

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

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

by

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**Thesis submitted in fulfillment of the
requirements for the degree of
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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·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 membentuk 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 kebolehasahan 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 kebolehasahan yang baik, saiz liang yang seragam dan kekasaran yang sederhana (52.9 nm). Ia menambah baik kememilihan NaCl membran TFC ke 0.691 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) ($2.506 \text{ L/m}^2 \cdot \text{h} \cdot \text{bar}$) nyata sekali bertambah baik berbanding dengan kebolehtelapan air tulen membran TFC ($1.110 \text{ L/m}^2 \cdot \text{h} \cdot \text{bar}$) dan membran TFN yang disintesiskan tanpa TEA ($1.159 \text{ L/m}^2 \cdot \text{h} \cdot \text{bar}$). 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.

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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