POLYAMIDE/ZEOLITIC IMIDAZOLATE FRAMEWORK-8/POLYSULFONE THIN FILM NANOCOMPOSITE MEMBRANE FOR THE TREATMENT OF PRODUCED WATER VIA FORWARD OSMOSIS

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by

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TABLE OF CONTENTS

CHAPTER ONE: INTRODUCTION

CHAPTER TWO: LITERATURE REVIEW

CHAPTER THREE: MATERIALS AND METHODOLOGY

CHAPTER FOUR: RESULTS AND DISCUSSION

CHAPTER FIVE: CONCLUSIONS AND RECOMMENDATIONS

APPENDICES

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AFM	Atomic Force Microscopy
ATR-FTIR	Attenuated Total Reflectance-Fourier Transform Infrared
BET	Brunauer-Emmett-Teller
BTEC	3,3’,5,5’-biphenyl tetraacyl chloride
CNTs	Carbon nanotubes
CTAB	Cetyltrimethylammonium bromide
DAHP	1,3-diamino-2-hydroxypropane
DETA	Diethylenetriamine
DLS	Dynamic Light Scattering
DMAc	N,N-dimethylacetamide
DMF	N,N-dimethylformamide
DSPM	Donnan Steric Pore Model
EDADMBSA	3,3’-(ethane-1,2-diylbis(azanediyl))bis(2,6-dimethylbenzenesulfonic acid)
FESEM	Field Emission Scanning Electron Microscopy
FO	Forward osmosis
FTIR	Fourier Transform Infrared
GO	Graphene oxide
hcp	Hexagonal close packed
HRTEM	High Resolution Transmission Electron Microscopy
HSP	Hansen Solubility Parameters
ICP	Internal concentration polarization
IPC	Isophthaloyl dichloride
IR	Infrared

MD	Membrane distillation
MF	Microfiltration
MPD	m-phenylenediamine
MWCNTs	Multiwalled carbon nanotubes
MXDA	m-xylylenediamine
NF	Nanofiltration
NIPS	Nonsolvent induced phase inversion
NMP	N-methylpyrrolidone
PAN	Polyacrylonitrile
PDA	Polydopamine
PEG	Polyethylene glycol
PEI	Polyethylenimine
PEIm	Polyetherimide
PES	Polyethersulfone
PIP	Piperazine
PSf	Polysulfone
PSS	Poly(sodium 4-styrenesulfonate)
PVDF	Polyvinylidene fluoride
PVP	Polyvinylpyrrolidone
RMS	Root mean square
RO	Reverse osmosis
RT	Room temperature
S-BAPS	Bis[4-(3-aminophenoxy)phenyl]sulfone
TA	Tannic acid
TEA	Triethylamine

TEG	Triethyleneglycol
TEM	Transmission Electron Microscopy
TEPA	Tetraethylenepentamine
TETA	Triethylenetetramine
TFC	Thin film composite
TFN	Thin film nanocomposite
TGA	Thermogravimetric Analysis
TMC	Trimesoyl chloride
TOC	Total Organic Carbon
UF	Ultrafiltration
UV	Ultraviolet
UV-Vis	Ultraviolet-Visible
VIPS	Vapor induced phase inversion
XRD	X-Ray Diffraction
ZIF-8	Zeolitic imidazolate framework-8

LIST OF SYMBOLS

A	Pure water permeability	$L/m^2 \cdot h \cdot bar$
$A_{i,j}$	HSP term for component pair of *i* and *j*	MPa
A_m	Effective membrane area	m^2
B	Salt permeability	$L/m^2 \cdot h$
B_{DS}	Draw solute permeability	$L/m^2 \cdot h$
C	Solute concentration	M
$C_{D,f}$	Final concentration of draw solute in draw solution	M
$C_{D,i}$	Initial concentration of draw solute in draw solution	M
C_f	Bulk feed concentration	M
C_o	Equilibrium solute concentration	M
C_p	Permeate concentration	M
D_{DS}	Diffusivity of draw solute in water	m^2/s
f_s	Solid fraction	-
i	van't Hoff's factor	-
J_s	Reverse salt flux	$mol/m^2 \cdot h$
$J_{v,FO}$	FO flux	$L/m^2 \cdot h$
J_w	Water flux	$L/m^2 \cdot h$
k	Boltzmann constant	J/K
k_3	Third order rate constant	$M^{-2}s^{-1}$
m	Number of ZIF-8 units that dissolve in water	-
n	Number of ZIF-8 units that form a ZIF-8 particle	-
n_i	Number of mole of component *i*	mol
P/P_o	Relative pressure	-
R	Universal gas constant	$J/mol \cdot K$

R_s	Salt rejection	-
r	Roughness ratio factor	-
r^*	Critical size	m
S	Structural parameter of support membrane	mm
T	Temperature	K
T_e	Solid-liquid equilibrium temperature	K
$V_{D,f}$	Final volume of draw solution	L
$V_{D,i}$	Initial volume of draw solution	L
V_m	Molar volume of the reference segment	cm^3/mol
γ	Surface energy of solid phase nucleated	J/m^2
ΔG_m	Gibbs free energy of mixing	J
ΔG_v	Gibbs free energy per unit volume	J/m^3
ΔH_f	Latent heat of fusion per unit volume	J/m^3
Δm_D	Change of mass of draw solution	g
ΔP	Transmembrane pressure	bar or Pa
ΔT	Supercooling	K
Δt	Time	h
ΔV	Permeate volume	L
ΔV_D	Change of volume of draw solution	L
$\Delta \pi$	Osmotic pressure difference	bar
δ_D	HSP for dispersion interaction	$(MPa)^{0.5}$
δ_{Di}	HSP for dispersion interaction of component *i*	$(MPa)^{0.5}$
δ_{Dj}	HSP for dispersion interaction of component *j*	$(MPa)^{0.5}$
δ_H	HSP for hydrogen bonding interaction	$(MPa)^{0.5}$
δ_{Hi}	HSP for hydrogen bonding interaction of component *i*	$(MPa)^{0.5}$
δ_{Hj}	HSP for hydrogen bonding interaction of component *j*	$(MPa)^{0.5}$

δ_P	HSP for polar interaction	$(MPa)^{0.5}$
δ_{Pi}	HSP for polar interaction of component *i*	$(MPa)^{0.5}$
δ_{Pj}	HSP for polar interaction of component *j*	$(MPa)^{0.5}$
θ_{CB}	Apparent contact angle	°
θ_Y	Young contact angle	°
π	Osmotic pressure	bar
$\pi_{D,b}$	Osmotic pressure of bulk draw solution	bar
$\pi_{F,m}$	Osmotic pressure of feed solution at the membrane surface	bar
ρ_F	Density of feed solution	g/L
σ	Supersaturation	-
ϕ_i	Volume fraction of component *i*	-
ϕ_j	Volume fraction of component *j*	-
$\chi_{i,j}$	Flory-Huggins interaction parameter between component *i* and *j*	-
Ω	Atomic volume	m^3

MEMBRAN NANOKOMPOSIT FILEM TIPIS POLIAMIDA/KERANGKA IMIDAZOLAT ZEOLITIK-8/POLISULFON UNTUK RAWATAN AIR TERHASIL MELALUI OSMOSIS HADAPAN

ABSTRAK

Penggunaan membran osmosis hadapan (FO) untuk rawatan air terhasil telah menghadapi cabaran seperti isipadu air sisa yang tinggi dan kestabilan kimia membran yang rendah terhadap air terhasil. Oleh itu, membran nanokomposit filem tipis (TFN) poliamida/kerangka imidazolat zeolitik-8 (ZIF-8) yang mempunyai kebolehtelapan air dan kestabilan kimia yang lebih baik dibangunkan dalam kajian ini. Partikel ZIF-8 bersaiz nano dan mempunyai taburan saiz unimodal berjaya disintesiskan pada suhu tindak balas yang rendah (5 °C) dengan menggunakan kepekatan ion zink (0.20 M) dan 2-metilimidazol (1.60 M) yang tinggi. Ia didapati bahawa salutan poli(natrium 4-stirenasulfonat) (PSS) menstabilkan partikel ZIF-8 daripada pelarutan dalam air dan seterusnya membolehkan pemuatannya melalui fasa berair semasa pempolimeran antaramuka. Pada masa yang sama, membran komposit filem tipis (TFC) yang mempunyai kememilihan NaCl yang tinggi disintesiskan dengan membentukkan filem poliamida di atas membran sokongan polisulfon (PSf) melalui pempolimeran antaramuka. Filem poliamida yang disediakan dengan menggunakan kepekatan m-fenilendiamina setinggi 3 w/v%, kepekatan trimesoil klorida setinggi 0.10 w/v% dan tempoh tindak balas sepanjang 60 s adalah nipis dan padat. Ia dicirikan melalui ujian penurasan osmosis berbalik dan mencapai kememilihan NaCl setinggi 0.673 bar^{-1}. Membran TFC ini selanjutnya disempurnakan secara pengubahan nisbah PSf/ polivinilpirolidon (PVP) dan penggunaan pelarut bersama semasa penyediaan dop

polimer untuk menambah baik kebolehbasahan permukaan membran sokongan dan pembentukkan filem poliamida di atasnya. Membran sokongan yang disediakan dengan menggunakan nisbah PSf/PVP setinggi 0.941 tanpa pelarut bersama mempunyai permukaan yang mempunyai kebolehbasahan yang baik, saiz liang yang seragam dan kekasaran yang sederhana (52.9 nm). Ia menambah baik kememilihan NaCl membran TFC ke 0.691 $\mathrm{bar^{-1}}$ berbanding dengan membran TFC yang disediakan di atas membran sokongan PSf tanpa pengubahsuaian dop polimer. Keadaan membran sokongan dan keadaan tindak balas membran TFC ini digabungkan dengan partikel ZIF-8 bersalut PSS untuk membangunkan membran TFN. Kebolehtelapan air tulen membran TFN yang disintesiskan dengan menggunakan trietilamina (TEA) (2.506 $\mathrm{L/m^2{\cdot}h{\cdot}bar}$) nyata sekali bertambah baik berbanding dengan kebolehtelapan air tulen membran TFC (1.110 $\mathrm{L/m^2{\cdot}h{\cdot}bar}$) dan membran TFN yang disintesiskan tanpa TEA (1.159 $\mathrm{L/m^2{\cdot}h{\cdot}bar}$). Peningkatan pengangkutan air membran TFN turut dipamerkan oleh fluks air yang lebih tinggi bagi membran TFN berbanding dengan membran TFC dalam penurasan air terhasil sintetik dan sebenar yang mempunyai kepekatan minyak setinggi 500 dan 377.8 ppm masing-masing melalui proses FO. Tambahan pula, membran TFN menunjukkan ketahanan pengampulan dan kestabilan kimia yang lebih baik terhadap air terhasil berbanding dengan membran TFC disebabkan partikel ZIF-8 yang stabil terhadap bahan kimia seperti hidrokarbon. Kesimpulannya, kajian ini berjaya membangunkan membran TFN poliamida/ZIF-8 yang mempunyai kebolehtelapan air yang tinggi, kestabilan kimia yang baik terhadap air terhasil serta penyingkiran minyak setinggi 99 % untuk rawatan air terhasil melalui proses FO.

POLYAMIDE/ZEOLITIC IMIDAZOLATE FRAMEWORK-8/ POLYSULFONE THIN FILM NANOCOMPOSITE MEMBRANE FOR THE TREATMENT OF PRODUCED WATER VIA FORWARD OSMOSIS

ABSTRACT

Produced water treatment using forward osmosis (FO) membrane has faced challenges such as high volume of wastewater and poor membrane chemical stability against produced water. Hence, a polyamide/zeolitic imidazolate framework-8 (ZIF-8) thin film nanocomposite (TFN) membrane with improved water permeability and chemical stability was developed in this work. Nanosized ZIF-8 particles with unimodal size distribution were successfully synthesized at low reaction temperature (5 °C) by using high zinc ion (0.20 M) and 2-methylimidazole (1.60 M) concentrations. Poly(sodium 4-styrenesulfonate) (PSS) coating was found to stabilize the ZIF-8 particles against dissolution in water, which enabled them to be dosed in via aqueous phase during interfacial polymerization. Concurrently, a thin film composite (TFC) membrane with high NaCl selectivity was synthesized by forming polyamide film above a polysulfone (PSf) support membrane via interfacial polymerization. The polyamide film prepared at 3 w/v% m-phenylenediamine concentration, 0.10 w/v% trimesoyl chloride concentration and 60 s reaction duration was thin and dense. It achieved high NaCl selectivity of 0.673 bar^{-1} as characterized via reverse osmosis filtration test. This TFC membrane was further refined by adjusting PSf/ polyvinylpyrrolidone (PVP) ratio and using co-solvent in preparing the polymer dope to improve support membrane surface wettability and polyamide film formation above it. The support membrane prepared at PSf/PVP ratio of 0.941 without co-solvent had a surface with good wettability, regular pore size and moderate roughness (52.9 nm). This improved the TFC membrane NaCl selectivity to 0.691 bar^{-1} compared to that prepared on PSf support membrane without polymer dope modification. The support and reaction conditions of this TFC membrane were combined with the PSS-coated ZIF-8 particles to develop the TFN membrane. The pure water permeability of TFN membrane synthesized with triethylamine (TEA) (2.506 $\text{L/m}^2\cdot\text{h}\cdot\text{bar}$) improved significantly over that of both TFC membrane (1.110 $\text{L/m}^2\cdot\text{h}\cdot\text{bar}$) and TFN membrane synthesized without TEA (1.159 $\text{L/m}^2\cdot\text{h}\cdot\text{bar}$). The enhanced water transport of TFN membrane was further manifested by its higher water flux relative to TFC membrane in filtering both synthetic and real produced water with oil concentration of 500 and 377.8 ppm respectively using FO process. Moreover, due to the chemically stable ZIF-8 particles against hydrocarbons, the TFN membrane demonstrated improved swelling resistance and chemical stability against produced water than the TFC membrane. In conclusion, this work successfully developed a polyamide/ZIF-8 TFN membrane with high water permeability, good chemical stability against produced water and high oil rejection of more than 99 % for produced water treatment using FO process.

CHAPTER ONE

INTRODUCTION

This chapter gives an overview of the background of this research project. In Section 1.1, the scenario on produced water pollution is presented. Forward osmosis (FO) membrane process is then introduced as a superior solution for its treatment in Section 1.2. Next, Section 1.3 discusses thin film nanocomposite (TFN) membrane as the current technology advancement in improving the membrane performance. Based on the latest research progress, the problem statement of this work is then highlighted in Section 1.4. This is followed by the formulation of research objectives of this work in Section 1.5. Finally, Section 1.6 and Section 1.7 present the scope of this study and the organization of this thesis.

1.1 Produced Water

The oil and gas industry has experienced an unprecedented growth due to the ever increasing global energy demand resulting from worldwide development. This has unfortunately led to the generation of large quantity of produced water. Currently, produced water is generated at an alarming rate of 250 million barrels worldwide daily along with 80 million barrels of oil, giving a high water to oil volume ratio of 3:1 (Fakhru'l-Razi et al., 2009, Igunnu and Chen, 2012, Jiménez et al., 2018). The volume of produced water is expected to keep increasing with time due to the growing oil and gas industry as well as maturing wells (Fakhru'l-Razi et al., 2009, Jiménez et al., 2018). Therefore, there is an urgent need of an effective technology to treat the large quantity of produced water to minimize its negative impact to the environment.

In general, produced water has a very complex composition. This includes dissolved and dispersed oil, dissolved minerals (salt ions, heavy metals and naturally occurring radioactive materials) with salinity ranging from a few ppm to 300000 mg/L, production chemicals and solids as well as dissolved gases (Fakhru'l-Razi et al., 2009, Igunnu and Chen, 2012, Jiménez et al., 2018). The main constituents of produced water from an oilfield are summarized in Appendix A. The generation of produced water has led to serious environmental problem such as pollution resulted from the discharge of produced water to the environment (Yu et al., 2017). It is reported that around 40 % of produced water is released to the environment (Igunnu and Chen, 2012).

Among the constituents of produced water, oil compounds have the strictest discharge concentration limit (Jiménez et al., 2018). The general oil concentration limit is 40 ppm (Igunnu and Chen, 2012). However, an increase of environmental awareness has gradually led to a stricter standard imposed by countries around the world (Igunnu and Chen, 2012). Table 1.1 summarizes the oil concentration limit in water for safe discharge in different countries. In view of the stringent regulations in place globally, produced water treatment gradually gains more attention from oil and gas producers with focus on zero pollutant release (Igunnu and Chen, 2012, Jiménez et al., 2018).

Table 1.1: Global legal oil concentration limit in water of various countries.

Country	Oil concentration limit (ppm)	Reference
Argentina and Venezuela	15	(Arnold and Stewart, 2008)
Brazil, Colombia and Ecuador	30	(Arnold and Stewart, 2008)
Indonesia	25	(Arnold and Stewart, 2008)
Middle East countries	30	(Arnold and Stewart, 2008)
North Sea countries	30	(Arnold and Stewart, 2008)
United States of America	29	(Arnold and Stewart, 2008)
Australia and Canada	30	(Neff, 2002)
Nigeria	40	(Neff, 2002)
China	10	(Tellez et al., 2002)
Malaysia	10	(Wan Ikhsan et al., 2017)

1.2 Forward Osmosis (FO) for Produced Water Treatment

Among the many technologies available for the treatment of produced water, membrane technology stands out as an attractive option. This is due to its better ability in removing the highly stable emulsified oil from water compared to other treatment methods. However, produced water still poses three challenges to using membrane technology for its treatment: membrane fouling, high volume of produced water to be treated and poor membrane chemical stability against produced water. Membrane fouling tends to be severe in treating produced water with high salinity as the stability of oil emulsion in produced water is low under saline condition and thus can induce a more serious membrane surface fouling especially under high pressure operation like reverse osmosis (RO) process (Fakhru'l-Razi et al., 2009, Igunnu and Chen, 2012, Wan Ikhsan et al., 2017, Jiménez et al., 2018).

In view of the membrane fouling problem, FO has emerged as a superior membrane technology over other membrane processes. FO offers unrivalled benefits over other membrane processes in terms of lower fouling propensity due to the absence of hydraulic pressure in its process (Chen et al., 2015, Bell et al., 2017, Chowdhury et al., 2017, Lv et al., 2017). Principally, FO process recovers water through the osmotic pressure difference created between both sides of membrane by a highly concentrated draw solution (Morales-Torres et al., 2016). An effective FO process requires a high draw solute retention in order to prevent the loss of osmotic pressure difference for water recovery. In view of this, the typical membrane used in a FO process is thin film composite (TFC) membrane. TFC membrane is comprised of a very thin and dense polyamide rejection layer residing above a porous support layer with the purpose of providing mechanical strength to the membrane. The dense polyamide rejection layer is vital in a FO process because it helps to retain the draw solutes from being lost to the feed solution thus preserving the osmotic pressure difference for effective water recovery.

Over the past decades, the water flux and solute rejection of TFC membrane have improved significantly as a result of its continuous advancement via global research efforts (Jeong et al., 2007). This includes optimization of polyamide rejection layer via the control of interfacial polymerization conditions as well as modification of support layer morphology by the control of phase inversion in preparing the support membrane. Nevertheless, with the gradually increasing amount of produced water and poor membrane chemical stability against produced water, further TFC membrane enhancement is necessary to achieve a better treatment outcome.

1.3 Thin Film Nanocomposite (TFN) Membrane

In order to handle high volume of produced water, high water permeability is an essential requirement of membrane. In this context, TFN membrane development represents a significant breakthrough in overcoming the inadequacy of TFC membrane. TFN membrane involves the introduction of nanofiller into the polyamide rejection layer that is formed via the typical interfacial polymerization above a porous support membrane (Jeong et al., 2007). Zeolite, carbon nanotubes (CNTs) and graphene oxide (GO) are some of the examples of nanofiller used for TFN membrane synthesis.

The water transport enhancement of TFN membrane is achieved via several ways. Firstly, a nanofiller provides less tortuous nanochannels for preferential water transport compared to the dense polyamide film (Jeong et al., 2007). For zeolite and CNTs, the nanochannels originate from their interconnected crystalline pore network (Azelee et al., 2017, Ghaee et al., 2017). Meanwhile, GO is often used in a multilayer configuration for improved mechanical strength. For a multilayered GO, the interlayer spacings act as the nanochannels for water transport (Jin et al., 2018, Lai et al., 2018, Shi et al., 2018a). Apart from nanochannels, a nanofiller can enhance the membrane water transport by improving the TFN membrane hydrophilicity (Dong et al., 2015, Lai et al., 2018, Ma et al., 2019). The enhanced membrane hydrophilicity is mostly resulted from the hydrophilic and charged groups present in the nanofiller structure such as hydroxyl and carboxyl groups (Dong et al., 2015, Lai et al., 2018, Ma et al., 2019). These groups can appear inherently in a nanofiller or are integrated into the nanofiller via functionalization.

Apart from water transport improvement, a nanofiller is generally beneficial for separating salt ions and water by functioning as a molecular sieve. By selecting a nanofiller with pore size that is between the size of common hydrated salt ions (0.66-0.86 nm) (Nightingale Jr., 1959) and the size of water molecule (0.27 nm) (Fathizadeh et al., 2011), the separation of salt ions and water can be achieved. Moreover, a charged nanofiller also helps to promote the separation between salt ions and water by inducing a stronger Donnan exclusion effect to reject the salt ions more effectively (Zarrabi et al., 2016, Mahdavi et al., 2017, Lai et al., 2018).

However, as is often the case for inorganic nanofillers, agglomeration occurs at high nanofiller loading due to incompatibility between the inorganic nanofillers and the organic polyamide. This causes interfacial defects that are detrimental to the salt rejection of TFN membrane (Dong et al., 2015, Mahdavi et al., 2017, Lai et al., 2018). In view of this, attention has been shifted towards hybrid organic-inorganic material, which can improve the compatibility between nanofiller and polyamide. For instance, zeolitic imidazolate framework-8 (ZIF-8), which constitutes both inorganic zinc ions and organic imidazolate ions, is proven to have better compatibility with the polyamide matrix (Duan et al., 2015, Xiao et al., 2018). Figure 1.1 illustrates the repeating unit of

ZIF-8 framework. Apart from the better nanofiller-polyamide compatibility, ZIF-8 has a pore size of 3.4 Å (Duan et al., 2015, Wang et al., 2015, Lee et al., 2019), which is ideal for water/salt separation. Low tortuosity nanochannels also exist within the ZIF-8 framework for rapid water transport. More importantly, ZIF-8 has excellent chemical stability against hydrocarbons such as alkanes and benzene, which are typically found in the produced water (Park et al., 2006). Hence, there is strong potential for ZIF-8 to be used as nanofiller in producing a TFN membrane with improved chemical stability for produced water treatment.

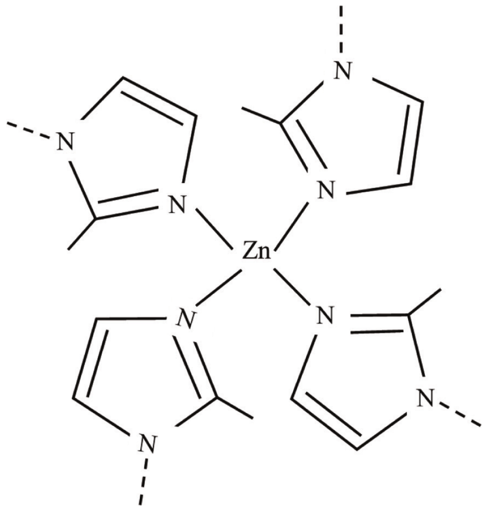

Figure 1.1: Repeating unit of ZIF-8 framework (Tan et al., 2017).

1.4 Problem Statement

FO, which has a lower fouling tendency than other membrane processes, has been selected in this work for the treatment of produced water. In order to achieve an effective treatment using FO process, it is important to develop a TFN membrane with the following criteria: high water permeability, high draw solute selectivity, high oil rejection and excellent chemical stability against produced water.

Prior to producing a TFN membrane via incorporation of nanofiller into the polyamide film, it is essential to first produce a TFC membrane with good structural integrity and high selectivity suitable for FO process. Past researches always reported that the TFC membrane separation properties hinge on its polyamide film structure, which is closely related to the interfacial polymerization conditions (Song et al., 2005, Soroush et al., 2012). However, the evolution process of polyamide film into its final structure is often neglected. Principally, this knowledge is essential as it allows the conceptualization of membrane structure at various stages of reaction, which may not be easily characterized due to the instantaneous nature of interfacial polymerization. With a better understanding on the polyamide film formation, it is easier to select the proper synthesis conditions for TFC membrane.

Apart from polyamide film, the support membrane of TFC membrane also plays a role in governing the polyamide film structure and TFC membrane separation properties (Ghosh and Hoek, 2009, Tiraferri et al., 2011). Although seldom reported, good support membrane surface wettability is the key to obtaining a structurally sound polyamide film as the synthesis of polyamide film involves the step of impregnating amine monomers into the support membrane surface pores before interfacial polymerization. The support membrane surface wettability can be tailored by tuning the casting dope composition to alter the phase inversion behavior during support membrane formation. Principally, polymer and additive interact differently with the solvent and nonsolvent. Similarly, different solvents also interact differently with the polymer and nonsolvent. This can change the support membrane surface properties including pore size, roughness and porosity to alter the support membrane surface wettability. Hence, it is of interest to study polymer/additive ratio and use of co-solvent in improving the support membrane surface wettability to achieve a better polyamide film formation and TFC membrane separation properties for later FO process.

ZIF-8 is chosen as the nanofiller in developing the TFN membrane in this work due to its beneficial properties including low tortuosity nanochannels for rapid water transport, pore size suitable for molecular sieving, improved compatibility with polyamide and good chemical stability against hydrocarbons. It is highly desirable to incorporate ZIF-8 particles with the size lower than the polyamide film thickness. This is to ensure that the ZIF-8 particles can fit well within the polyamide film to avoid the formation of defects in TFN membrane (Lee et al., 2019). Meanwhile, ZIF-8 particles with the size similar to the polyamide film thickness can also help to minimize the tortuosity of membrane. Since the polyamide film thickness is often around 50 to 200 nm (Lind et al., 2009), it is vital to tailor the ZIF-8 particle size to nanoscale.

The charged ions in the ZIF-8 framework are expected to aid its dispersion in water, which facilitates its incorporation into the TFN membrane via aqueous phase dosing. Unfortunately, ZIF-8 has been shown to degrade in water (Zhang et al., 2015), which makes it unstable and unsuitable for interfacial polymerization. Principally, ZIF-8 framework degradation indicates the loss of its nanochannels and molecular sieving effect, which is detrimental to water transport and solute rejection respectively. Hence, it is necessary to modify the ZIF-8 particle surface to prevent its degradation. Besides, ZIF-8 is also shown to be degraded by the hydrogen chloride formed during interfacial polymerization (Van Goethem et al., 2018). As such, acid acceptor must be introduced to remove the hydrogen chloride in order to protect the ZIF-8 framework. While acid acceptor has been widely used in forming TFC membrane, the role of acid acceptor in governing the TFN membrane synthesis remains unexplored. As such, it is of interest to study the interfacial polymerization of TFN membrane using acid acceptor to better understand the TFN membrane formation and separation properties.

It is commonly known that polyamide membrane can be easily swelled by hydrocarbons (Albo et al., 2014). In contrast, ZIF-8 offers excellent chemical stability against hydrocarbons (Park et al., 2006). In spite of this, ZIF-8 has never been explored for its ability in improving the chemical stability of polyamide against hydrocarbons such as alkanes, which are the typical oil compounds in produced water. Hence, the potential of ZIF-8 in improving the membrane chemical stability against hydrocarbons requires further detailed investigation.

1.5 Research Objectives

The aim of this study is to develop a polyamide/ZIF-8 TFN membrane with high water permeability, high NaCl (draw solute) selectivity, high oil rejection and improved chemical stability for produced water treatment. The research objectives are formulated as below:

1. To synthesize nanosized ZIF-8 particles with unimodal size distribution for TFN membrane development.
2. To synthesize a TFC membrane with high salt rejection for operation under FO process via interfacial polymerization.
3. To prepare a polysulfone (PSf) support membrane with enhanced surface wettability for improved polyamide film formation.
4. To develop a polyamide/ZIF-8 TFN membrane with high water permeability using surface-modified ZIF-8 particles and acid acceptor during interfacial polymerization.
5. To evaluate the performance and chemical stability of TFN membrane for the treatment of produced water using FO process.

1.6 Scope of Study

ZIF-8 particles are tailored to nanosize by performing reactant concentration study followed by reaction temperature study. The concentration of zinc ion (Zn^{2+}) and

2-methylimidazole (2-mIm^{-}) is first tuned systematically at a range of 0.025 to 0.20 M for Zn^{2+} concentration and 1 : 2 to 1 : 16 for Zn^{2+} : 2-mIm^{-} ratio (Cravillon et al., 2009, Kida et al., 2013). Increasing reactant concentration is expected to form smaller ZIF-8 particles by inducing higher supersaturation to favor ZIF-8 nucleation (Snyder and Richardson, 1993). Next, ZIF-8 particles are synthesized in ice bath condition (5 °C) by using reactant concentration that shows promising size control in reactant concentration study. The low reaction temperature is chosen because reducing reaction temperature can provide effective ZIF-8 size control by favoring nucleation via higher supercooling but hindering particle growth via lower reaction rate (Mullin, 2001).

A TFC membrane with good structural integrity and high NaCl (draw solute) selectivity should first be produced for the subsequent TFN membrane development. In this work, TFC membranes were synthesized at 1 to 3 w/v% m-phenylenediamine (MPD) concentration, 0.05 to 0.15 w/v% trimesoyl chloride (TMC) concentration and 30 to 90 s reaction duration (Soroush et al., 2012, Xie et al., 2012). The concentration of monomers and reaction duration are altered because they define the rate and extent of reaction respectively, in which a proper balance is required to obtain a structurally sound polyamide film. RO filtration test is carried out to characterize the membrane separation properties (pure water permeability and NaCl rejection). It is important to first characterize these properties before moving onto FO filtration of produced water. Firstly, a defective polyamide film with poor structural integrity (low NaCl rejection) can be avoided from being used in FO filtration test where rapid loss of driving force is expected. Besides, screening can be made based on pure water permeability so that only the membrane that shows promising improvement in water transport is tested for FO filtration of produced water. This can help to avoid meaningless FO experiments that require plenty of time, materials and effort. Based on the separation properties characterized through RO filtration test, the TFC membrane with the highest NaCl selectivity is chosen for the subsequent study.

Next, the PSf support membrane surface wettability is tailored by modifying PSf/polyvinylpyrrolidone (PVP) ratio as well as using N,N-dimethylformamide (DMF) and N,N-dimethylacetamide (DMAc) as co-solvent with N-methylpyrrolidone (NMP) as the main solvent in preparing the casting dopes. The PSf/PVP ratio is adjusted at 0.833 (15 wt% PSf and 18 wt% PVP), 0.941 (16 wt% PSf and 17 wt% PVP) and 1.063 (17 wt% PSf and 16 wt% PVP) while 10 wt% DMF and DMAc are added to the casting dope at the expense of NMP in this study (Han and Nam, 2002, Tiraferri et al., 2011). The casting dope composition is fine-tuned in only small quantity to avoid excessive membrane morphology change, which might cause undesirable effect on the structure and separation properties of TFC membrane. The phase inversion process is evaluated thermodynamically and kinetically using Flory-Huggins theory of polymer solution (Flory, 1953, Tompa, 1956, Kurada and De, 2017) and casting dope viscosity measurement respectively to explain the changes in support membrane surface properties governing its surface wettability (pore size, porosity and roughness), which are then correlated to the TFC membrane separation properties as characterized by RO filtration test. Again, the TFC membrane with the highest NaCl selectivity is chosen for subsequent TFN membrane development.

TFN membranes were synthesized by incorporating ZIF-8 particles through dosing into the aqueous phase monomer solution. The water stability of ZIF-8 particles is improved by coating them with poly(sodium 4-styrenesulfonate) (PSS) molecules using pure or mixture of methanol and water as the coating solvent. The negatively charged PSS is expected to interact well with the Zn^{2+} ions at the ZIF-8 outer surface thus preventing the Zn^{2+} ions from dissolving into water. Both methanol and water are needed in the coating solvent to balance the need of stabilizing the ZIF-8 particles and dissolving the PSS. 2 w/v% triethylamine (TEA) is further added into the aqueous phase monomer solution as the acid acceptor to prevent ZIF-8 from being degraded by the hydrogen chloride generated during interfacial polymerization of TFN membrane (Sharabati et al., 2019). After that, the TFC and TFN membranes with high pure water permeability are chosen to be compared for FO filtration of produced water.

The TFC and TFN membranes selected above are tested for FO filtration of synthetic and real produced water with oil concentration of 500 ppm and 377.8 ppm respectively. The oil concentration of synthetic produced water is chosen arbitrarily to be higher than that of real produced water considering that the oil concentration will increase with time during FO filtration due to water permeating from the feed to draw solution. The real produced water is provided by Petronas Penapisan (Terengganu) Sdn. Bhd., Kerteh. In order to evaluate the complex composition of produced water, pure water and synthetic seawater are run for comparison. The flow rate of feed and draw solutions is set at 0.757 L/min (12 GPH) and 0.505 L/min (8 GPH) respectively. These flow rates are chosen such that stable flow can be provided by the pumps within their operating limit. Three key requirements of produced water treatment are assessed and compared between TFC and TFN membranes: water flux, oil rejection and membrane chemical stability. The membrane chemical stability is characterized by performing Thermogravimetric Analysis (TGA) on the membranes before and after FO filtration to evaluate the membrane swelling behavior.

1.7 Thesis Organization

There is a total of five chapters in this thesis. The contents of every chapter are briefly summarized below.

In Chapter One, the overview on produced water and its treatment using FO membrane technology is first provided. Next, based on the problems associated with produced water treatment using FO process, the problem statement is outlined along with the formulation of research objectives to address the problem statement. This is followed by the scope of this study and finally the organization of this thesis.

Chapter Two provides the detailed literature review on the latest development of research pertaining to the current work. The conventional and membrane treatment methods of produced water is first discussed. Next, the development of TFC membrane is reviewed from two aspects: tuning of polyamide film via interfacial polymerization control and tuning of support membrane via phase inversion control. Subsequently, TFN membrane is introduced with the common nanofillers used discussed along with their performance and limitations. ZIF-8, which is the nanofiller selected in this work, is also reviewed in detail on the aspect of TFN membrane performance as well as the importance of size control and chemical stability. The challenges in FO treatment of produced water and the techniques employed in previous works in solving the issues are then presented. Lastly, the research gaps are highlighted.

Chapter Three begins with the details of raw materials and chemicals used in this project. This is followed by the experimental flow chart. Next, all major procedure in this work are presented in a systematic manner. The synthesis of ZIF-8 particles is first described together with the surface modification procedure and characterizations performed. Next, the steps in preparing PSf support membranes are presented along with the methods in analyzing the thermodynamics and kinetics of casting dope. This is followed by the description on the synthesis of TFC and TFN membranes. After that, all membrane characterizations performed are detailed with their purpose and steps in obtaining the results. Lastly, the procedure on RO and FO filtration tests in evaluating the TFC and TFN membranes are described.

Chapter Four presents the core findings of this study based on the formulated research objectives. The synthesis of nanosized ZIF-8 particles with unimodal size distribution is first reported. Next, the TFC membrane synthesized at different reaction conditions is discussed with focus on the evolution of polyamide film structure and the selection of TFC membrane with high NaCl selectivity. This is then followed by the findings on the tuning of TFC membrane separation properties via modification of support membrane surface properties by altering polymer/additive ratio and using co-solvent in preparing the casting dope. The corresponding thermodynamics and kinetics changes of phase inversion are reported. The development of polyamide/ZIF-8 TFN membrane is then discussed. The study on ZIF-8 stability in water is first presented. The findings on the separation characteristics of TFN membrane synthesized under PSS coating of ZIF-8 particles and with the aid of TEA follow subsequently along with the characterization results. This chapter ends with the findings on the FO performance of TFN membrane for the filtration of synthetic and real produced water with focus on three key requirements: water flux, oil rejection and membrane chemical stability.

Finally, Chapter Five recaps the major findings of this study in accordance to the formulated research objectives. Several recommendations are then provided based on the current research findings in improving the future works.

CHAPTER TWO

LITERATURE REVIEW

This chapter summarizes the latest development of researches closely related to the current project. Section 2.1 introduces the common produced water treatment methods including conventional methods and membrane technology. Next, Section 2.2 discusses the past development of TFC membrane including the optimization of both support membrane and polyamide active layer by the control of phase inversion and interfacial polymerization respectively. This is followed by Section 2.3, which reviews the latest progress of TFN membrane and the types of nanofiller introduced. Besides, focus is placed on ZIF-8, which is the nanofiller selected in this project, on the aspect of its size control and chemical stability. After that, Section 2.4 discusses the treatment of produced water using FO process with focus on the limitations faced in previous works. Finally, the research gaps are identified and highlighted in Section 2.5.

2.1 Produced Water Treatment Technologies

Produced water is a serious pollutant that requires effective treatment in this highly urbanized and industrialized world. This section reviews the technologies that have been developed for produced water treatment.

2.1.1 Conventional Produced Water Treatment Methods

Conventionally, many methods have been developed to treat produced water. Generally, produced water treatment techniques can be classified into a few categories: physical treatment, chemical treatment and biological treatment. In some of the cases, different treatment methods are combined for a better treatment outcome in order to abide to the stringent regulations on the discharge limit of oil compounds (Fakhru'l-Razi et al., 2009, Igunnu and Chen, 2012, Yu et al., 2017, Jiménez et al., 2018).

The common physical methods for the treatment of produced water include adsorption and flotation (Fakhru'l-Razi et al., 2009, Igunnu and Chen, 2012, Wan Ikhsan et al., 2017, Yu et al., 2017, Jiménez et al., 2018). In adsorption, adsorbents are used to adsorb the oil compounds from produced water. The typical adsorbents are activated carbon, organoclay and zeolite (Fakhru'l-Razi et al., 2009, Igunnu and Chen, 2012, Jiménez et al., 2018). This method can achieve high water quality (Jiménez et al., 2018) but requires the regeneration of adsorbent and is prone to adsorbent plugging by the suspended solids (Igunnu and Chen, 2012, Jiménez et al., 2018). Meanwhile, in flotation technique, fine air bubbles are introduced into the wastewater to attach to the oil. This reduces the density of oil to make them float in water. The floated oil can then be skimmed off from the water (Yu et al., 2017). This method does not require any chemicals (Igunnu and Chen, 2012) but is not suitable for produced water having emulsified oil and high salinity (Jiménez et al., 2018).

In the context of chemical treatment, the most common techniques include coagulation and electrochemical processes. In coagulation, coagulants are added to the wastewater to destabilize colloidal oil (Wan Ikhsan et al., 2017). This method is often combined with flocculation to produce large agglomerates that can be removed easily thereafter (Wan Ikhsan et al., 2017). The typically used coagulants are ferric chloride, aluminium sulfate and polyaluminium chloride (Wan Ikhsan et al., 2017). This method is suitable for removing colloidal and suspended oil but not dissolved oil (Fakhru'l-Razi et al., 2009, Jiménez et al., 2018). Besides, this method produces sludge, which requires further handling and treatment. Meanwhile, electrochemical processes make use of the chemical reaction to achieve oil removal from produced water while producing electricity simultaneously (Igunnu and Chen, 2012, Jiménez et al., 2018). This method does not require additional chemicals and produces no secondary waste although it may need to couple with other treatment methods to achieve a high quality discharge water (Igunnu and Chen, 2012, Jiménez et al., 2018).

On the other hand, biological treatment makes use of microbial metabolism to convert organic contaminants into harmless materials (Igunnu and Chen, 2012, Wan Ikhsan et al., 2017, Yu et al., 2017). As of today, the most widely applied biological treatment method is activated sludge (Fakhru'l-Razi et al., 2009, Igunnu and Chen, 2012, Wan Ikhsan et al., 2017, Yu et al., 2017). In this technique, an aeration tank is utilized to sustain the microbial growth while the wastewater is flowed through the tank for a predetermined retention time in order for microbial metabolism to occur. In general, biological treatment is rather effective for the removal of hydrocarbons (Fakhru'l-Razi et al., 2009, Jiménez et al., 2018). However, it is shown to have minimal impact on the dissolved solids in wastewater (Jiménez et al., 2018). Besides, its effectiveness reduces significantly at higher salinity (Tellez et al., 2002) thus may not be suitable for treating produced water with very high salinity.

Although all conventional treatment methods aforementioned are relatively well-developed, their widespread application on the treatment of oily wastewater has been restricted by some disadvantages such as uneconomical process, requirement for space and chemicals as well as secondary pollution (Fakhru'l-Razi et al., 2009, Padaki et al., 2015). In addition, emulsified oil, which is very stable in water, cannot be treated effectively with the conventional techniques. Furthermore, the environmental standard on oil discharge is becoming stricter in response to the increased global environmental awareness. All these factors drive the development of a more effective technology for produced water treatment such as membrane technology.

2.1.2 Membrane Technology for Produced Water Treatment

Membrane technology has gradually emerged as a promising alternative for treating produced water in the 21st century (Fakhru'l-Razi et al., 2009, Padaki et al., 2015). In general, a membrane is a thin film with specific pore size range that allows the selective separation of fluid from its constituents (Fakhru'l-Razi et al., 2009, Igunnu and Chen, 2012). The membrane can be made up of polymer such as polyvinylidene fluoride (PVDF) (Jiménez et al., 2018) or inorganic material such as zeolite (Fakhru'l-Razi et al., 2009, Jiménez et al., 2018). Membrane technology offers many advantages over the conventional treatment methods including higher quality of effluent, no chemical addition, no phase change thus less energy and cost demand, low sludge production thus less secondary pollution and easy operation (Wan Ikhsan et al., 2017, Yu et al., 2017, Jiménez et al., 2018). However, fouling remains the major drawback in membrane technology (Fakhru'l-Razi et al., 2009, Igunnu and Chen, 2012, Wan Ikhsan et al., 2017, Jiménez et al., 2018).

As of today, the most well-established membrane technology for treating oily wastewater is the pressure-driven membrane processes such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and RO (Fakhru'l-Razi et al., 2009, Igunnu and Chen, 2012, Silva et al., 2017, Wan Ikhsan et al., 2017, Jiménez et al., 2018). From MF, UF, NF to RO processes, the effluent quality increases along with the energy and cost requirement (Jiménez et al., 2018). Therefore, the selection of the type of pressure-driven membrane process depends on the water discharge quality required and the composition of oily wastewater. For instance, RO is a more suitable process in obtaining pure water as it can remove the high salinity of typical produced water via its very small membrane pores. On the other hand, MF and UF membranes have much larger pores that are effective in removing suspended solids and oil but not the salt contents of produced water (Igunnu and Chen, 2012). Hence, MF and UF processes are mainly designed for pretreatment instead of final water polishing.

Besides pressure-driven membrane processes, there are two other emerging membrane technologies, which are membrane distillation (MD) and FO. MD is a temperature-driven membrane process, which works based on the vapor pressure difference between both sides of membrane (Silva et al., 2017). Specifically, the thermally vaporized water permeates through a hydrophobic membrane and is then condensed at the other side of membrane to obtain water with improved quality (Silva et al., 2017). At the same time, the non-volatile pollutants in wastewater are selectively separated (Silva et al., 2017). MD process avoids the direct contact between membrane and non-volatile contaminants of oily wastewater (Silva et al., 2017). However, mineral scaling is discovered in the MD treatment of produced water in some studies (Cho et al., 2016, Zhong et al., 2016).

Meanwhile, in FO process, a highly concentrated draw solution is separated from the feed solution by a membrane in between them. By principle, this creates an osmotic pressure difference between both sides of membrane, which drives the water through the membrane (Morales-Torres et al., 2016) while retaining the pollutants in wastewater. The schematic diagram of FO process for produced water treatment is shown in Figure 2.1. FO process cannot generate a pure effluent and needs to be coupled with other membrane processes such as UF, NF, RO and MD to obtain pure water while regenerating the draw solution for reuse at the same time (Ge et al., 2013). However, FO process has distinct advantages over pressure-driven and temperature-driven membrane processes as it does not require high pressure and temperature thus reducing the energy demand (Silva et al., 2017). More importantly, the absence of hydraulic pressure lowers the membrane fouling propensity significantly (Chen et al., 2015, Bell et al., 2017, Chowdhury et al., 2017, Lv et al., 2017). Hence, FO process is an attractive option among all membrane processes for the treatment of produced water. TFC membrane is the typical membrane used in FO process owing to the need of a dense rejection layer to retain the draw solute in draw solution. In view of this, substantial research effort has been dedicated to improving the TFC membrane performance particularly on the water flux and solute rejection.

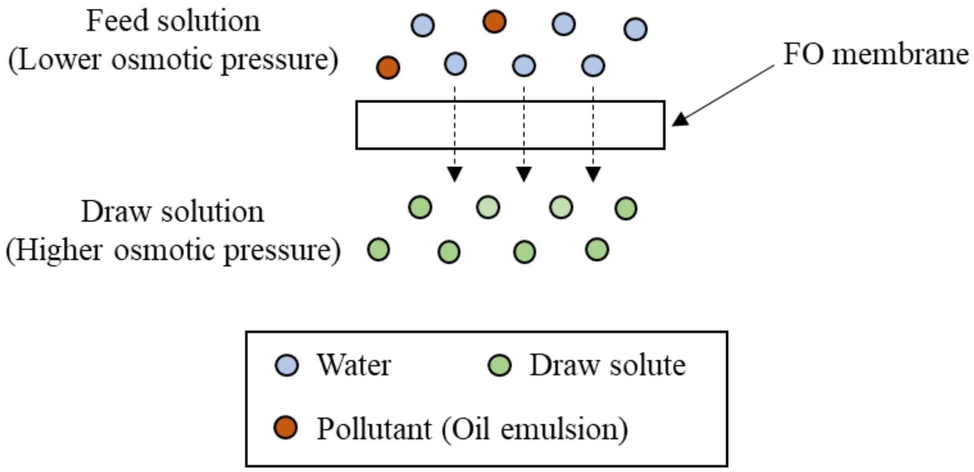

Figure 2.1: Schematic diagram of FO process for produced water treatment.

2.2 Development of Thin Film Composite (TFC) Membrane

TFC membrane consists of a very thin and dense polyamide film residing on a porous support membrane. Figure 2.2 shows the structure of a typical TFC membrane. For pressure-driven membrane processes such as NF and RO, it is generally accepted that polyamide film plays a more dominant role in governing the membrane water flux and salt rejection compared to the support membrane (Xu et al., 2017a). However, the support membrane can also influence the TFC membrane performance as it provides the surface for interfacial polymerization and attachment of polyamide film (Xu et al., 2017a). Meanwhile, for osmotically driven membrane process such as FO, the support membrane further controls the TFC membrane performance by dictating the severity of internal concentration polarization (ICP) during FO filtration (Xu et al., 2017a). ICP occurs as the support membrane creates resistance for the draw solute to diffuse across it, which lowers the effective osmotic pressure difference for water recovery. In short, both polyamide film and support membrane are equally important in developing a TFC membrane with proper structure and good performance. It is widely accepted that the polyamide film and support membrane can be optimized separately (Ghosh and Hoek, 2009, Han et al., 2012). This section summarizes the methods and findings of literature in seeking for a better TFC membrane performance via the tuning of polyamide film and support membrane respectively.

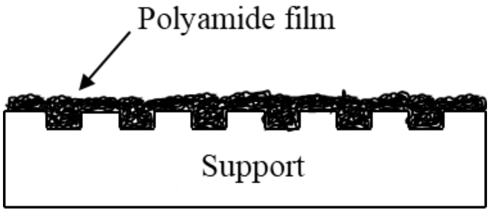

Figure 2.2: Illustration of TFC membrane structure.

2.2.1 Polyamide Film Tuning via Control of Interfacial Polymerization

Generally, polyamide film is formed via interfacial polymerization between amine monomer in water and acid chloride monomer in organic solution. The synthesis of polyamide film generally involves two steps. In the first step, amine monomers are impregnated into the support membrane surface pores. Next, acid chloride monomers are poured onto the support membrane surface for interfacial polymerization to take place for a predetermined duration (Tomaschke, 2000). The resulting TFC membrane can also undergo optional heat curing treatment to promote further reaction between amine and acid chloride monomers (Soroush et al., 2012). Principally, polyamide film morphology can be altered by varying the synthesis conditions of polyamide film. For instance, manipulating amine and acid chloride monomers, altering reaction conditions, controlling heat curing conditions and using additives in reaction.

Tuning of monomer content provides an easy and direct means in controlling the polyamide film synthesis. Wei et al. (2011) studied MPD concentration in their TFC membrane preparation. They found that increasing MPD concentration from 0.5 to 2 w/v% improved the polyamide film crosslinking to form a denser membrane. Hence, water permeability decrement and salt rejection increment were concomitantly observed (Wei et al., 2011). Meanwhile, Xie et al. (2012) reported an optimum MPD concentration of 1.5 w/v% for achieving high water flux. A higher (up to 3 w/v%) and lower (down to 0.5 w/v%) MPD concentration gave rise to a thicker and denser polyamide film respectively, which resulted in a lower water flux (Xie et al., 2012). Similarly, an optimum MPD concentration was found in the work of Xu et al. (2017b). At low MPD concentration (0.1 to 0.2 w/v%), the TFC membrane was not permeable to water due to the closely packed polyamide chains. On the other hand, a thicker and looser polyamide film with defects was formed at high MPD concentration of 20 w/v% to culminate in a lower water flux and salt rejection. Meanwhile, at optimum MPD concentration of 2 w/v%, a high water flux of 60 $L/m^2 \cdot h$ and salt rejection of 98.8 % was attained (Xu et al., 2017b). Interestingly, Park et al. (2018) obtained opposite result, where increasing MPD concentration did not affect the TFC membrane performance. Due to the strong interaction between MPD and hydrophilic polyacrylonitrile (PAN) support, the diffusion of MPD into organic phase was suppressed. This thus minimized the impact of MPD on membrane formation (Park et al., 2018).

Besides MPD, sulfonated amines have been investigated for TFC membrane synthesis. Xie et al. (2012) utilized bis[4-(3-aminophenoxy)phenyl]sulfone (S-BAPS) as the amine monomer in TFC membrane preparation. The high molecular weight and hydrophilicity of S-BAPS slowed down the diffusion of S-BAPS into organic phase. This lowered the membrane crosslinking to produce a membrane with high water flux but low NaCl rejection (Xie et al., 2012). 3,3’-(ethane-1,2-diylbis(azanediyl))bis(2,6-dimethylbenzenesulfonic acid) (EDADMBSA) was employed in another work as the amine monomer in synthesizing the TFC membrane. EDADMBSA was specially engineered by Zheng et al. (2018) to contain two bulky methyl groups beside the phenylamino group in EDADMBSA. The methyl groups restricted the packing of polyamide chains due to steric hindrance to increase the amount of water pathways within the membrane. Besides, the methyl groups served to fill up the membrane voids. As a result, the TFC membrane attained a higher water flux while retaining a reasonably high salt rejection (Zheng et al., 2018). Meanwhile, Li et al. (2014) compared the TFC membranes produced from different amine monomers including diethylenetriamine (DETA), triethylenetetramine (TETA), tetraethylenepentamine (TEPA) and piperazine (PIP). They concluded that the amine with higher solubility in organic phase favored the formation of membrane with higher porosity, electrical charges and larger nodules to give a higher water permeability (Li et al., 2014).

Compared to the single amine system, mixed amine monomers can provide greater control of TFC membrane performance by introducing two amine monomers with desirable characteristics into the membrane structure. For instance, Vyas and Ray (2015) controlled the balance between the linear PIP and the aromatic MPD in TFC membrane synthesis. It was found that a higher PIP content improved the water flux while a higher MPD content increased the NaCl rejection (Vyas and Ray, 2015). Perera et al. (2015) used a more hydrophilic 1,3-diamino-2-hydroxypropane (DAHP) together with MPD as the amine monomers. The use of DAHP led to a thinner membrane with higher chain mobility and internal porosity thus increasing the water permeability (Perera et al., 2015). In another work, melamine was used as the co-monomer with polyethylenimine (PEI) in TFC membrane synthesis (Hoseinpour et al., 2017). The use of melamine not only improved the water flux by forming a looser membrane but also improved the PEI resistance against acidic attack (Hoseinpour et al., 2017). Carboxylic monoamine and polydopamine (PDA) are some other examples of co-monomer used together with PIP in producing a TFC membrane (Ang et al., 2017, Zhu et al., 2018). In both researches, the mixed amine systems produced a TFC membrane with higher hydrophilicity and negative charges to give a higher water permeability and Na_2SO_4 rejection (Ang et al., 2017, Zhu et al., 2018).

TFC membrane performance can also be tuned by adjusting the acid chloride monomer. TMC is by far the most dominating acid chloride used for TFC membrane synthesis due to its ability to endow the membrane with crosslinking ability. Wei et al. (2011) adjusted TMC concentration in preparing the TFC membrane. They found that higher TMC concentration produced more unreacted -COCl crosslinking sites in the polyamide film. As a result, a membrane with lower crosslinking degree and thus higher permeability and lower salt rejection was obtained (Wei et al., 2011). In another work, Xie et al. (2012) reported that the highest water flux was attained at 0.05 w/v% TMC concentration. Film density increase was observed at higher TMC concentration of up to 0.13 w/v% while lower TMC concentration (0.025 w/v%) gave a thicker polyamide film. Both factors subsequently reduced the water flux (Xie et al., 2012). Xu et al. (2017b) studied the correlation between TFC membrane morphology and performance. They concluded that 0.1 w/v% TMC concentration was optimum as a membrane with lower water flux was formed at both lower and higher TMC concentration attributed to the formation of void-free and thicker polyamide film, respectively (Xu et al., 2017b). In the work of Park et al. (2018), a lower water flux but higher NaCl rejection was obtained at increasing TMC concentration owing to the enhanced membrane crosslinking as more TMC could take part in the reaction.