	79.11	19.01	1.81	0.07	100
HMDA	83.47	14.1	2.43		100

Table 4-2 shows the main elements of PSF membrane, and TFC membranes as seen from the EDX spectrum (See figure 4-3 of PSF and 1,2-BIS TFC membrane, and other TFC membranes spectrum in the appendix figures A-3, A-4, A-5, A-6, A-7, and A-8). Carbon (C), Oxygen (O), and Sulfur (S) are the main elements in the PSF membrane, while TFC membranes share the same PSF membranes' main elements with additional Nitrogen (N). The nitrogen (N) element is not detected in this spectrum due to lower concentration compared to Carbon (C) and Oxygen (O). The presence of Chloride (Cl) atoms in TFC membranes are either due to remaining uncross-linked of TMC with a polyamine or remaining salts on the membrane surface. The atomic percentage of carbon and sulfur increased as the thickness of the membrane increased with interfacial polymerization (IP) of PA layer on the PSF membrane. This confirms the PA layer is present on the top of the membrane. The Atomic percentage of sulfur was increased due to the presence of surfactant (SDS, Sodium dodecyl Sulfate) in an aqueous mixture of polyamide.

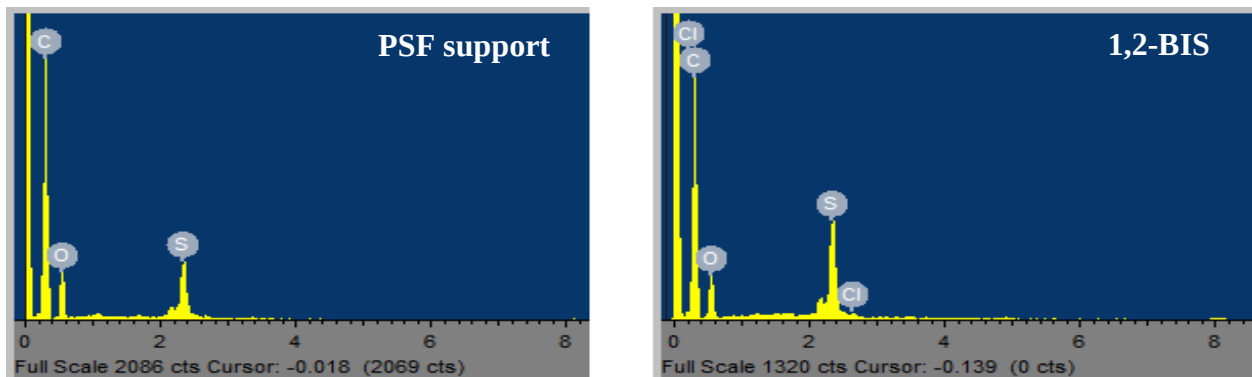


Figure 4-3: EDX Analysis Results of PSF support layer (left figure), and 1,2-BIS TFC membrane (Right figure).

4.3. Membrane morphology

The surface morphologies of the PSF support layer, and fabricated membranes with PA composite layers (BAPA, 1,2-BIS, M-XDA, DAPP, and HMDA) were investigated using a field emission scanning electron microscope (FESEM). Figure 4-4 illustrates the membrane surface FESEM morphologies with a scale of 500 nm. As shown in Figure 4-4, the PSF support layer is distinguished as an asymmetric structure with nonuniform pores distributed on the surface. The higher formation of pore size in the PSF support layer is mainly because of the polyvinylpyrrolidone (PVP) presence in the casting solution [103-105]. The pores support layer of PSF was covered by a polyamide layer in the interfacial polymerization (IP) process as it showed in Figure 4-4. The surface morphology difference is caused by different types of amines used in aqueous mixture preparation [106]. These differences were attributed to different amine monomers used in this study, which were classified as aliphatic compounds, and aromatic compounds. Even each type had different subclassification as per short or long chain as it showed previously in Figure 3-1, and Table 3-2 in the previous section of 3.3.2. Aliphatic compounds of Bis(3-aminopropyl) amine (BAPA), 1,2-Bis(3-aminopropylamino) ethane (1,2-BIS), and Hexamethylenediamine (HMDA) were contributed to smooth and firm PA layer, while the aromatic compounds of m-Xylylenediamine (M-XDA), and 1,4-Bis(3aminopropyl) piperazine (DAPP) affected altering the PA layer surface due to bulky structure [53,107-111]. The five different fabricated membranes with different amines were successfully deposited as revealed in the FESEM images, with a defect-free PA layer.

Also, the presence of surfactant (SDS, Sodium dodecyl Sulfate) and additive (TEA, Triethylamine) in an aqueous mixture of polyamide affect the PA layer as it caused cracks in the

PA layer, and facilitate the amine monomer diffusion rate into the organic solution respectively. TEA is more nucleophilic - compared to other amines - towards the carbonyl group in 1,3,5-Benzenetricarbonyl trichloride (TMC). So, the acylation of amines by TMC is faster in the presence of TEA, and avoiding violent reactions might occur between amine and acyl chloride [112-114]. In addition, adding surfactant helps to enhance the cross-linking between two monomers in the PA layer [88,115-116]. Both SDS and TEA help to improve the overall membrane performance compared without or with one of them [61,73,81,116,118].

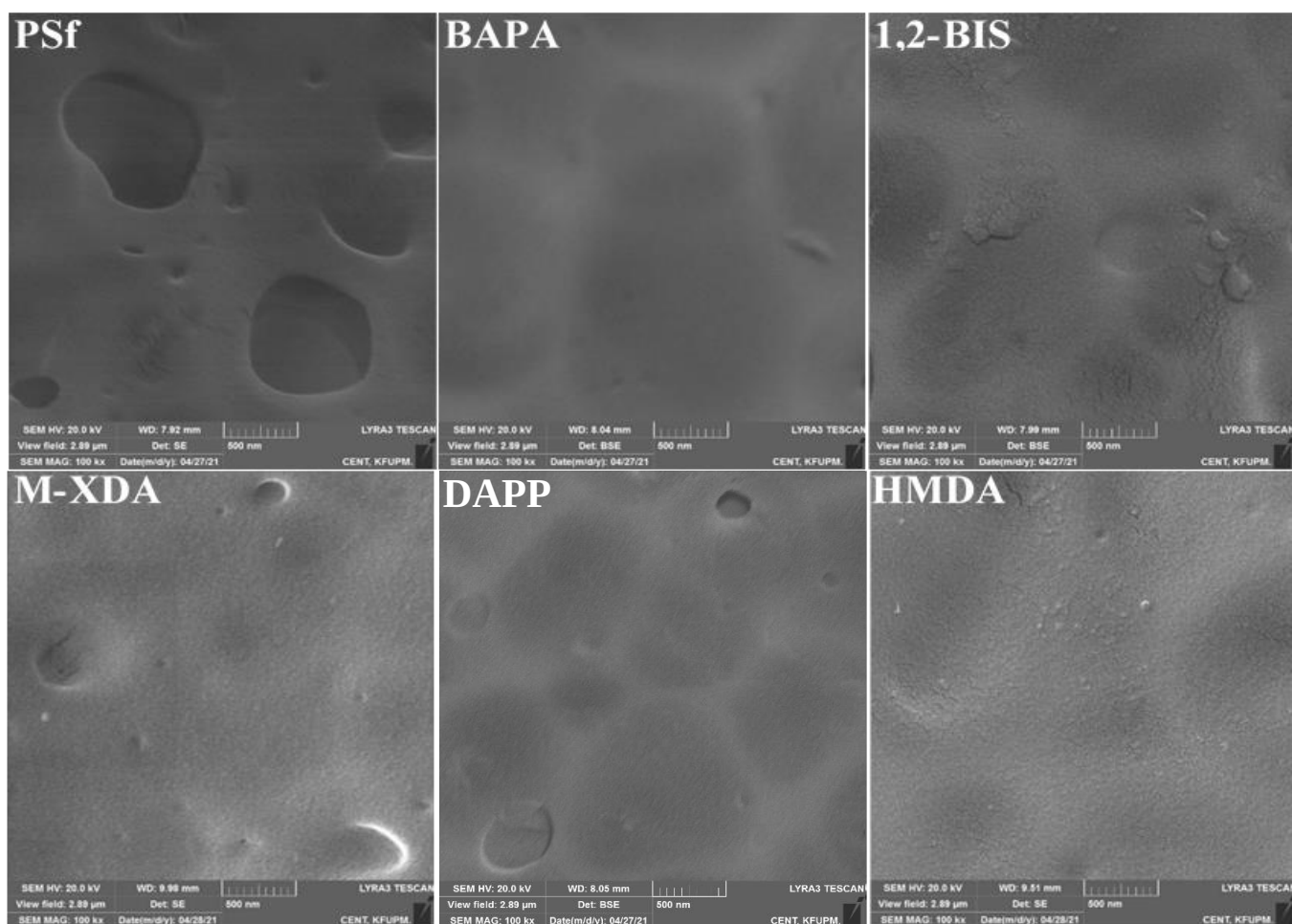


Figure 4-4: The surface SEM image of the PSf support layer, and five different fabricated polyamide thin-film composite (TFC) membranes, with scale of a 500 nm per one.

4.4. X-ray diffraction (XRD)

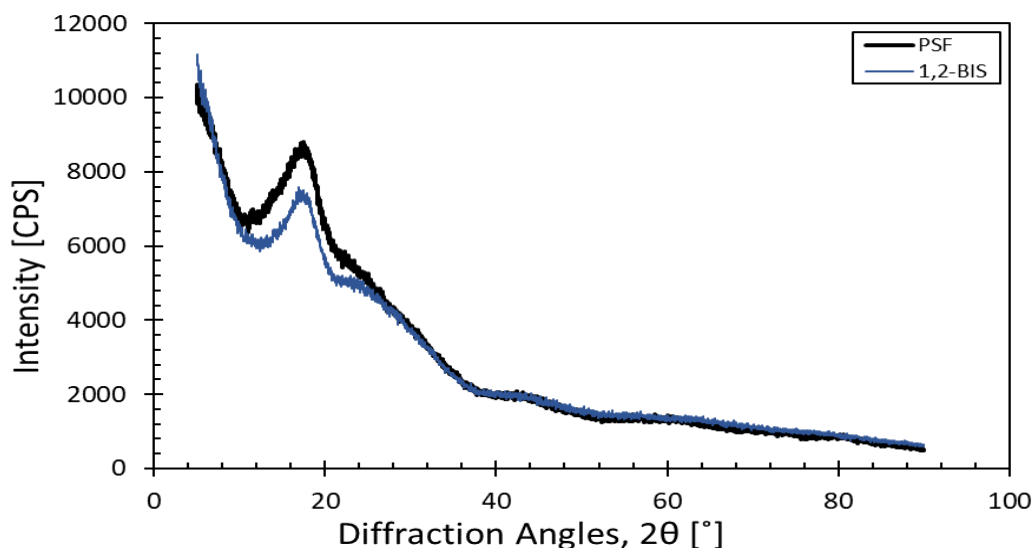


Figure 4-5: XRD pattern of PSF support layer (Black line) and 1,2-BIS TFC membrane (Dark blue line).

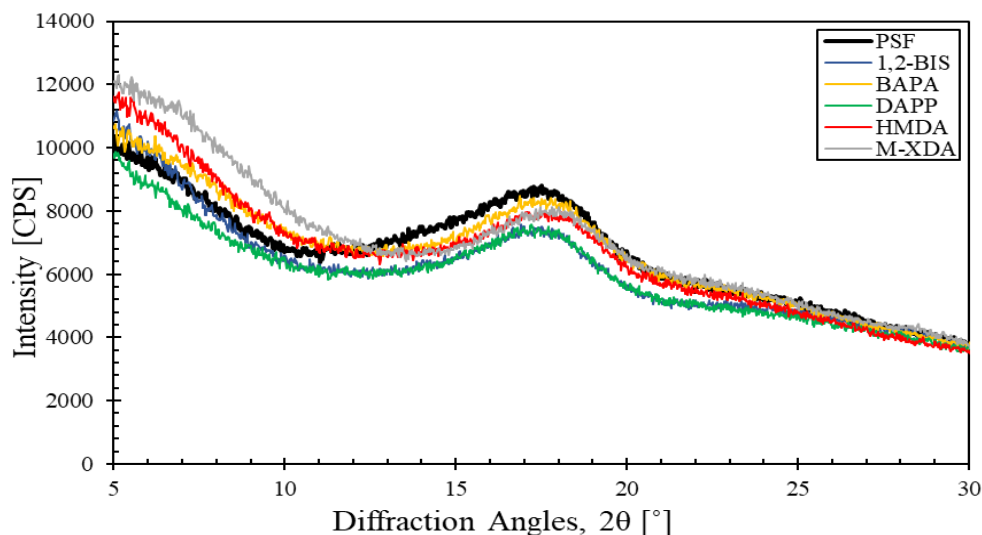


Figure 4-6: XRD pattern of PSF support layer (Black line) and five different fabricated thin-film composite (TFC) membranes (BAPA TFC: yellow line, 1,2-BIS TFC: Dark blue line, M-XDA TFC: grey line, DAPP TFC: green line, and HMDA TFC: red line).

X-ray diffraction (XRD) pattern was used to investigate the possible crystalline formation of the PSF support layer and fabricated TFC membranes (BAPA, 1,2-BIS, M-XDA, DAPP, and HMDA). As shown in Figure 4-5, and Figure 4-6 (See more figures of XRD spectra in the appendix of other fabricated TFC membranes in Figures A-9, A-10, A-11, and A-12), all membranes

exhibited no crystallinity, with a demonstration of amorphous with rigid polymer structure [119,120]. As shown in the XRD spectra of the PSF support layer and fabricated TFC membranes, the broad peak appeared ranging between 2θ values of 15° to 20° . The broad peak of fabricated TFC membranes was decreased gradually, and was more amorphous compared to the PSF support layer. These changes are attributed to the restriction of polymer chain mobility due to polyamide addition. Similar findings of PSF support layer and polyamide layer effects on crystalline properties were reported in the literature [121-124].

4.5. Thermogravimetric analysis (TGA)

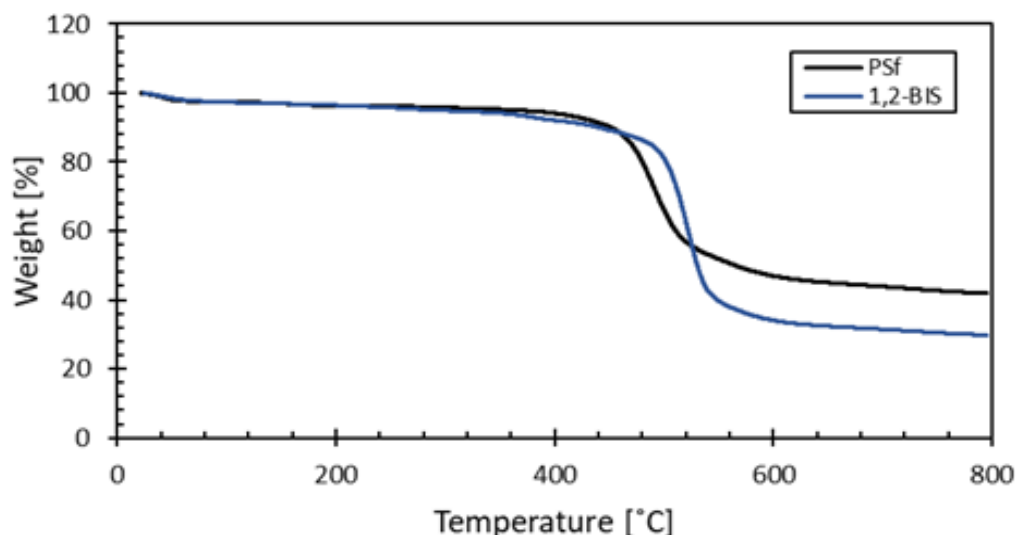


Figure 4-7: TGA Spectra of PSF support layer (Black line) and 1,2-BIS TFC membrane (Dark blue line) with the heating rate of 10 °C/min.

The thermal behavior of the PSF support layer, and 1,2-BIS TFC membrane was studied by using thermogravimetric analysis (TGA). Both samples were studied separately under the same operating conditions as explained in the materials and methods section. The mass of both membranes is slightly different due to the extra layer of PA on the PSF support layer, where the mass of the PSF support layer, and 1,2-BIS TFC membrane are 8.32 mg and 8.49 mg, respectively. Figure 4-7 illustrates the TGA curves of the PSF support layer, and 1,2-BIS TFC membrane. Both membranes showed excellent thermal stability, and resistivity below the temperature of 362 °C, where the degradation happens after that. However, the major weight loss of both membranes was seen at the temperature range of 460 °C - 610 °C. The added layer of PA to fabricate the TFC membrane led to long thermal resistance compared to the bare membrane as shown in Figure 4-7. Similar observations were already reported in the literature, where the chain scission of the carbon-sulfur bond (The weakest link in polysulfone repeat unit) occurs at the temperature range of 400-

500 °C [125]. The chemical structure of the TFC membrane which is composed of such as amide groups and aromatic moieties played a major role to be highly resistant to elevated temperature [126]. Also, the PA layer increased the polymer chain rigidity and, hence, the amount of energy needed to chain breakage or movement increased as well [127].

4.6. Contact angle measurement studies

Table 4-3: Contact angles of DI water for PSF support layer and five different fabricated TFC membranes at ambient conditions.

Type of membrane	Average Contact Angle Value [°]
PSF support layer	41.23 ± 4.63
HMDA TFC	18.61 ± 1.25
DAPP TFC	35.09 ± 2.93
M-XDA TFC	38.36 ± 1.57
1,2-BIS TFC	40.77 ± 0.36
BAPA TFC	57.06 ± 2.31

Deionized water contact angle measurements were carried out to study the effect of different polyamide layers at the top of the PSF support layer on membrane wettability. Table 4-3 summarizes contact angle observations (See image of the PSF support layer and five different fabricated TFC membranes contact angles in the appendix with Figure A-13), where all membranes values are below 90° which indicates all membranes are hydrophilic [128]. The typical PSF support layer contact angle value is around 80° [129, 130] while it was reported in this study with a lower value of $41.23 \pm 4.63^\circ$, attributable to the addition of polyvinylpyrrolidone (PVP). As can be observed in the surface morphology of the PSF support layer FESEM image (Figure 4-4), the pore distribution and pore size presence contributed to a low water contact angle [131,132]. The contact angles of different fabricated TFC membranes were varied in the order of HMDA TFC < DAPP TFC < M-XDA TFC < 1,2-BIS TFC < BAPA TFC, where they corresponded to the opposite permeation fluxes trend as expected in the order of HMDA TFC > DAPP TFC > M-XDA TFC > 1,2-BIS TFC > BAPA TFC (See the permeation results in next sub-section of 4.8). The hydrophilicity enhancement of the TFC membranes could be attributed to different factors. Surface roughness, porosity, and the weight ratio of polar groups present on the membrane surface are

factors that may play a major role in contact angle variations [133-135]. The presence of amide bond, amine end group, and carboxylic acid end group in the PA layer as a result of completing the interfacial polymerization (IP) reaction affects the surface hydrophilicity to be a wettable, and it can be more wettable as it increases in the membrane surface [53,136,137].

4.7. Zeta Potential

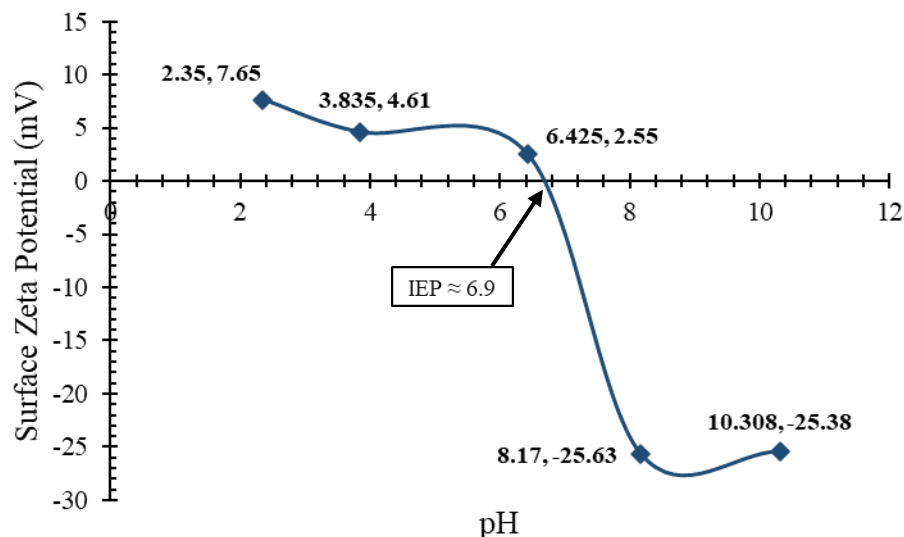


Figure 4-8: Surface zeta potential, and isoelectric point (IEP) of 1,2-BIS TFC membrane at pH = 2–11 and 25 °C.

The surface zeta potential of 1,2-BIS TFC membrane was analyzed by using Malvern Zetasizer Nano ZS, Zen3600 at the temperature of 25° C with a variation of electrolyte solution pH from 2.35 to 10.308. Figure 4-8 indicates the surface zeta potential of 1,2-BIS TFC membrane, and isoelectric point (IEP) of 6.9. The surface zeta potential of the membrane below the isoelectric point (IEP) is positively charged due to a large amount of residual amino group, secondary, and tertiary amines that exist on the membrane surface, where they easily protonate in the acidic condition, while 1,2-BIS TFC membrane exhibits a negative charge of surface zeta potential above the membrane isoelectric point (IEP). The negative surface charge in the basic condition is attributed to the deprotonation of their carboxylic acid functional group ($-\text{COOH}$) to be ($-\text{COO}^-$) [48,138-142]. The surface zeta potential analysis plays a critical role in the membrane separation efficiency, whereby understanding the acid-base properties of the membrane can influence salt rejection selectivity, and the fouling propensity too [143]. In 1,2-BIS TFC membrane analysis, pH condition above 6.9 is recommended to be more selective for anions rejecting, such as sulfate ions

(SO₄²⁻) (See the rejection results in next sub-section of 4.8, especially 4.8.3, and 4.8.4). This is due to the Donnan exclusion theory and Steric hindrance, where the membrane surface charge plays a major role in the repulsive interactions toward the ions, and the narrow pore size of the membrane can remove more salts and lower permeate flux [144-150].

4.8. Performance Evaluation of the TFC Membranes

4.8.1. Permeate flux, and salts rejection of PSF and five TFC membranes

Nanofiltration performance of the PSF support layer, and different fabricated TFC membranes (BAPA, 1,2-BIS, M-XDA, DAPP, and HMDA) were evaluated with a crossflow filtration system (Experimental set-up was described in the previous section of 3.5.1). PSF support layer, and different fabricated TFC membranes were analyzed with deionized (DI) water, 1000 ppm NaCl solution, and 1000 ppm MgSO₄ solution separately. Figure 4-9, and Tables 4-4 and 4-5 indicate the effect of operating pressures (10 bar, 20 bar, 30 bar) on permeate flux, J , ($\frac{L}{m^2h}$, LMH), and salts rejection (%) on three different feed streams. The deionized (DI) water, NaCl solution, and MgSO₄ solution fluxes and salts rejection had a positive correlation with operating pressures, which is well established in literatures and other similar studies on membranes. The first preliminary trial experiment of each fabricated TFC membrane was indicated that 1,2-BIS TFC had the highest MgSO₄ rejection of 93 % with permeate flux of 95 LMH at the pressure of 30 bar, while the NaCl rejection reached 76.2 % with permeate flux of 97 LMH at the pressure of 30 bar. In addition to 1,2-BIS TFC membrane, BAPA TFC membrane showed an excellent performance with an acceptable value of MgSO₄ and NaCl rejections, while the rest of the fabricated TFC membranes had poor performance. The flux of fabricated membranes showed a similar trend as contact angle membrane, where the high flux is associated with low contact angle (See table 4-3 in section 4.6). The operating pressure elevation resulted in higher flux, and salt rejection in the PSF support layer, and fabricated TFC membranes were due to the solution-diffusion theory. The salt passage through the membrane gets declined or stays at a constant level as the water diffuses at a higher rate. So,

the permeate concentration was diluted at higher pressure, resulting in an increase in flux and salt rejection [151-153].

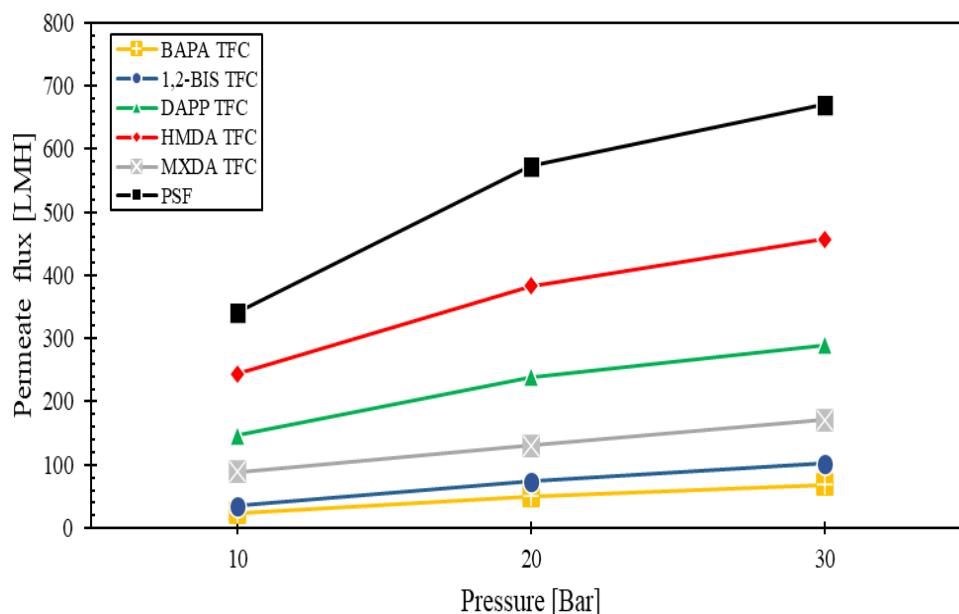


Figure 4-9: Effect of operating pressures on permeate flux, J, (LMH) of PSF support layer, and different fabricated TFC membranes. Operating conditions: Cross-flow rate: 360 LPH, pH: 6.92 $\pm$ 0.09, and Temperature: 22.14 $^{\circ}$ C $\pm$ 0.28 $^{\circ}$ C.

Table 4-4: Effect of operating pressures (10 bar, 20 bar, 30 bar) on the permeate flux, J, (LMH) [Left Table], and salts rejection (%) [Right Table] of TFC membranes (BAPA, 1,2-BIS, M-XDA, DAPP, and HMDA). Operating conditions: 1000 ppm NaCl solution, Cross-flow rate: 360 LPH, pH: 6.96 $\pm$ 0.04, and Temperature: 22.39 $^{\circ}$ C $\pm$ 0.29 $^{\circ}$ C.

1000 ppm NaCl solution Permeate Flux [LMH]						1000 ppm NaCl solution Rejection [%]					
Pressure [bar]	HMDA TFC	DAPP TFC	MXDA TFC	1,2-BIS TFC	BAPA TFC	Pressure [bar]	HMDA TFC	DAPP TFC	MXDA TFC	1,2-BIS TFC	BAPA TFC
10	201	121	76	35	24	10	20	18	23	68	52
20	281	198	122	71	48	20	17	19	25	67	53
30	280	213	135	97	66	30	20	23	29	76	64

Table 4-5: Effect of operating pressures (10 bar, 20 bar, 30 bar) on the permeate flux, J, (LMH) [Left Table], and salts rejection (%) [Right Table] of TFC membranes (BAPA, 1,2-BIS, M-XDA, DAPP, and HMDA). Operating conditions: 1000 ppm MgSO₄ solution, Cross-flow rate: 360 LPH, pH: 7.07 $\pm$ 0.03, and Temperature: 22.26 $^{\circ}$ C $\pm$ 0.07 $^{\circ}$ C.

1000 ppm MgSO ₄ solution Permeate Flux [LMH]						1000 ppm MgSO ₄ solution Rejection [%]					
Pressure [bar]	HMDA TFC	DAPP TFC	MXDA TFC	1,2-BIS TFC	BAPA TFC	Pressure [bar]	HMDA TFC	DAPP TFC	MXDA TFC	1,2-BIS TFC	BAPA TFC
10	176	118	67	35	23	10	17	22	30	88	87
20	239	181	107	68	46	20	19	25	31	91	90
30	255	207	125	95	64	30	21	31	35	93	91

4.8.2. Permeate flux and salts rejection of 1,2-BIS TFC membrane

Table 4-6: Effect of operating pressures (10 bar, 20 bar, 30 bar) on the permeate flux, J, (LMH), and salts rejection (%) of 1,2-BIS TFC membrane by using Deionized (DI) water, 1000 ppm NaCl solution, and 1000 ppm MgSO₄ solution with a cross-flow rate of 360 LPH. pH and Temperature conditions are in the range of 7 ± 0.5 and $22 \text{ }^{\circ}\text{C} \pm 1 \text{ }^{\circ}\text{C}$, respectively

1,2-BIS TFC	DI water	1000 ppm NaCl Solution		1000 ppm MgSO ₄ Solution	
Pressure [bar]	Permeate Flux [LMH]	Permeate Flux [LMH]	Rejection [%]	Permeate Flux [LMH]	Rejection [%]
10	47	45	50.6	39	67.7
20	87	84	57.2	76	73.4
30	112	108	64.9	103	92

Table 4-6 summarizes the further investigation which held on the best fabricated TFC membranes performance in the first preliminary trial experiment. As it was explained previously, 1,2-BIS TFC membrane showed the highest salts rejection with acceptable flux values. Further investigations were studied with additional replications of new synthesized 1,2-BIS TFC membranes. 1,2-BIS TFC membranes were analyzed with deionized (DI) water, 1000 ppm NaCl solution, and 1000 ppm MgSO₄ solution separately. The deionized (DI) water, 1000 ppm NaCl solution, and 1000 ppm MgSO₄ solution were run with crossflow filtration system (Experimental set-up was described in previous section of 3.5.1) in the following solution conditions: pH = 6.85 ± 0.07 and Temperature = $22.28 \text{ }^{\circ}\text{C} \pm 0.28 \text{ }^{\circ}\text{C}$, pH = 6.99 ± 0.01 and Temperature = $22.29 \text{ }^{\circ}\text{C} \pm 0.27 \text{ }^{\circ}\text{C}$, and pH = 7.09 ± 0.03 and Temperature = $22.40 \text{ }^{\circ}\text{C} \pm 0.18 \text{ }^{\circ}\text{C}$, respectively. 1,2-BIS TFC membrane exhibited an excellent salts rejection range at 30 bars, which are MgSO₄ rejection of 92%, and NaCl rejection of 65%. The decline occurred in the average values due to the non-homogeneity synthesizing of new 1,2-BIS TFC membranes. Permeate fluxes showed a linear correlation with elevated transmembrane pressure from 10-30 bar using a deionized (DI) water, 1000 ppm NaCl solution, and 1000 ppm MgSO₄ solution. Meanwhile, 1,2-BIS TFC membrane showed a better rejection of divalent ions (Mg^{2+} SO_4^{2-}) compared to monovalent ions (Na^+ Cl^-).

These results suggested that multivalent ions can be highly rejected in comparison with divalent, and monovalent ions. The result can be explained by the Donnan exclusion theory and Steric hindrance, where the membrane surface charge plays a major role in the repulsive interactions toward the ions, and the narrow pore size of the membrane can remove more salts and lower permeate flux [144-150].

4.8.3. Effect of pH and Temperature on 1,2-BIS TFC membrane performance

Figures 4-10, and 4-11 exhibit the influence of pH and temperature of feed tank solution on the nanofiltration performance of 1,2-BIS TFC membrane. Both 1000 ppm NaCl solution (Figure 4-10), and 1000 ppm MgSO₄ solution (Figure 4-11) separately were used to evaluate 1,2-BIS TFC membrane performance at pH values of 3, 7, and 10, and temperature values of 22°C, 30°C, 35°C, and 40°C, at the pressure of 30 bars with a cross-flow rate of 360 LPH. The solution pH was adjusted using HCl and NaOH solutions. The results showed that permeate flux of both 1000 ppm NaCl solution, and 1000 ppm MgSO₄ solution was affected strongly by changing pH and elevating the temperature of the feed tank, while the salt rejection was influenced by solution pH more than temperature. The permeate flux increased almost linearly as the feed tank temperature elevated from 22°C to 40°C. The feed solution viscosity decreases by the temperature elevation, which results in higher permeate flux. On the other hand, the elevated temperature ranges from 22°C to 40°C had minor significance on the salt rejection of NaCl, and MgSO₄. These results confirm 1,2-BIS TFC membrane applicability in the temperature range from 22°C to 40°C with salt rejection stability [48,53,154].

pH values increment had a strong effect on salt rejection in both 1000 ppm NaCl solution, and 1000 ppm MgSO₄ solution. As feed pH solution increased from 3 to 7, salt rejection increased, while salt rejection decreased at a pH value of 10. The observed decrement in both saline solutions separately was higher than salt rejection at a pH value of 3. Generally, salt rejection increased as the feed pH solution increased compared to the reported salt rejection at a pH value of 3. With increasing pH, the salt rejection of NaCl increased from 46.9% to 57.8% at 22°C, and 51.6% to 52.2% at 40°C, while MgSO₄ rejection increased from 50.3% to 71.9% at 22°C, and 50.5% to

67.8% at 40°C. The highest MgSO_4 rejection was reported at $\text{pH} = 7$ and $T = 40^\circ\text{C}$, with value of 78.2%, while NaCl rejection was 56.5% in the same conditions. The highest NaCl rejection was 63.2% at operating conditions of $\text{pH} = 7$ and $T = 22^\circ\text{C}$. In contrast to salt rejection, the permeate flux decreases as pH increases. As the feed tank solution got acidic ($\text{pH} = 3$), the amine groups are protonated, while the carboxyl groups are deprotonated when the feed tank solution became basic ($\text{pH} = 10$). Protonation, and deprotonation help the membrane to be more hydrophilic. As result, the permeate flux was enhanced as well [155,156]. The effect of feed pH solution on 1,2-BIS TFC membrane salt rejection can be explained by the Donnan exclusion theory, where membrane surface charge plays a major role in the salt rejection. Ions repulse or attract based on negatively, or positively surface membrane charge. As the feed pH solution increased, 1,2-BIS TFC membrane surface charge switched from positive to negative (See Figure 4-8 of 1,2-BIS TFC membrane surface zeta potential in the sub-section of 4.9). As a result, more anion rejection such as sulfate ions occurred at a higher feed pH solution value of 6.9 (isoelectric point (IEP) of 1,2-BIS TFC membrane). A huge permeate flux declining in both 1000 ppm NaCl solution, and 1000 ppm MgSO_4 solution separately at feed pH solution value of 10 lowered salt rejection compared to reported results at feed pH solution value of 7 as the effect of solution-diffusion theory was higher than the Donnan exclusion theory in this particular. The amount of transported water through the membrane at a feed pH solution value of 10 was fewer than at a feed pH solution value of 7, which impacted the salt concentration on the permeate stream. Lower salt rejection reported at a feed pH value of 3 was dominant by a positive surface membrane charge. In addition to deprotonation, protonation, and membrane surface charge, properties of the compounds, the solubility of the feed solution, presence of ionic particles, dissociation constant (pK_a), polarity, dipole moment, and

effective membrane charge density are other factors that affected by changing pH, which directly affected the membrane performance [148-150].

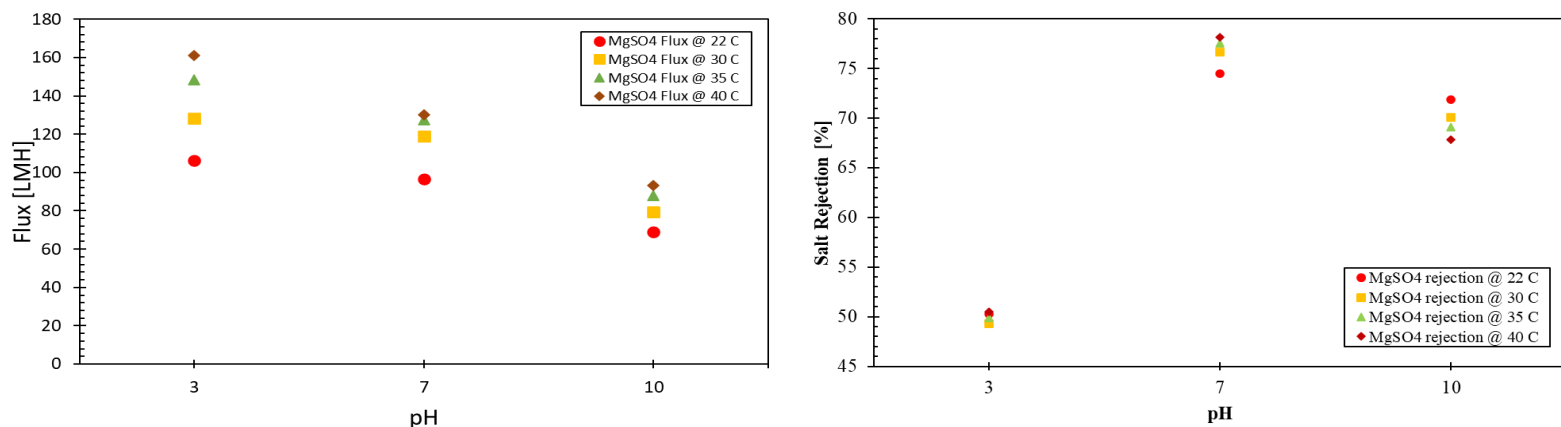


Figure 4-10: Effect of pH (3,7,10), and Temperature (22 °C, 30 °C, 35 °C, 40 °C) on the permeate flux, J, (LMH), and salts rejection (%) of 1,2-BIS TFC membrane. Operating conditions: 1000 ppm MgSO₄ solution, Pressure: 30 bar, and Cross-flow rate: 360 LPH.

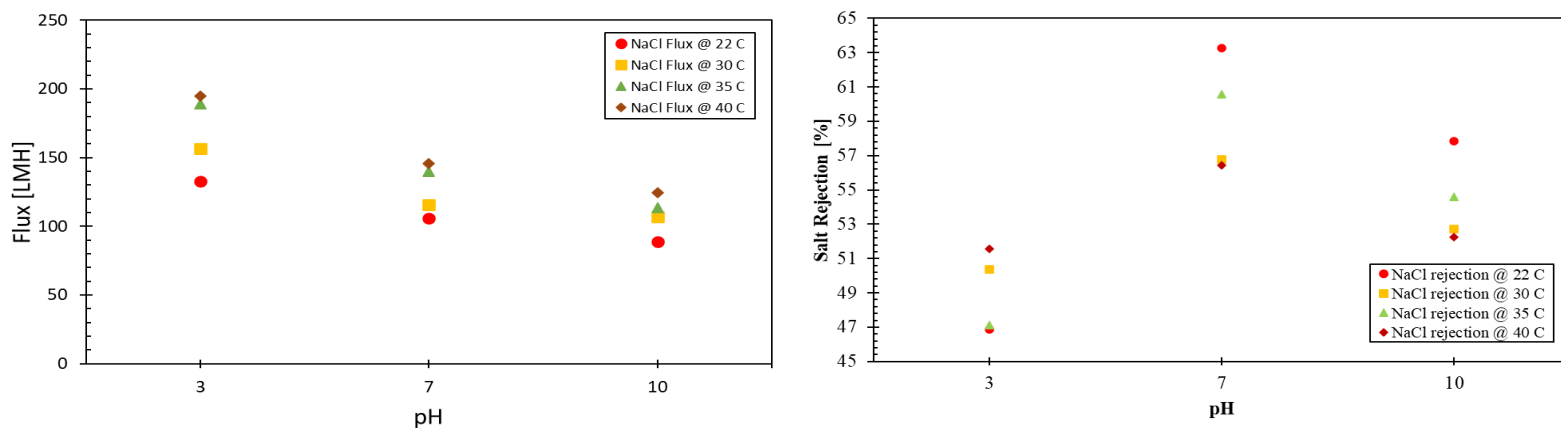


Figure 4-11: Effect of pH (3,7,10), and Temperature (22 °C, 30 °C, 35 °C, 40 °C) on the permeate flux, J, (LMH), and salts rejection (%) of 1,2-BIS TFC membrane. Operating conditions: 1000 ppm NaCl solution, Pressure: 30 bar, and Cross-flow rate: 360 LPH.

4.8.4. Effect of pH and Pressure on 1,2-BIS TFC membrane performance

1,2-BIS TFC membrane was evaluated at different values of feed tank solution pH (3,7, and 10), and transmembrane pressure (10 bar, 15 bar, 20 bar, 25 bar, 30 bar) at a feed solution temperature of 40°C with a cross-flow rate of 360 LPH. Both 1000 ppm NaCl solution, and 1000 ppm MgSO₄ solution separately were used in the performance evaluation, and solution pH was adjusted using HCl and NaOH solutions. Figures 4-12, and 4-13 prove a positive correlation between the transmembrane pressure and both permeate flux and salt rejection in both NaCl solution, and MgSO₄ solution. As the transmembrane pressure increased, the permeate flux increment was up to 56.7% in NaCl, and 60.2% in MgSO₄, while the salt rejection increased by 25.6% in NaCl, and 15.7% in MgSO₄. The effect of transmembrane pressure, and the solution pH variation on the membrane performance can be explained by solution-diffusion theory and the Donnan exclusion theory, where transported salt through the membrane was less compared to the amount of transported water as transmembrane pressure increases, and membrane surface charge plays a major role in the salt rejection, where the ions repulse based on negatively, or positively surface membrane charge [148-150].

The rejection of 1000 ppm NaCl solution, and 1000 ppm MgSO₄ solution was varied by modifying pH values with changing transmembrane pressure at a feed solution temperature of 40°C and a cross-flow rate of 360 LPH. 1,2-BIS TFC membrane exhibited increment rejection of MgSO₄ with increasing pH (3,7, and 10) as transmembrane pressure increased as well. NaCl rejection behaved similar to MgSO₄ rejection performance with increasing pH, and transmembrane pressure except when the pH value increased after 7, the NaCl rejection decreased. Figures 4-12, and 4-13 show that pH influence on the permeate flux of both 1000 ppm NaCl solution, and 1000

ppm MgSO_4 solution is directly proportional. These results aligned with previous performance results, which suggested that 1,2-BIS membrane operates well, and efficiently at $\text{pH} = 7$, and temperature = 40°C . pH influence on 1,2-BIS TFC membrane performance was explained previously in section 4.8.3.

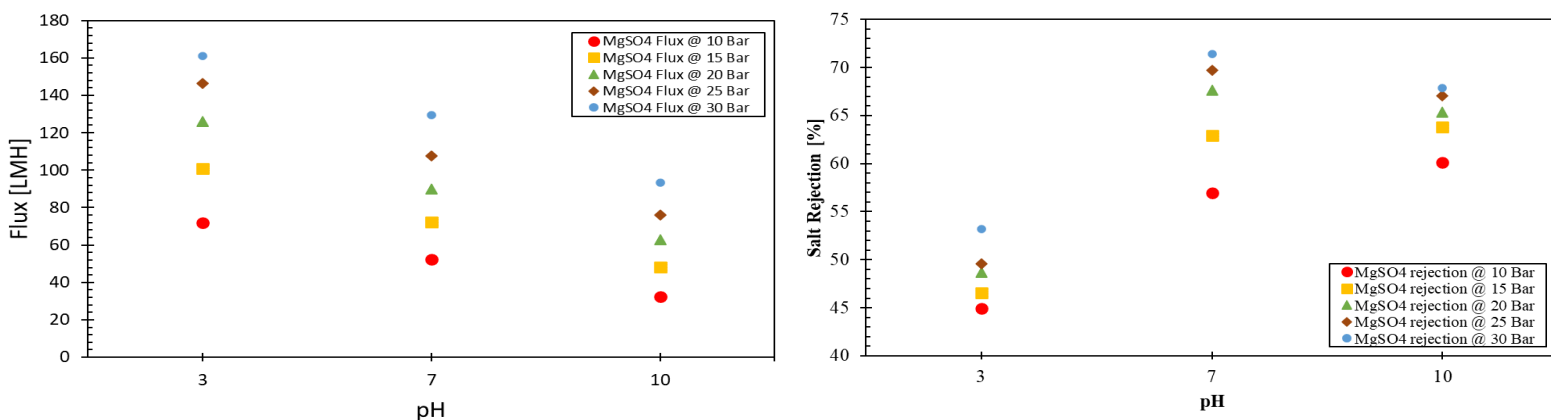


Figure 4-12: Effect of pH (3,7,10), and operating pressures (10 bar, 20 bar, 30 bar) on the permeate flux, J , (LMH), and salts rejection (%) of 1,2-BIS TFC membrane. Operating conditions: 1000 ppm MgSO_4 solution, Temperature: 40°C , and Cross-flow rate: 360 LPH.

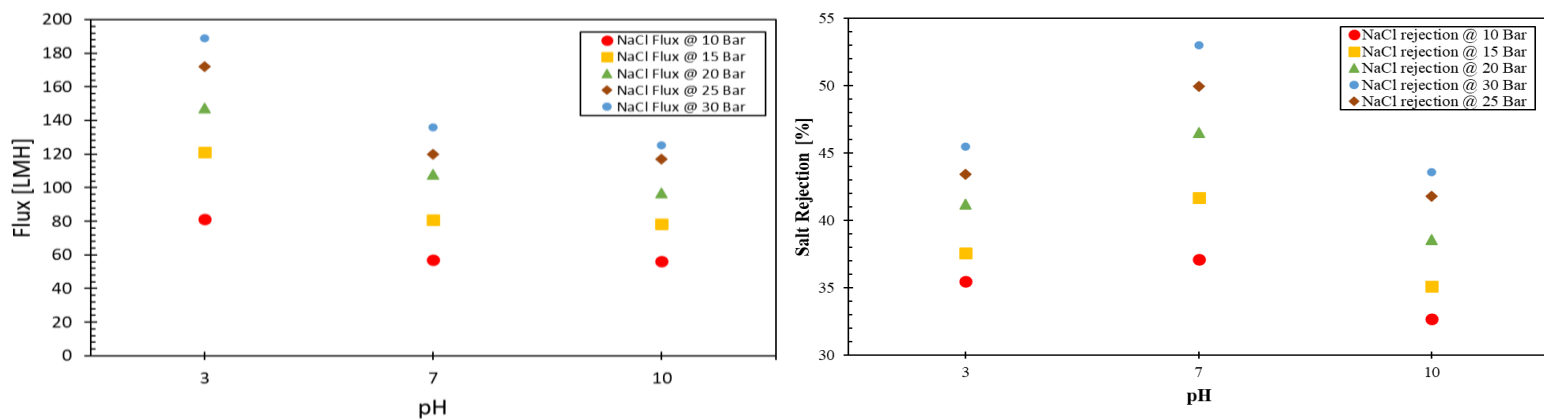


Figure 4-13: Effect of pH (3,7,10), and operating pressures (10 bar, 20 bar, 30 bar) on the permeate flux, J , (LMH), and salts rejection (%) of 1,2-BIS TFC membrane. Operating conditions: 1000 ppm NaCl solution, Temperature: 40°C , and Cross-flow rate: 360 LPH.

4.8.5. Effect of cross-flow velocity on 1,2-BIS TFC membrane performance

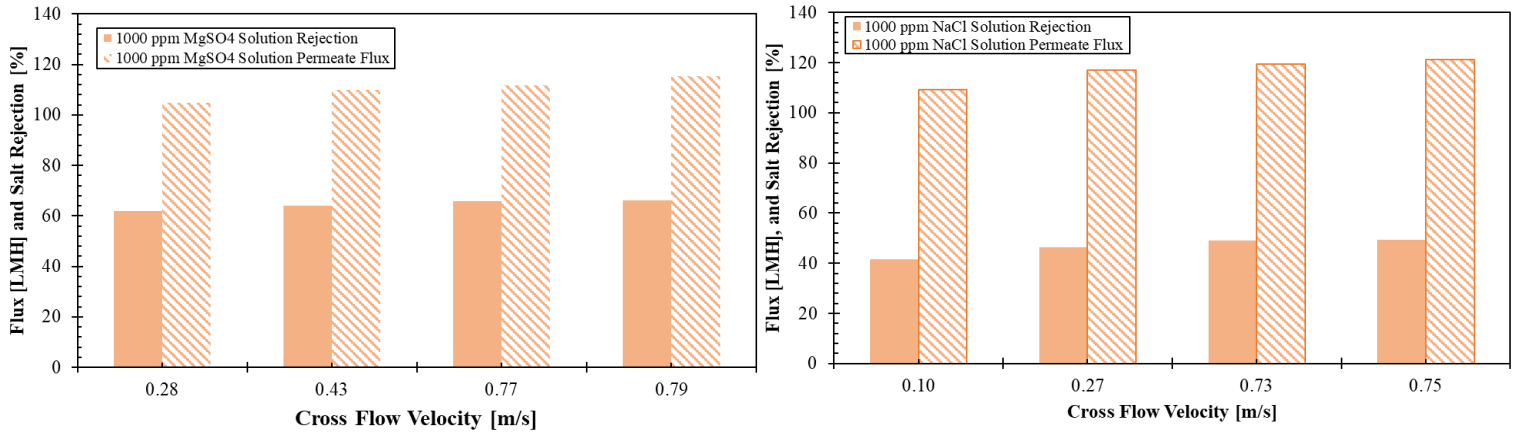


Figure 4-14: Effect of Cross-flow velocity on the permeate flux, J, (LMH), and salts rejection (%) of 1,2-BIS TFC membrane by using 1000 ppm MgSO₄ solution (Left Chart), and 1000 ppm NaCl solution (Right Chart). Operating conditions: Pressure: 30 bar, Temperature: 40 °C, and pH: 7.

The effectiveness of feed solution cross-flow velocity variation was studied on 1,2-BIS TFC membrane performance. Both 1000 ppm NaCl solution, and 1000 ppm MgSO₄ solution were used as feed solutions separately at a feed solution temperature of 40°C, a constant transmembrane pressure of 30 bar, and a pH value of 7. Figure 4-14 shows a positive correlation between feed solution cross-flow velocity and permeate flux and salt rejection. In 1000 ppm MgSO₄ Solution, the permeate flux increased from 104.7 to 115.3 LMH as the feed cross-flow velocity increased from 2.76×10^{-1} to $7.93 \times 10^{-1} \frac{\text{m}}{\text{s}}$, which is the maximum cross-flow velocity limit that can be reached in this setup. Whereas the permeate flux of 1000 ppm NaCl solution increased from 109.2 to 121.1 LHM as the feed cross-flow velocity increased from 1.04×10^{-1} to $7.48 \times 10^{-1} \frac{\text{m}}{\text{s}}$, which is the maximum cross-flow velocity limit that can be reached in this setup. Salt rejection increased by 6.7 %, and 18.5 % in 1000 ppm MgSO₄ solution, and 1000 ppm NaCl solution, respectively, as feed cross-flow velocity increased. 1,2-BIS TFC membrane performance with increasing cross-flow velocity using both saline solutions with a concentration of 1000 ppm separately showed a linear correlation, which anticipates a directly proportional relationship

between feed cross-flow velocity, and both permeate flux and salt rejection. Increasing the feed cross-flow velocity will help to reduce concentration polarization, which result results in greater convective force. The higher convective force will help water to permeate more than solute, which results in low salt in the permeate flux. Therefore, salt rejection is going higher as the feed cross-flow velocity increases. However, studying the variation of cross-flow velocity would help to maximize the membrane surface effectiveness for the separation. In addition, it can be helpful to find the critical flux in which the minimum fouling occurs [151,152,157-160].

4.8.6. Long-term performance and stability of 1,2-BIS TFC membrane

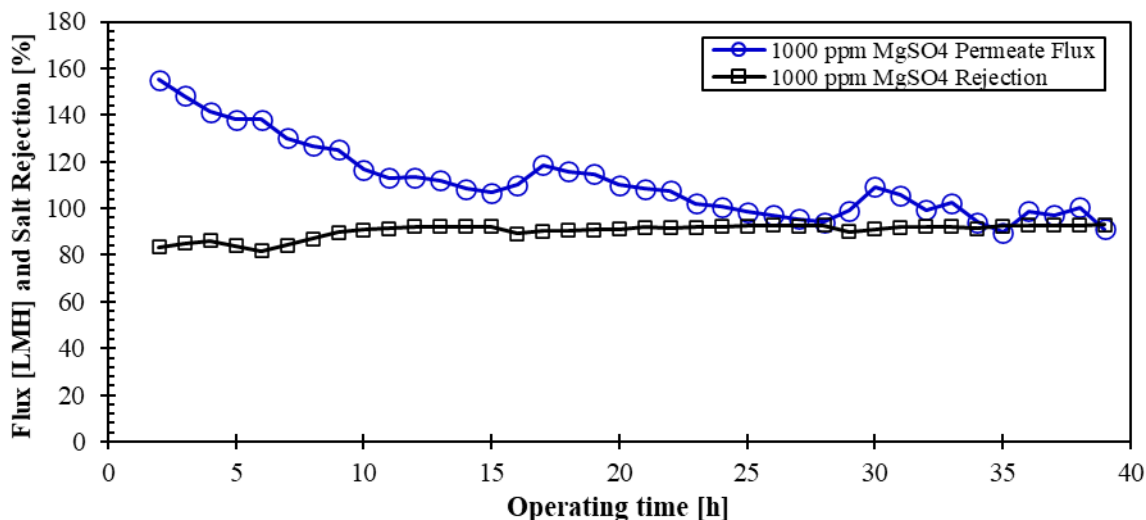


Figure 4-15: Stability test for 1,2-BIS TFC membrane. Operating conditions: 1000 ppm MgSO₄ solution, Pressure: 30 bar, Temperature: 40 °C, pH: 7, and Cross-flow rate: 360 LPH.

Figure 4-15 shows the long-term performance and stability analysis of 1,2-BIS TFC membrane using 1000 ppm MgSO₄ solution for 39 hours at a transmembrane pressure of 30 bar, feed temperature of 40 °C, feed pH of 7, and cross-flow rate 360 LPH. A long-term performance test was investigated to assess the stability, and fouling effects on the membrane surface, which will be critical for the potential commercial applications. As can be seen in Figure 4-15, the permeate flux decreased and fluctuated with time, while the MgSO₄ rejection was increased by approximately at around 10%, and maintained around 93% with time. This result showed a little fouling with acceptable permeate flux and rejection ranges by 1000 ppm MgSO₄.

4.8.7. Study Summary

Table 4-7 summarizes five different thin-film composite membranes that were used in this research study to investigate their role in removing sulfate ions (SO_4^{2-}). The summary table is intended to give an overview of geometry shape, and dimension, preparation, performance, and operating conditions. More detailed information about each thin-film composite membrane were fully addressed in the previous sections.

Table 4-7: A summary table of five thin-film composite membranes were investigated in this research study.

Membrane					
Characteristics	HMDA	DAPP	MXDA	1,2-BIS	BAPA
Geometry	Flat-sheet	Flat-sheet	Flat-sheet	Flat-sheet	Flat-sheet
Active area [cm^2]	16	16	16	16	16
Material	Polyamide	Polyamide	Polyamide	Polyamide	Polyamide
Substrate composition	15 wt. % Polysulfone (PSF), 4 wt. % polyvinylpyrrolidone (PVP), and 81 wt. % N,N-Dimethylacetamide (DMAc).				
Aqueous solution composition	2 wt. % Amine monomer, 2 wt. % Triethylamine (TEA), 0.1 wt. % Sodium dodecyl Sulfate (SDS), and 95.9 wt. % Deionized (DI) water.				
Organic solution composition	0.2 wt. % 1,3,5-Benzenetricarbonyl trichloride (TMC) in n-Hexane.				
Flux $\frac{\text{L}}{\text{m}^2 \text{ h bar}}$	19.6	12.1	7	4.73	2.4
Contact Angle ($^\circ$)	18.6 $\pm$ 1.2	35.1 $\pm$ 2.9	38.4 $\pm$ 1.6	40.8 $\pm$ 0.4	57.1 $\pm$ 2.3
Solute Rejection [%]					
MgSO ₄	21	31	35	92	91
NaCl	20	23	29	65	64
Tested pH range	7	7	7	3-10	7
Tested Temperature range ($^\circ\text{C}$)	22	22	22	22-40	22
Maxi ^m tested Pressure (bar)	30	30	30	30	30

4.9. Performance comparison

Table 4-8 summarizes the nanofiltration separation performance of the thin-film composite membrane of PSF-1,2-BIS/TEA/SDS-TMC with other similar TFC membranes. The different thin-film composite membranes in Table 4-7 shared the same used substrate (PSF) for the membrane supporting layer fabrication, and the same acyl chloride monomer (TMC) in the organic solution, with differences in the amine monomers and its additive. The comparison between different synthesized thin-film composite membranes showed that 1,2-BIS TFC membrane (this work) ranking was in the middle of mentioned membranes in Table 4-7. The MgSO_4 rejection of 1,2-BIS TFC membrane was reaching up to 93% while the permeability flux needs more improvements compared with other studies.

Table 4-8: Comparison between nanofiltration (NF) separation performance of different thin-film composite (TFC) membranes.

Membrane	Flux [$\frac{\text{L}}{\text{m}^2 \text{ h bar}}$]	Rejections [%]		Operating Conditions	Reference
		NaCl	MgSO_4		
PSF-1,2-BIS/TEA/SDS-TMC	4.73	65	92	Temperature: 22±1 °C Salt concentration: 1000 ppm	This Work
PSF-PIP-TMC	11.9	29.9	91.4	Temperature: 25 °C Salt concentration: 1000 ppm	[52]
PSF-PIP/ABA-TMC	70	15.5	62.5	Temperature: 25 °C Salt concentration: 1000 ppm	[52]
PSF-PIP/NaOH-TMC/BIBB	5.5	54.2	89	Temperature: 25 °C Salt concentration: 1000 ppm	[64]
PSF- PEI/CCh/tris(hydroxymethyl) aminomethane buffer solution-TMC	4.43	38.2 ± 1.0	92.7 ± 0.9	Temperature: 25 °C Salt concentration: 1000 ppm	[69]
PSF-SPEI _{0.3%} -TMC	20.9	5.5	—	Temperature: 25 °C Salt concentration: 1000 ppm	[71]
PSF-PEI-TMC	5.78	3.2	—	Temperature: 25 °C Salt concentration: 1000 ppm	[71]
PSF-PIP/GAZ-TMC	30.5	Low	74	Temperature: 25 °C Salt concentration: 1000 ppm	[66]

CHAPTER 5

Conclusion and Recommendation

5.1. Conclusion

Different active layers of polyamide were successfully fabricated on the Polysulfone substrate by the interfacial polymerization reaction. The five different thin-film composite membranes were characterized by using different methods and techniques. Field Emission Scanning Electron Microscope (FESEM) confirmed the formation of defect-free active layers of polyamide on top of Polysulfone substrate for each fabricated TFC membrane. Typical absorption peaks of polyamide functional groups were verified by using the Fourier-transform infrared spectroscopy (FTIR), which confirmed the successful formation of polyamide active layers. Moreover, X-ray powder diffraction (XRD) patterns showed no crystallinity, with a demonstration of amorphous and rigid polymer structure in all five fabricated TFC membranes.

The performance of all fabricated membranes was evaluated and analyzed using a crossflow filtration system with deionized water, 1000 ppm NaCl solution, and 1000 ppm MgSO₄ solution separately. 1,2-BIS TFC membrane showed a promising separation performance among other fabricated TFC membranes with the highest permeate flux and salt rejection. Up to 92%, and 64.9% were MgSO₄, and NaCl rejections, respectively, with permeate flux of 103 LMH, and 108 LMH in 1000 ppm MgSO₄ solution, and 1000 ppm NaCl solution, respectively, while the

deionized (DI) water permeate flux reported 112 LMH at the pressure of 30 bar. The performance results of other fabricated TFC membranes were not encouraging for further investigations. The trend of permeation fluxes for the fabricated TFC membranes was in the order of HMDA TFC > DAPP TFC > M-XDA TFC > 1,2-BIS TFC > BAPA TFC, where they corresponded to the opposite contact angles trend as expected.

Moreover, the effect of various operating conditions (feed pH, feed temperature, transmembrane pressure, and feed cross-flow velocity) have a significant impact on separation performance. The permeate flux was increased with increasing feed temperature, transmembrane pressure, and feed cross-flow velocity, while the feed pH is inversely proportional to the permeate flux. In general, salt rejection increases as feed pH, transmembrane pressure, and feed cross-flow velocity increase, while it showed stability with increasing feed temperature. The effects of feed pH, and feed temperature were alleged with findings in both Zeta Potential and Thermogravimetric Analysis (TGA), where the higher salt rejection of negatively divalent ions is more pronounced at pH values higher than the isoelectric point (IEP) of 1,2-BIS TFC membrane (IEP = 6.9). The long-term performance, and stability analysis suggested that 1,2-BIS TFC membrane can be qualified for further investigations to address other areas that might be needed before moving forward for large-scale purposes.

The present study attempted to investigate new amine monomers to synthesize TFC nanofiltration membranes with excellent performance, especially higher Sulfate ions (SO_4^{2-}) rejection. Both 1,2-BIS TFC membrane, and BAPA TFC membrane demonstrated the ability to

reject more than 90% of Sulfate ions (SO_4^{2-}) from 1000 ppm MgSO_4 feed solution. Therefore, this composite membrane can play a crucial role in reducing scale formation in the field of oil and gas.

5.2. Recommendation

The main objectives of this study were achieved by introducing and investigating new amine monomers in synthesizing thin-film composite (TFC) nanofiltration membranes. Accordingly, the results of both 1,2-Bis(3-aminopropylamino) ethane (1,2-BIS), and Bis(3-aminopropyl) amine (BAPA) showed good Sulfate ions (SO_4^{2-}) rejection, while the rest of amine monomers showed poor rejection performance. However, additional investigations, and future developments may need for each fabricated thin-film composite (TFC) nanofiltration membrane, which can be helpful to be economically feasible for large-scale purposes. Some recommendations that can be helpful for future work:

- 1) Studying the effect of amine concentration, additive, or surfactant on the permeate flux, salts rejection, surface morphology, and others.
- 2) Investigating new additives, and/or surfactants instead of using Triethylamine (TEA) as an additive, and Sodium dodecyl sulfate (SDS) as a surfactant in the aqueous solution of amine.
- 3) Evaluating the performance of TFC nanofiltration membranes at higher salinity (1500 ppm, 2000 ppm, 3000 ppm) and new saline solutions such as Na_2SO_4 , MgCl_2 , and others. Also, a sample of brackish water or seawater can be used too.

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Appendix: More figures, and Pictures.

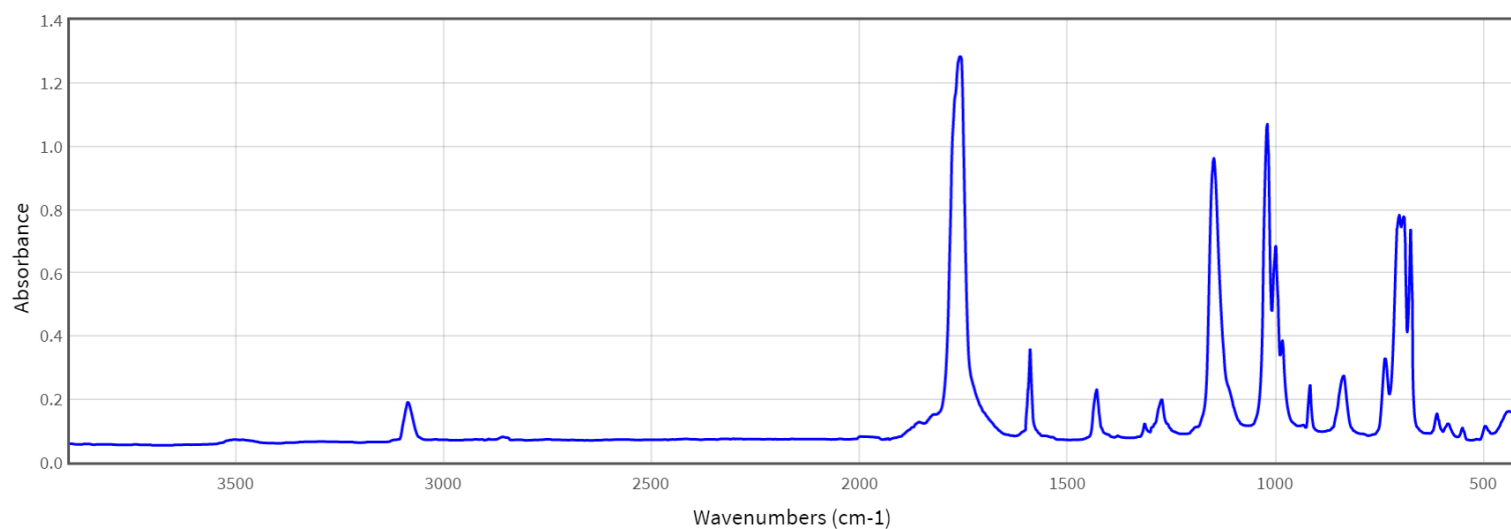


Figure A-1: FTIR spectra of pure 1,3,5-Benzenetricarbonyl Trichloride (TMC) [161].

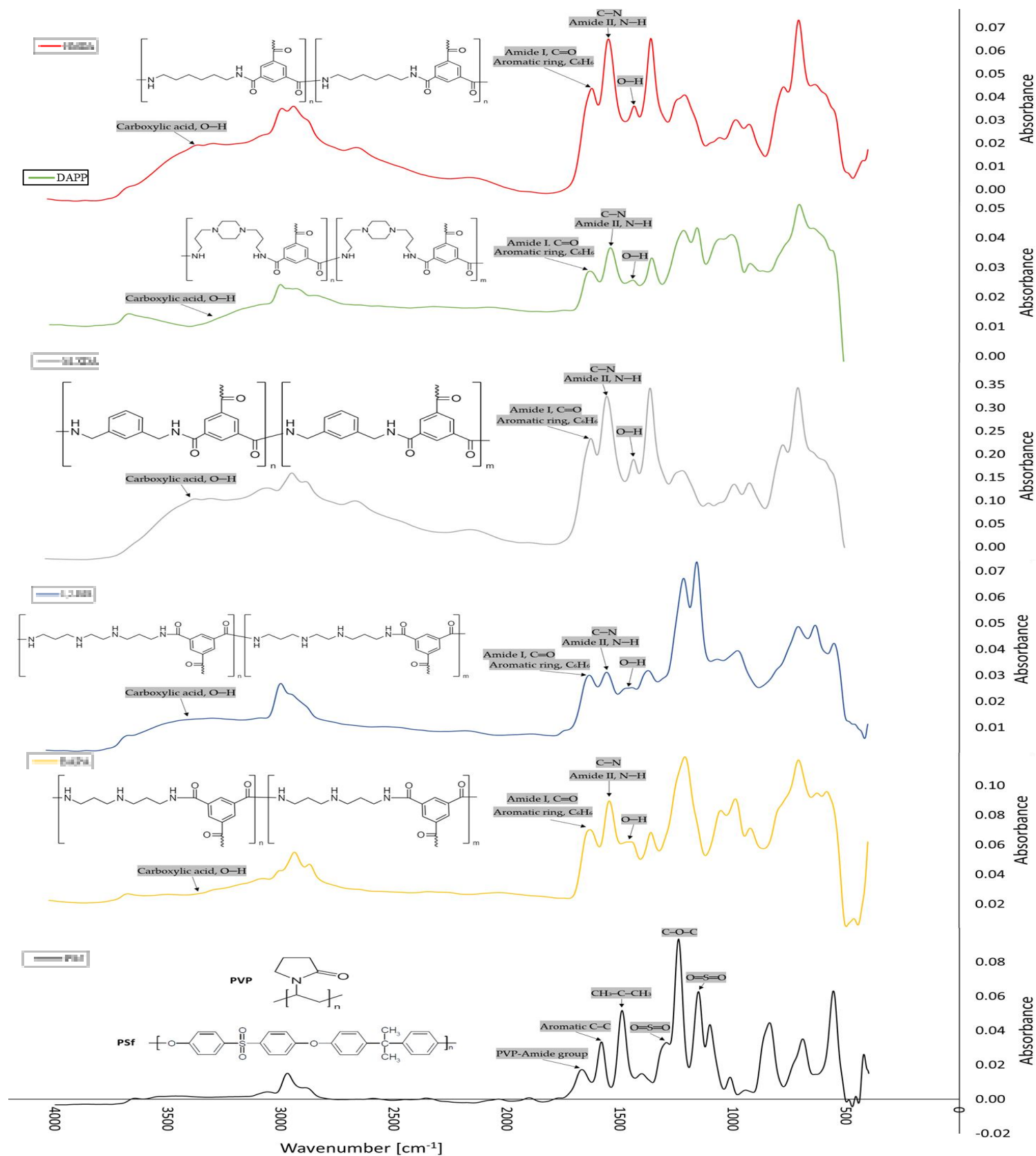


Figure A-2: FTIR spectra of the PSF support layer, and five different active layers of polyamide (PA) that interfacial polymerized with 0.2% (w/v) TMC with the presence 2% (w/v) TEA, and 0.1% (w/v) SDS in an aqueous solution.

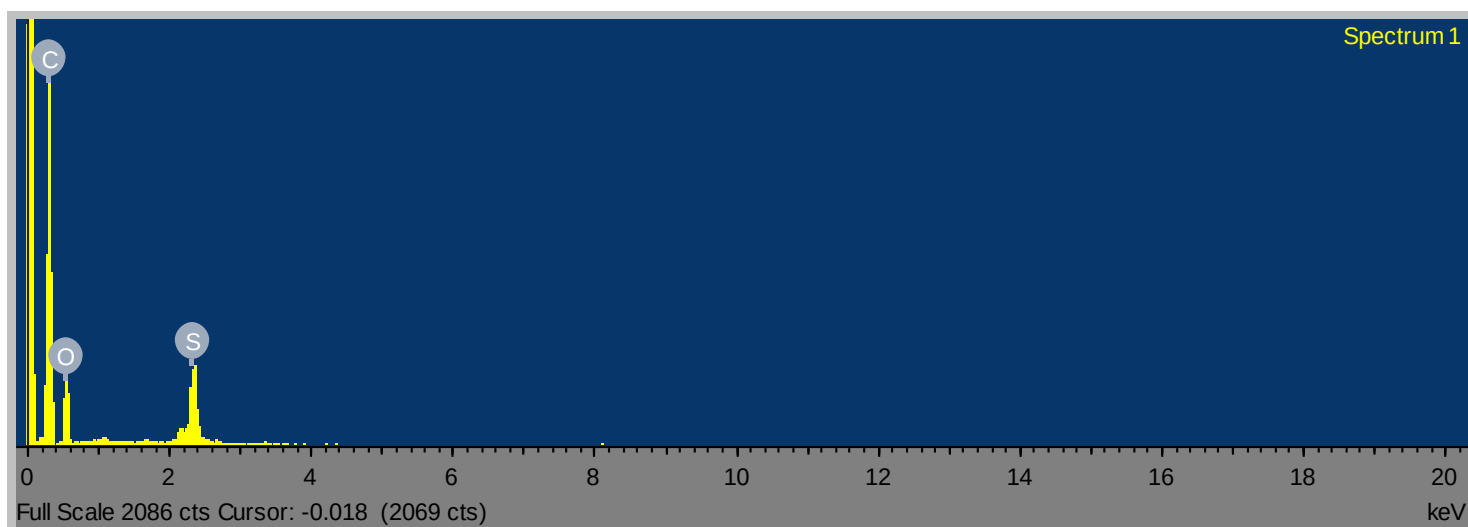


Figure A-3: EDX Analysis result of the PSF support layer.

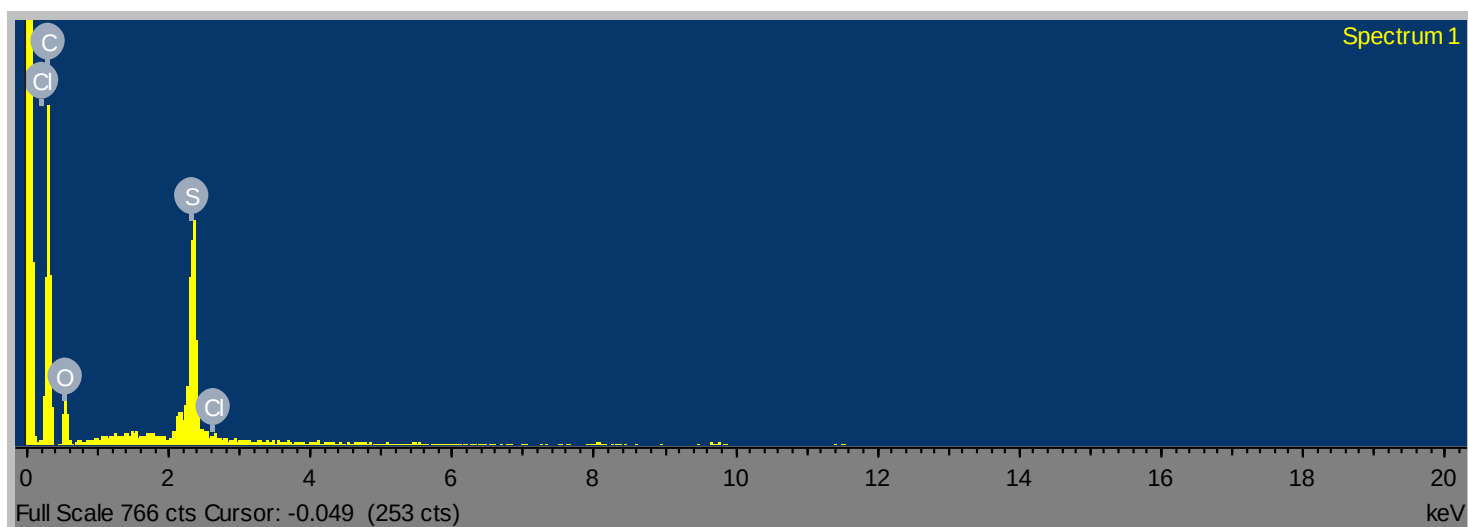


Figure A-4: EDX Analysis result of Bis(3-aminopropyl) amine (BAPA) TFC membrane.

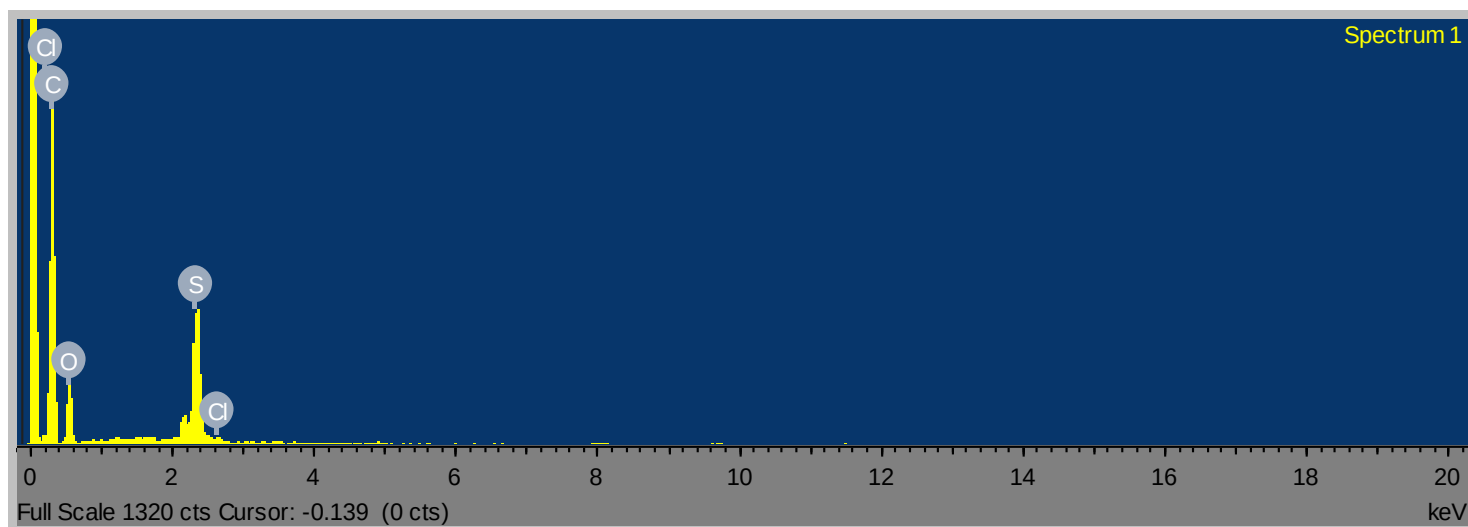


Figure A-5: EDX Analysis result of 1,2-Bis(3-aminopropylamino) ethane (1,2-BIS) TFC membrane.

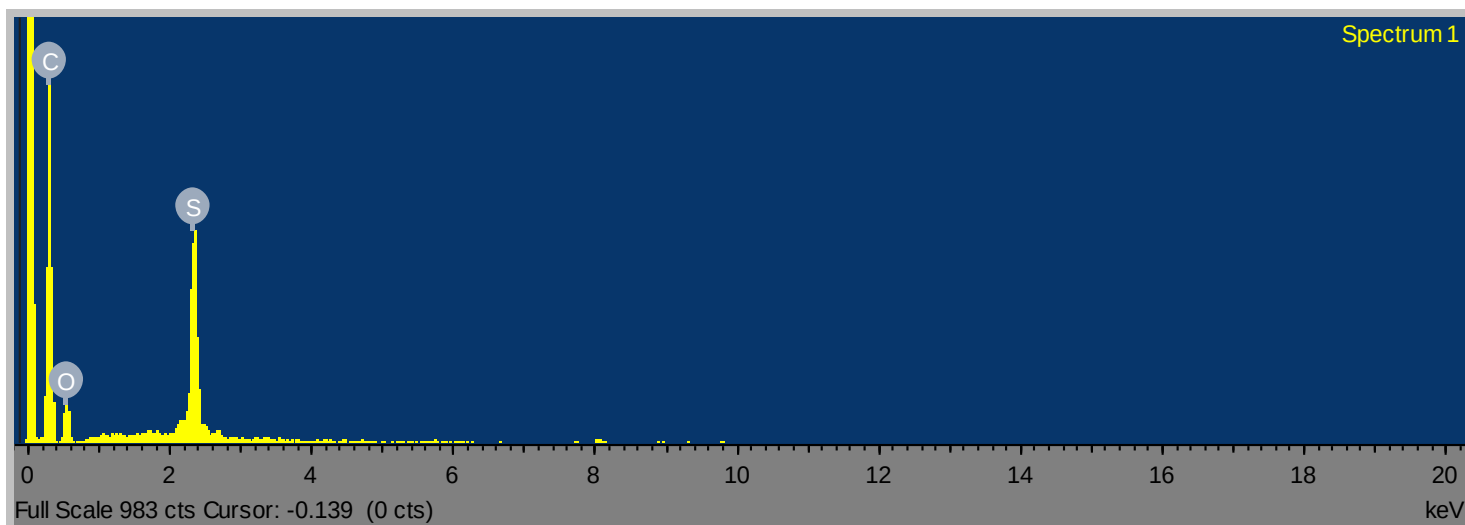


Figure A-6: EDX Analysis result of m-Xylylenediamine (m-XDA) TFC membrane.

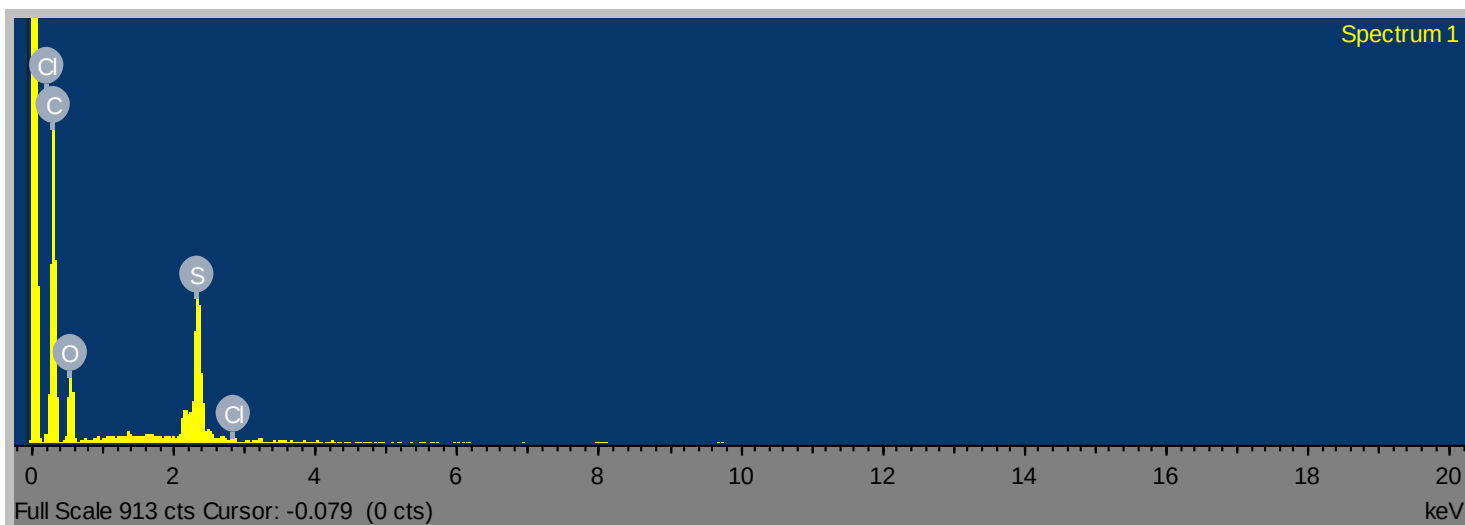


Figure A-7: EDX Analysis result of 1,4-Bis(3-aminopropyl) piperazine (DAPP) TFC membrane.

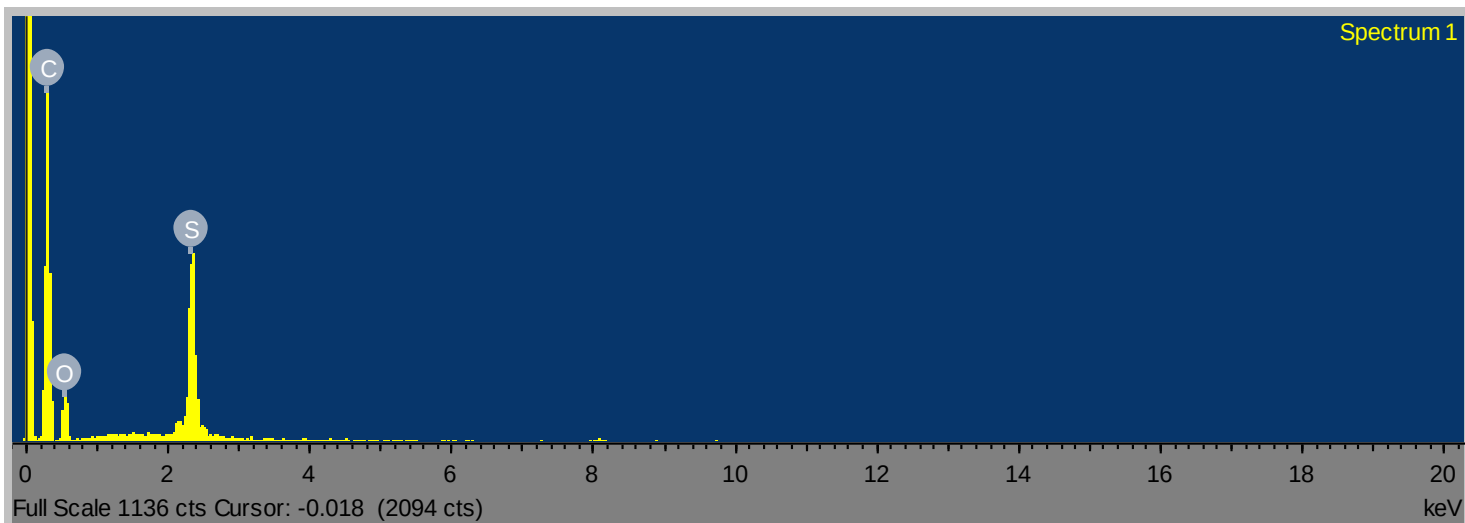


Figure A-8: EDX Analysis result of Hexamethylenediamine (HMDA) TFC membrane.

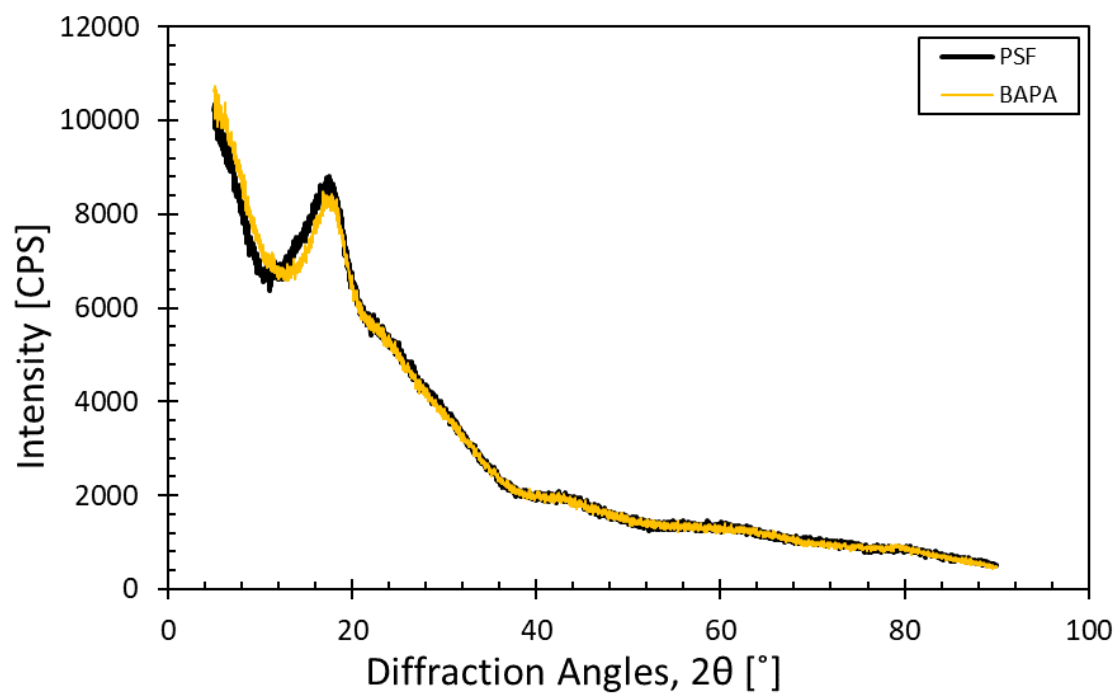


Figure A-9: XRD pattern of the PSF support layer (Black line) and Bis(3-aminopropyl) amine (BAPA) TFC membrane (Yellow line).

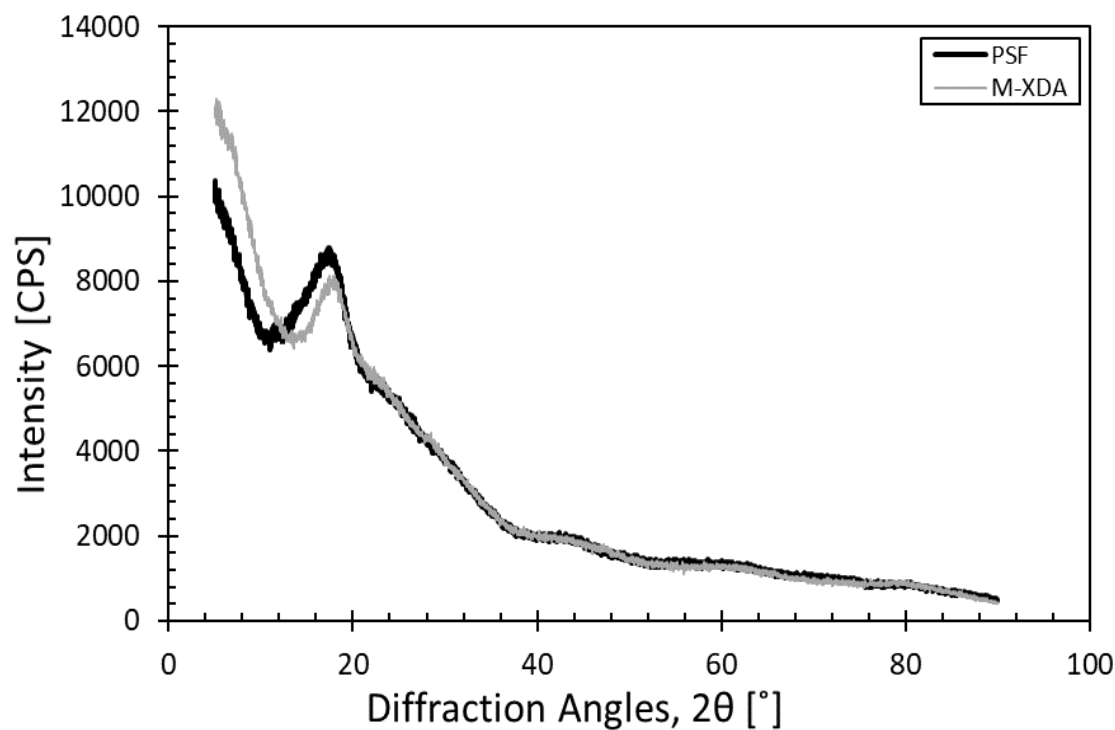


Figure A-10: XRD pattern of the PSF support layer (Black line) and m-Xylylenediamine (m-XDA) TFC membrane (Grey line).

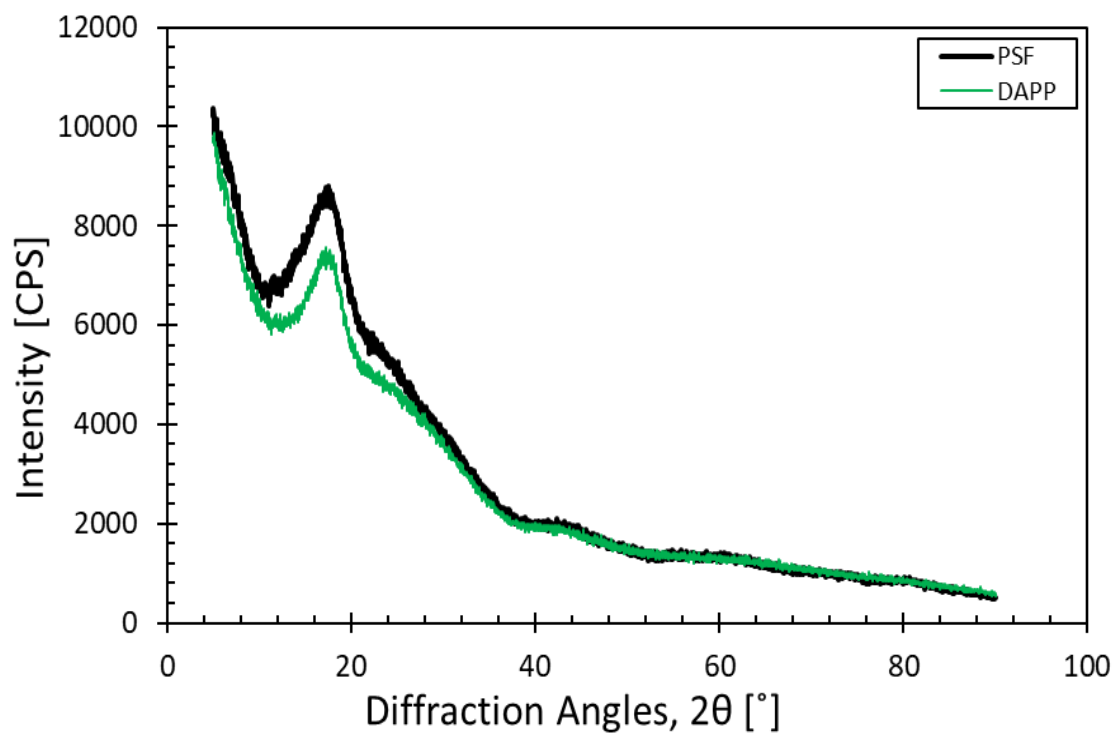


Figure A-11: XRD pattern of the PSF support layer (Black line) and 1,4-Bis(3-aminopropyl) piperazine (DAPP) TFC membrane (Green line).

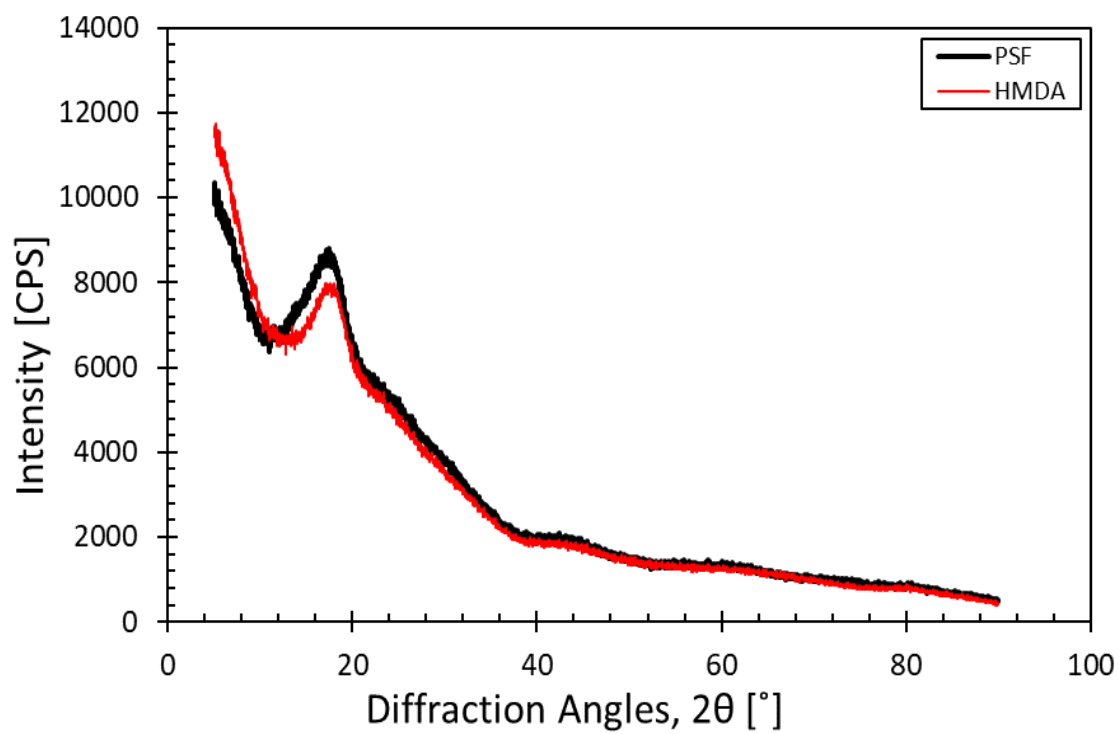


Figure A-12: XRD pattern of the PSF support layer (Black line) and Hexamethylenediamine (HMDA) TFC membrane (Red line).

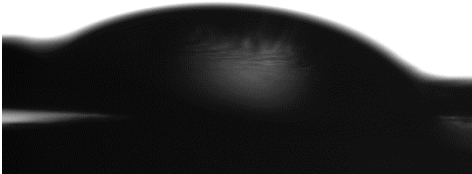
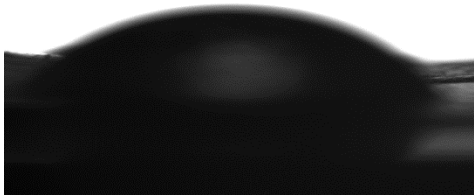
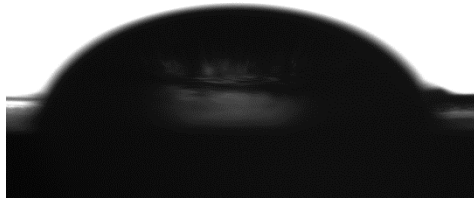
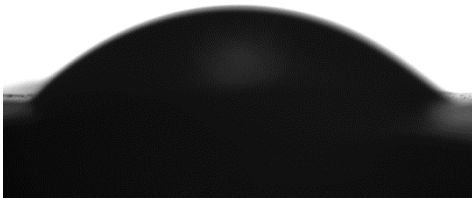
	
PSF support layer	m-Xylylenediamine (m-XDA) TFC
	
Bis(3-aminopropyl) amine (BAPA) TFC	1,4-Bis(3-aminopropyl) piperazine (DAPP) TFC
	
1,2-Bis(3-aminopropylamino) ethane (1,2-BIS) TFC	Hexamethylenediamine (HMDA) TFC

Figure A-13: Image of the PSF support layer and five different fabricated TFC membranes contact angles by using a DI water at ambient conditions.

Vitae

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