

SYNTHESIS, CHARACTERIZATION AND PERFORMANCE  
ASSESSMENT OF THIN FILM COMPOSITE NANOFILTRATION  
(TFC-NF) MEMBRANES FOR TREATING DYES WASTEWATER

NORHIDAYAH BINTI ABDULL

MASTER OF SCIENCE  
UNIVERSITI MALAYSIA TERENGGANU

2009

0/7199

1100071230

Perpustakaan Sultanah Nur Zahirah  
Universiti Malaysia Terengganu (UMT)



tesis

TP 248.25 .M46 N6 2009



1100071230

Synthesis, characterization and performance assessment of thin film composite nanofiltration (TFC-NF) membranes for treating dyes wastewater / Norhidayah Abdull.

PERPUSTAKAAN SULTANAH NUR ZAHIRAH  
UNIVERSITI MALAYSIA TERENGGANU (UMT)  
21030 KUALA TERENGGANU

1100071230		

Lihat sebelah

HAK MILIK  
PERPUSTAKAAN SULTANAH NUR ZAHIRAH UMT

**SYNTHESIS, CHARACTERIZATION AND PERFORMANCE  
ASSESSMENT OF THIN FILM COMPOSITE  
NANOFILTRATION (TFC-NF) MEMBRANES  
FOR TREATING DYES WASTEWATER**

**NORHIDAYAH BINTI ABDULL**

**Thesis Submitted in Fulfillment of the Requirements for the  
Degree of Master of Science in the Faculty of Science and Technology  
Universiti Malaysia Terengganu**

**March 2009**

**1100071239**

Abstract of thesis presented to the Senate of Universiti Teknologi  
Malaysia in fulfillment of the requirement for the degree of Master of  
Science

**SYNTHESIS, CHARACTERIZATION AND PERFORMANCE  
ASSESSMENT OF THIN FILM COMPOSITE NANOFILTRATION  
(TFC-NF) MEMBRANES FOR TREATING DYES WASTEWATER**

**NORIDAYAH BINTI ABDULL**

March 2009

Chairperson : Associate Professor Dr. NorZalida bt Abd. M.P.H.  
They (angels) said: "Glory be to You, we have no knowledge except what  
you have taught us. Verily, it is You, the All-Knower, the All-Wise."  
Member : Associate Professor Dr. Ahmad bin Abdul  
Faculty : Science and Technology

**This thesis is dedicated to**

My parents (Hj Abdull bin Said and Hj Zahaliah bt Daud),

my sisters (NorZaliza and Nor Asyikin),

Mohammad Aryf bin Yusuff

**And**

All those noble and sublime personalities whose serenity,

courage and wisdom lead me to the *Path of Guidance*

Abstract of thesis presented to the Senate of Universiti Terengganu Malaysia in fulfillment of the requirement for the degree of Master of Science.

**SYNTHESIS, CHARACTERIZATION AND PERFORMANCE  
ASSESSMENT OF THIN FILM COMPOSITE NANOFILTRATION  
(TFC-NF) MEMBRANES FOR TREATING DYES WASTEWATER**

**NORHIDAYAH BINTI ABDULL**

**March 2009**

**Chairperson : Associate Professor Dr. Nora`aini binti Ali, Ph.D.**  
**Member : Associate Professor Ir. Ahmad bin Jusoh**  
**Faculty : Science and Technology**

In this study, the influence of dipping times of aqueous phase, reaction times in organic phase, and curing times on the preparation of thin film composite nanofiltration (TFC-NF) membranes were examined. Membranes were interfacially polymerized of m-phenylene diamine and trimesoyl chloride on ultrafiltration membrane and then were characterized by means of permeability coefficient, charged solutes separation and membrane morphologies. All membranes characteristics are in the range of NF membrane. SEM micrographs show that most of the membranes have typical composite structure. The prepared membranes within 3 min dipping time (TFC-NF-D3), 30 sec reaction time (TFC-NF-R30) and curing time (TFC-NF-C15) reveal the superior charged solute separation with the trade off between permeate fluxes and rejections. These membranes were further investigated to obtain a general understanding of the possibility of membrane to separate the dye-based wastewater. Results indicate

membranes have good quality of permeates (up to about 95%) and higher fluxes (1.957 to 17.977 m<sup>3</sup>/m<sup>2</sup>.s.bar) as well as to those observed with commercial membranes.

Among the dominant obstacles of NF membrane process is the declination of flux over time. Therefore, the effect of dye concentration (100 mg/L, 200 mg/L, 300 mg/L and 400 mg/L) and dye – salt mixture concentration (0.1 g/L, 1.0 g/L and 10.0 g/L) at fixed dye concentration of 100 mg/L on the flux decline behavior of dye wastewater were examined. The membrane properties and the percentages of flux decline (total flux decline, irreversible and reversible fouling, and concentration polarization) were investigated to explain the flux decline behavior. The highest dye and dye –salt mixture concentration exposes that the most accelerates of flux decline, but the lowest flux recovery for all membranes. Fluxes were sharply decreased at the initial stage of filtration. It is believed that the flux decline behavior at this stage is controlled by the irreversible fouling (pore blockage and pore constriction mechanisms). When more dyes accumulated on the membrane surface, the flux decline mechanism transited to cake formation mechanism (reversible fouling). At this stage, a steady state was achieved. Thus, it is demonstrated that most of the filtration process was dominated by a reversible fouling.

Abstrak tesis yang dikemukakan kepada Senat Universiti Malaysia Terengganu sebagai memenuhi keperluan untuk ijazah Sarjana Sains.

**SISTESIS, PENCIRIAN DAN PENILAIAN PRESTASI MEMBRAN  
PENURAS NANO SELAPUT NIPIS (TFC NF) DALAM MERAWAT  
AIR SISA BAHAN PENCELUP**

**NORHIDAYAH BINTI ABDULL**

**Mac 2009**

**Pengerusi : Profesor Madya Dr. Nora`aini binti Ali, Ph.D.**

**Ahli : Profesor Madya Ir. Ahmad bin Jusoh**

**Fakulti : Sains and Teknologi**

Dalam kajian ini, pengaruh masa celupan pada fasa akues, masa tindakbalas pada fasa organik, dan masa rawatan terhadap penyediaan membran komposit selaput nipis penuras nano (TFC NF). Membran dipolimerkan secara antara muka antara *m*-fenelin diamina and trimesoil klorida pada membran penuras ultra dan kemudian dicirikan terhadap pekali kebolehtelapan, pemisahan bahan bercas dan morfologi membran. Keseluruhan ciri-ciri membran berada di dalam julat penuras nano (NF). Mikrograf pengimbas elektron mikroskopik (SEM) menunjukkan hampir keseluruhan membran mempunyai struktur tipikal komposit. Membran yang dibangunkan pada masa pencelupan 3 minit (TFC-NF-D3), masa tindakbalas 30 saat (TFC-NF-R30) dan masa rawatan 15 minit (TFC-NF-C15) menunjukkan pemisahan bahan bercas yang terbaik dengan kesinambungan di antara fluks dan penyingkiran. Membran-membran ini dijalankan penyelidikan selanjutnya untuk mendapatkan pemahaman umum terhadap kebolehan membran memisahkan air sisa berasaskan bahan

pencilup. Keputusan membuktikan bahawa membran mempunyai air keluar yang berkualiti tebaik (penyingkiran mencapai sehingga 95%) dan fluks yang tinggi (1.957 to 17.977 m<sup>3</sup>/m<sup>2</sup>.s.bar) seperti mana ia sejajar dengan membran komersial.

Antara permasalahan utama membran NF ialah penurunan fluks terhadap masa. Oleh itu, pengaruh kepekatan bahan pencilup (100 mg/L, 200 mg/L, 300 mg/L dan 400 mg/L) dan kepekatan campuran bahan pencilup - garam (0.1 g/L, 1.0 g/L dan 10.0 g/L dengan kepekatan bahan pencilup yang tetap pada 100 mg/L) terhadap kelakuan penurunan fluks air sisa bahan pencilup dikaji. Ciri-ciri membran dan peratusan penurunan fluks (jumlah penurunan fluks, penyumbatan ketakterbolehbalikan dan kebolehterbalikan dan kepekatan polarisasi) dikaji untuk menerangkan kelakuan penurunan fluks. Kepekatan yang tertinggi bagi bahan pencilup dan campuran bahan pencilup – garam mempamerkan penurunan fluks berlaku dengan lebih pantas, tetapi paling rendah bagi perolehan semula fluks untuk semua membran. Fluks menurun secara drastik pada permulaan peringkat penurasan. Ini dipercayai bahawa kelakuan penurunan fluks pada peringkat ini dikawal oleh penyumbatan tidak boleh balikan (mekanisme penyumbatan liang dan penjerutan liang). Apabila lebih banyak bahan pencilup termendak pada permukaan membran, mekanisme penurunan fluks bertukar kepada mekanisme pembentukan kek (penyumbatan boleh balikan). Pada peringkat ini, keadaan stabil dicapai. Maka, ini membuktikan bahawa hampir keseluruhan proses penurasan didominasi oleh penyumbatan boleh balikan.



## ACKNOWLEDGEMENT

*In the name of Allah, the Most Gracious, the Most Merciful Read! In the Name of your Lord Who has created (all that exists). He has created man from a clot (a piece of thick coagulated blood). Read! And your Lord is the Most Generous. Who has taught (the writing) by the pen. He has taught man which has known not.*

*Al-Quran, Surah Al-Alaq: 1-5*

*(The Quran, Chapter 96: 1-5)*

All Praises and thanks are for Allah (Subhanau-wa-Ta`alla), the Lord of the entire creation that exists (in earth and in Heavens). May his peace and Blessing be upon all His Messengers, Prophets, their Companions and all Muslims (alive or dead) – Amin. I am extremely grateful to Almighty Allah who alone made this accomplishment possible. Research is basically unveiling the mysteries of the universe by trying to understand the laws of nature as set by Creator. I was found a miracle in the Holy Al – Quran that can be elaborated to my research theory (separation concept of membrane).

*He released the two seas meeting (side by side); between them is barrier (so) neither of them transgress. So which of the favors of your Rabb would you deny?*

*(Al – Quran, Surah Ar – Rahman (55); 19 -21)*

*And it is He who released (simultaneously) the two seas, one fresh and sweet and one salty and bitter, and He placed between them a barrier and prohibiting barrier.*

*(Al – Quran, Surah Al – Furqan (25); 52 – 53).*

I am indebted to my parents with all my heart. I submit that all my successes and achievements drew that inspiration from their blessings, endless love, encouragements and support. Hence, it is to them, whom I ever owe my self and liable to, that I dedicate this work of mine. I would also like to thank my sisters for their support and love. I have been lucky to have such a wonderful family, a family that is an integral part of my existence. I would like to offer my deepest gratitude to Mr. Aryf bin Yusuf. Thank you for your preserving support and encouragement.

Thanks are due to University Malaysia Terengganu (Faculty of Science and Technology, and Graduate Research Center) for providing the support for this research. This research project was financially supported by the Ministry of Science and Technology Malaysia.

With deep sense of gratitude and appreciate, I would like to express my sincere thanks to my research supervisor, Associate Professor Dr. Nora`aini bt Ali, for her inspiring guidance, help and excellent cooperation in supervising this research work. It was her keen interest which made this research work presentable in this format. Thank you very much for the unending help throughout the course of my research. I am also very grateful


to my co-supervisor Ass. Prof. Ir. Ahmad bin Jusoh for his great help and support.

I am thankful to the current Head of Engineering Science Department Dr. Zamri bin Ibrahim, all staff members and Mr. Nasir, Mrs. Norita and Ms. Zurah from the Institute of Oceanography, for they assistance while I am working with SEM and TOC Analyzer. I wish to show appreciation to all supportive post-graduate students (Nurud Suria Suhaimi, Sofia Hamzah and Nurul Syazana Abdul Halim, Nur Baiti Abdul Hanid) for their kind and cheerful cooperation. Thank you for making my life interesting and cheerful.

Finally and humbly, I offer my sincere thanks again to my lovely parents, my sisters, Mr. Aryf bin Yusuf Rauf and other members for their great encouragement, support and prayers.

Associate Professor  
Faculty of Science and Technology  
University Malaysia Terengganu  
(Member)

Abdul Latif Ahmad, Ph.D.  
Professor / Dean of School of Chemical Engineering,  
Universiti Sains Malaysia  
(Independent Examiner)

  
Prof. Dr. Wan Saifun Wang Abdullah, Ph.D.  
Professor / Dean of Graduate School  
University Malaysia Terengganu

Date: 07 JUL 2009

## APPROVAL

I certify that an Examination Committee has met on 25<sup>th</sup> November 2008 to conduct the final examination of Norhidayah bt Abdull on her Master of Science thesis entitled "Synthesis, Characterization and Performance Assessment Of Thin Film Composite Nanofiltration (TFC-NF) Membrane For Treating Dyes Wastewater" in accordance with the regulations approved with the regulations approved by the Senate of Universiti Malaysia Terengganu. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follow:

Zamri Ibrahim, Ph.D  
Faculty of Science and Technology  
University Malaysia Terengganu  
(Chairperson)

Nor`aini Ali, Ph.D  
Associate Professor / Research Supervisor  
Faculty of Science and Technology  
University Malaysia Terengganu  
(Member)

Ahmad Jusoh, Ir.  
Associate Professor  
Faculty of Science and Technology  
University Malaysia Terengganu  
(Member)

Abdul Latif Ahmad, Ph.D  
Professor / Dean of School of Chemical Engineering,  
Universiti Sains Malaysia  
(Independent Examiner)



---

Prof. Dr. Wan Salmin Wong Abdullah, Ph.D.  
Professor /Dean of Graduate School  
University Malaysia Terengganu

Date: 07 JUL 2009

## APPROVAL

This thesis submitted to the Senate of University Malaysia Terengganu and has been accepted as fulfillment of the requirement for the degree of Master of Science.



---

Prof. Dr. Wan Salihin Wong Abdullah, Ph.D.  
Professor /Dean of Graduate School  
University Malaysia Terengganu

Date: 10 7 JUL 2009

## DECLARATION

I hereby declare that the thesis is based on my original work except for quotation and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any degree at University Malaysia Terengganu or other institutions.



Norhidayah binti Abdull

Date: 05 JULAI 2009

## TABLE OF CONTENTS

DEDICATION	ii	
ABSTRACT	iii	
ABSTRAK	v	
ACKNOWLEDGEMENT	vii	
APPROVAL	x	
DECLARATION	xii	
LIST OF TABLES	xviii	
LIST OF FIGURES	xx	
LIST OF ABBREVIATIONS	xxiii	
<b>CHAPTER</b>		
1	INTRODUCTION	
1.1	Background of the Research	1
1.2	Statement of the Problem	7
1.3	Significance of the Research	8
1.4	Objectives of the Research	10
1.5	Scope of the Research	11
2	LITERATURE REVIEW	
2.1	General Aspect of Dye	15
2.1.1	Classification of Dye	15
2.1.2	Environmental Concerns	18
2.1.3	Regulations	19
2.1.4	Conventional Treatment of Dye wastewater	20
2.2	Membrane Definition	22
2.3	Membrane Classification	22
2.4	Nanofiltration (NF) Membrane	23
2.4.1	Characteristic of Nanofiltration (NF) Membrane	24
2.4.2	Application of Nanofiltration (NF) Membrane	25
2.5	Origin and development of TFC membrane	27
2.6	Structure of TFC membrane	29
2.7	Interfacial Polymerization Technique	29
2.8	Fabrication parameters of TFC Membrane	30
2.8.1	Kinetic Control	30
2.8.2	Material Selection	31
2.8.2.1	Material Selection for UF Support Layer Membrane	32
2.8.2.2	Material Selection for the Development Of Thin Film Layer	32
2.8.3	Preparation Condition of TFC membrane	36
2.9	Characterization of Membrane	38
2.10	Transport model of Nanofiltration (NF) Membrane	39

2.10.1	Kedem and Katchalsky (KK) Model	40
2.10.2	Spiegler and Kedem (SK) Model	41
2.10.3	Steric Hindrance Pore (SHP) Model	42
2.10.4	Teorell–Meyer–Sievers (TMS) Model	43
2.11	Nanofiltration (NF) Membrane for Dye Wastewater Treatment	43
2.12	Advantages and Disadvantages of Membrane Separation Process	44
2.13	Membrane Flux Decline	45
2.13.1	Concentration Polarization	47
2.13.2	Fouling	48
2.14	Membrane Flux Decline with Textile Wastewater	49
2.15	Factors Influencing of Flux Decline	51
2.15.1	Membrane Properties	52
2.15.2	Operating Condition	53
2.15.2.1	Feed Concentration	54
2.15.2.2	Feed Mixture Concentration	55
3	<b>METHODOLOGY</b>	
3.1	Material	57
3.2	Membrane Preparation	59
3.2.1	Preparation of UF support layer membrane	60
3.2.1.1	Material selection for preparing UF support layer membrane	61
3.2.1.2	Preparation of Polymer Solution	63
3.2.1.3	Preparation of UF Support Layer Membrane	65
3.2.2.	Preparation of Thin Film Composite (TFC) Membrane	66
3.2.2.1.	Preparation of TFC Membrane with Various Dip Time in Aqueous Phase	66
3.2.2.2.	Preparation of TFC Membrane with Various Reaction Time in Organic Phase	67
3.2.2.3.	Preparation of TFC membrane with Various Curing Time	68
3.3	Membrane Characterization	68
3.3.1	Determination of Permeability Coefficient	68
3.3.2	Separation of Charged Solute	70
3.3.3	Separation of Uncharged Solutes	71
3.3.4	Analysis of Membrane Surface And Membrane Cross-Section Morphology	71
3.3.5	Determination Of Membrane Fine Structural Details Using Theoretical Approach	72
3.3.5.1.	Determination of Membrane Pore Radius	72
3.3.5.2	Determination of Solute Permeability And Membrane Thickness	74
3.3.5.3	Determination of Membrane Porosity and Ratio of Effective Membrane Thickness	



		To Membrane Porosity	74
	3.3.5.4	Determination of Effective Membrane Charge Density and Ratio Of Fixed Charge Density To Bulk Concentration	75
	3.4	Membrane Performance Evaluation: Synthetic Dye Wastewater	75
	3.5	Study Of Flux Decline Behavior On The Dye Removal Application	77
	3.6	Membrane Chemical Cleaning	78
4	RESULTS AND DISCUSSION		
	4.1	Development of UF Support Layer Membrane	80
	4.1.1.	Permeability Coefficient	80
	4.1.2.	Membrane Cross-Section and Membrane Surface	81
	4.1.3.	Separation Performance of Charged Solute	82
	4.2.	Effect of Dipping Time on TFC NF Membrane	83
	4.2.1.	Permeability Coefficient	84
	4.2.2.	Membrane Cross-Section and Membrane Surface	85
	4.2.3.	Separation Performance Of Charged Solute	88
	4.2.4.	Characterization of Membrane In Terms of Membrane Fine Structural Details	90
	4.2.5.	Separation of Uncharged Solute	96
	4.3	Effect of Reaction Time in Organic Phase on TFC NF Membrane	97
	4.3.1.	Permeability Coefficient	98
	4.3.2.	Membrane Cross-Section and Membrane Surface	99
	4.3.3	Effect of Reaction Time on The Separation Performance of Charged Solute	102
	4.3.4	The Characterization Of Membrane In Terms Of Membrane Fine Structural Details Membrane	104
	4.3.5	Separation Of Uncharged Solute	108
	4.4	Effect of Curing Time on TFC NF Membrane	109
	4.4.1.	Permeability Coefficient	109
	4.4.2.	Membrane Cross-Section and Membrane Surface	110
	4.4.3.	Separation Performance of Charged Solute	114
	4.4.4.	Characterization of Membrane in Terms Of Membrane Fine Structural Details	116
	4.4.5.	Separation of Uncharged Solute	118
	4.5	Membrane Performances Evaluation for Dye Wastewater Application	119
	4.5.1	TFC-NF-D3 Membrane	120
	4.5.2	TFC-NF-R30 Membrane	123
	4.5.3	TFC-NF-C15 Membrane	125
	4.5.4	Effect of Membrane Properties on the Effectiveness of Dye Wastewater Removal	127
	4.6	Effect of Dye Concentration on the Flux Decline Behavior	129
	4.6.1	Initial Value of Membrane Fluxes	130
	4.6.2	The Percentages of Flux Decline	136
	4.6.2.1	Reactive Black 5 (RB 5)	136

	4.6.2.2	Reactive Orange (RO 16)	136
	4.6.2.3	Acid Yellow 17 (AY 17)	138
	4.6.3	Effect of Dye Concentration	139
	4.6.4	Effect of Membrane Properties	140
	4.6.5	Mechanism of Flux Decline	142
	4.6.5	Flux Recovery	144
	4.6.6	Permeate Quality	145
4.7		Effect Of Dye-Salt Mixture On The Flux Decline Behavior	147
	4.7.1	Initial Value of Membrane Fluxes	152
	4.7.2	The Percentages of Flux Decline	152
	4.7.3	Effect of Dye – Salt Mixture	157
	4.7.4	Effect of Membrane Properties	160
	4.7.4	Mechanism of Flux Decline	162
	4.7.5	Flux Recovery	162
	4.7.6	Permeate Quality	165
4.8		Design protocol for optimum TFC membrane	171
5	CONCLUSION AND RECOMMENDATION		
	5.1	Conclusion	172
	5.2	Recommendation	176
	REFERENCES		178
	APPENDICES		
Appendix A	Example of permeation data and pure water permeability of TFC-NF-D3		191
Appendix B	Example of permeation data of sodium chloride (0.01 M) and its calculation of $R_{real}$ , wall concentration and mass transfer coefficient for TFC-NF-D3		192
Appendix C	Flux and rejection of membranes at various applied pressure		193
Appendix D	Estimation of membrane parameters and membrane properties for TFC-NF-D3		196
Appendix E	Example of permeation data of Uncharged Solute for TFC-NF-D3		201
Appendix F	Example of permeation data of Reactive Black 5, Reactive Orange 16 and Acid Yellow 17 for TFC-NF-D3		202
Appendix G	Example of permeation data (within 400 minutes) of Reactive Black 5 for TFC-NF- D3		205
Appendix H	Example of pure water permeability before, after permeation and after cleaning process data for TFC-NF-D3		206

FIGURES	PAGE
<b>PUBLICATIONS</b>	<b>207</b>
<b>BIODATA OF AUTHOR</b>	<b>209</b>
4.16 SEM micrographs of membrane surface at magnification of 500x	113
4.17 Flux and rejection of sodium chloride at various curing times	114
4.18 Rejection of PEG at various molecular weights for optimum curing time	115
4.19 Effect of applied pressure on flux of RB 5, RO 16 and AY 17 for TFC-NF-D3	121
4.20 Effect of applied pressure on rejection of RB 5, RO 16 and AY 17 for TFC-NF-D3	122
4.21 Effect of applied pressure on flux of RB 5, RO 16 and AY 17 for TFC-NF-R30	124
4.22 Effect of applied pressure on rejection of RB 5, RO 16 and AY 17 for TFC-NF-R30	125
4.23 Effect of applied pressure on flux of RB 5, RO 16 and AY 17 for TFC-NF-C15	126
4.24 Effect of applied pressure on rejection of RB 5, RO 16 and AY 17 for TFC-NF-C15	126
4.25 Flux as a function of time for the separation of RB 5 solutions using TFC-NF-D3	131
4.26 Flux as a function of time for the separation of RB 5 solutions using TFC-NF-R30	131
4.27 Flux as a function of time for the separation of RB 5 solution using TFC-NF-C15	132
4.28 Flux as a function of time for the separation of RO 16 solutions using TFC-NF-D3	132
4.29 Flux as a function of time for the separation of RO 16 solutions using TFC-NF-R30	133
4.30 Flux as a function of time for the separation of RO 16 solution using TFC-NF-C15	133
4.31 Flux as a function of time for the separation of AY 17 solutions using TFC-NF-D3	134
4.32 Flux as a function of time for the separation of AY 17 solutions using TFC-NF-R30	134
4.33 Flux as a function of time for the separation of AY 17 solution using TFC-NF-C15	135
4.34 Rejection of RB 5 solutions using TFC-NF-D3	146
4.35 Rejection of RB 5 solutions using TFC-NF-R30	146
4.36 Rejection of RB 5 solutions using TFC-NF-C15	147
4.37 Rejection of RO 16 solutions using TFC-NF-D3	147
4.38 Rejection of RO 16 solutions using TFC-NF-R30	148
4.39 Rejection of RO 16 solutions using TFC-NF-C15	148
4.40 Rejection of AY 17 solutions using TFC-NF-D3	149
4.41 Rejection of AY 17 solutions using TFC-NF-R30	149
4.42 Rejection of AY 17 solutions using TFC-NF-C15	150

**FIGURES****LIST OF TABLES****PAGE**

4.16	SEM micrographs of membrane surface at magnification of 500x	113
4.17	Flux and rejection of sodium chloride at various curing times	114
4.18	Rejection of PEG at various molecular weights for optimum curing time	115
4.19	Effect of applied pressure on flux of RB 5, RO 16 and AY 17 for TFC-NF-D3	121
4.20	Effect of applied pressure on rejection of RB 5, RO 16 and AY 17 for TFC-NF-D3.	122
4.21	Effect of applied pressure on flux of RB 5, RO 16 and AY 17 for TFC-NF-R30	124
4.22	Effect of applied pressure on rejection of RB 5, RO 16 and AY 17 for TFC-NF-R30.	125
4.23	Effect of applied pressure on flux of RB 5, RO 16 and AY 17 for TFC-NF-C15	126
4.24	Effect of applied pressure on rejection of RB 5, RO 16 and AY 17 for TFC-NF-C15	126
4.25	Flux as a function of time for the separation of RB 5 solutions using TFC-NF-D3.	131
4.26	Flux as a function of time for the separation of RB 5 solutions using TFC-NF-R30.	131
4.27	Flux as a function of time for the separation of RB 5 solution using TFC-NF-C15	132
4.28	Flux as a function of time for the separation of RO 16 solutions using TFC-NF-D3.	132
4.29	Flux as a function of time for the separation of RO 16 solutions using TFC-NF-R30.	133
4.30	Flux as a function of time for the separation of RO 16 solution using TFC-NF-C15	133
4.31	Flux as a function of time for the separation of AY 17 solutions using TFC-NF-D3.	134
4.32	Flux as a function of time for the separation of AY 17 solutions using TFC-NF-R30.	134
4.33	Flux as a function of time for the separation of AY 17 solution using TFC-NF-C15	135
4.34	Rejection of RB 5 solutions using TFC-NF-D3	146
4.35	Rejection of RB 5 solutions using TFC-NF-R30	146
4.36	Rejection of RB 5 solutions using TFC-NF-C15	147
4.37	Rejection of RO 16 solutions using TFC-NF-D3	147
4.38	Rejection of RO 16 solutions using TFC-NF-R30	148
4.39	Rejection of RO 16 solutions using TFC-NF-C15	148
4.40	Rejection of AY 17 solutions using TFC-NF-D3	149
4.41	Rejection of AY 17 solutions using TFC-NF-R30	149
4.42	Rejection of AY 17 solutions using TFC-NF-C15	150

## LIST OF TABLES

TABLE	PAGE
2.1 Dye classification, application, dye-fiber attachment mechanism and dyeing method	17
2.2 The metallic compounds and their effect to human health	20
2.3 Advantages and disadvantages of the current methods of dye removal from industrial wastewater	21
2.4 Different membrane processes based on driving force	23
2.5 Summary of RO, NF, and UF membrane process	24
2.6 Areas and industrial application of NF membranes	26
3.1 List of chemicals and reagents used	59
3.2 Summary of membrane formulation and processing condition	61
3.3 Summary of the preparation condition of TFC NF membrane	67
3.4 Ions, ion atomic or molecular weights, ion diffusivities and Stokes radii	73
3.5 Simple mathematical equations that used to evaluate the flux decline behaviors	78
4.1 Numerical results of membrane parameters TFC-NF membranes at various dipping times in aqueous phase	92
4.2 Modeling results of membrane parameters TFC-NF membranes at various dipping times in aqueous phase	93
4.3 Summary of the characteristic of 29 commercial NF membranes	93
4.4 Numerical results of membrane parameters TFC-NF membranes at various reaction times in organic phase	105
4.5 Modeling results of membrane parameters TFC-NF membranes at various reaction times in organic phase	106
4.6 Numerical results of membrane parameters TFC-NF membranes at various curing times	116
4.7 Modeling results of membrane parameters TFC-NF membranes at various curing times	117
4.8 A summary of the characteristics of TFC-NF membranes	120
4.9 The percentages of flux decline behavior of RB 5 for TFC NF membranes	137
4.10 The percentages of flux decline behavior of RO 16 for TFC NF membranes	138
4.11 The percentages of flux decline behavior of AY 17 for TFC NF membranes	139
4.12 Ratio of radius solute of dye to the membrane pore size	143
4.13 The flux recoveries of dyes for TFC-NF membranes	145
4.14 The percentages of flux decline behavior of RB 5 – Salt mixture for TFC NF membranes	148
4.15 The percentages of flux decline behavior of RO 16 – Salt mixture for TFC NF membranes	159

TABLE	LIST OF FIGURES	PAGE
4.16	The percentages of flux decline behavior of AY 17 – Salt mixture for TFC NF membranes	160
4.17	The flux recoveries of dyes-salt mixtures for TFC-NF membranes	164
4.18	A summary of the range of membrane characteristics that prepared at optimum condition	171
2.1	Chemical structure of <i>o</i> -phenylene diamine	33
2.2	Chemical structure of trimethyl chloride	35
2.3	Chemical structure of aromatic polyamide membrane	35
2.4	Profile of time-dependent flux	40
3.6	Irreversible fouling, reversible fouling and fouling	49
3.1	Methodology overview (Design of experiments)	58
3.2	Preparation steps of UF support layer membrane	57
3.3	Chemical structure of polysulfone	61
3.4	The apparatus set up for polymer solution preparation	62
3.5	A semi-automated electrically casting machine	64
3.6	The apparatus set up for permeation experiments	70
3.7	Chemical structure of Reactive Black 5	76
3.8	Chemical structure of Reactive Orange 16	76
3.9	Chemical structure of Acid Yellow 17	76
4.1	Pure water flux at various applied pressures for the UF support layer membrane	81
4.2	SEM micrograph on the UF membrane support layer	82
4.3	Rejection and flux of sodium chloride (0.01 M) at various applied pressures on the UF support layer membrane	83
4.4	Pure water permeability of membranes that prepared with various dipping times in aqueous phase	85
4.5	SEM micrographs of membrane cross-section at magnification of 1500x	86
4.6	SEM micrographs of membrane surface at magnification of 500x	87
4.7	Flux and rejection of sodium chloride at various dip times	89
4.8	Retention of PEG at various molecular weights for optimum dipping time in aqueous phase	97
4.9	Pure water flux at various applied pressure on the various reaction times in organic phase	98
4.10	SEM micrographs of membrane cross-section at magnification of 1500x	100
4.11	SEM micrographs of membrane surface at magnification of 500x	101
4.12	Flux and rejection of sodium chloride at various reaction times	102
4.13	Rejection of PEG at various molecular weights for the optimum reaction time in organic phase	108
4.14	Pure water permeability at various curing time	110
4.15	SEM micrographs of membrane cross-section at magnification of 1500x	112

## LIST OF FIGURES

<b>FIGURES</b>		<b>PAGE</b>
2.1	The chromophores that introduced colour property of dye	15
2.2	Chemical structure of <i>m</i> -phenylene diamine	35
2.3	Chemical structure of trimesoyl chloride	35
2.4	Chemical structure of aromatic polyamide membrane	35
2.5	Profile of time-dependent flux	46
2.6	Irreversible fouling, reversible fouling and fouling	49
3.1	Methodology overview (Design of experiment)	58
3.2	Preparation steps of UF support layer membrane	57
3.3	Chemical structure of polysulfone	61
3.4	The apparatus set up for polymer solution preparation	62
3.5	A semi automated electrically casting machine	64
3.6	The apparatus set up for permeation experiments	70
3.7	Chemical structure of Reactive Black 5	76
3.8	Chemical structure of Reactive Orange 16	76
3.9	Chemical structure of Acid Yellow 17	76
4.1	Pure water flux at various applied pressures for the UF support layer membrane	81
4.2	SEM micrograph on the UF membrane support layer	82
4.3	Rejection and flux of sodium chloride (0.01 M) at various applied pressures on the UF support layer membrane	83
4.4	Pure water permeability of membranes that prepared with various dipping times in aqueous phase	85
4.5	SEM micrographs of membrane cross-section at magnification of 1500x	86
4.6	SEM micrographs of membrane surface at magnification of 500x	87
4.7	Flux and rejection of sodium chloride at various dip times	89
4.8	Retention of PEG at various molecular weights for optimum dipping time in aqueous phase	97
4.9	Pure water flux at various applied pressure on the various reaction times in organic phase	98
4.10	SEM micrographs of membrane cross-section at magnification of 1500x	100
4.11	SEM micrographs of membrane surface at magnification of 500x	101
4.12	Flux and rejection of sodium chloride at various Reaction times.	102
4.13	Rejection of PEG at various molecular weights for the optimum reaction time in organic phase	108
4.14	Pure water permeability at various curing time.	110
4.15	SEM micrographs of membrane cross-section at magnification of 1500x	112

**FIGURES****LIST OF ABBREVIATIONS****PAGE**

4.43	Flux as a function of time for the separation of RB 5 + Salt mixture solutions using TFC-NF-D3.	153
4.44	Flux as a function of time for the separation of RB 5 + Salt mixture solutions using TFC-NF-R30	153
4.45	Flux as a function of time for the separation of RB 5 + Salt mixture solutions using TFC-NF-C15	154
4.46	Flux as a function of time for the separation of RO 16 + Salt mixture solutions using TFC-NF-D3.	154
4.47	Flux as a function of time for the separation of RO 16 + Salt mixture solutions using TFC-NF-R30	155
4.48	Flux as a function of time for the separation of RO 16 + Salt mixture solutions using TFC-NF-C15	155
4.49	Flux as a function of time for the separation of AY 17 + Salt mixture solutions using TFC-NF-D3.	156
4.50	Flux as a function of time for the separation of AY 17 + Salt mixture solutions using TFC-NF-R30	156
4.51	Flux as a function of time for the separation of AY 17 + Salt mixture solutions using TFC-NF-C15	157
4.52	Rejection of RB 5 + Salt mixture solutions using TFC-NF-D3.	157
4.53	Rejection of RB 5 + Salt mixture solutions using TFC-NF-R30.	165
4.54	Rejection of RB 5 + Salt mixture solutions using TFC-NF-C15.	166
4.55	Rejection of RO 16 + Salt mixture solutions using TFC-NF-D3.	166
4.56	Rejection of RO 16 + Salt mixture solutions using TFC-NF-R30.	167
4.57	Rejection of RO 16 + Salt mixture solutions using TFC-NF-C15.	167
4.58	Rejection of AY 17 + Salt mixture solutions using TFC-NF-D3.	168
4.59	Rejection of AY 17 + Salt mixture solutions using TFC-NF-R30.	169
4.60	Rejection of AY 17 + Salt mixture solutions using TFC-NF-C15.	169



## LIST OF ABBREVIATIONS

$A_k$	Membrane porosity
$c$	Concentration, mol/m <sup>3</sup>
$C_i$	Concentration in the bulk solution, mol/m <sup>3</sup>
$c_i$	Concentration of component $i$ , mol/m <sup>3</sup>
$c_{i,p}$	Concentration of component $i$ in the permeate, mol/m <sup>3</sup>
$C_{\text{total}}$	Total charge concentration in bulk solution (of -ve or +ve solutes) permeate, mol/m <sup>3</sup>
$D_i$	Diffusivity of ion $i$ in free solution, m <sup>2</sup> /s
$D_s$	Solute diffusivity for neutral molecule, or generalized diffusivity for 1-1 type of electrolyte defined as $D_s = 2 (D_1/D_2) / (D_1+D_2)$ , m <sup>2</sup> /s
$F$	Faraday constant, 96487 C/mol
$H_F, H_D$	Steric parameters related to wall correction factors under diffusion and convection conditions, respectively
$J_s$	Averaged solute flux over membrane surface, mol/m <sup>2</sup> s
$J_v$	Averaged solute volume over membrane surface, m/s
$k_i$	Averaged distribution coefficient of ion $i$ by the electrostatic effects
$L_p$	Pure water permeability, m/s
$P$	Applied pressure, bar
$P_s$	Solute permeability, m/s
$R$	Rejection, %
$R_i$	Rejection of component $i$ , %
$r_p$	Pore radius, m
$r_s$	Solute radius, m
$S_F, S_D$	Distribution coefficient of solute by steric hindrance effect under diffusion and convection condition, respectively
$u_x$	Velocity in the axial direction to the membrane, m/s
$X_d$	Effective membrane charge density, mol/m <sup>3</sup>
$z_i$	Valence of ion

## GREEK LETTER

$\Delta x$	Effective membrane thickness, m
$\varepsilon$	Membrane porosity (dimensionless)
$\eta$	Ratio of solute radius to membrane pore radius
$\sigma$	Reflection coefficient, %
$\tau$	Tortuosity (dimensionless)
$\xi$	Ratio of fixed charge