

THE MARYLAND STATE BOARD OF
EDUCATION APPROVED

BY THE STATE BOARD OF EDUCATION

APPROVED FOR USE IN SCHOOLS

BY THE STATE BOARD OF EDUCATION

BY THE STATE BOARD OF EDUCATION

APPROVED FOR USE IN SCHOOLS

BY THE STATE BOARD OF EDUCATION

2007

china

Perbadanan Universiti Malaysia Terengganu (UMT)
1100051082

Perdustakaan

Universiti Malaysia Terengganu (UMT)

LP 14 FST 1 2007



1100051082

Thin film composite (tfc) membranes : effects of monomer and solvents in interfacial polymerization process for dye removal / Mashitah Abdullah.



**PERPUSTAKAAN
UNIVERSITI MALAYSIA TERENGGANU (UMT)
21030 KUALA TERENGGANU**

110005108

Lihat sebelah

HAK MILIK
PERPUSTAKAAN UMT

**THIN FILM COMPOSITE (TFC) MEMBRANES:EFFECTS OF MONOMER
AND SOLVENTS IN INTERFACIAL POLYMERIZATION PROCESS
FOR DYE REMOVAL**

Oleh
Mashitah Abdullah

Laporan Penyelidikan ini disediakan untuk mematuhi
sebahagian keperluan bagi
Ijazah Sarjana Muda Teknologi (Alam Sekitar)

Jabatan Sains Kejuruteraan
Fakulti Sains Dan Teknologi
UNIVERSITI MALAYSIA TERENGGANU
2007

1100051082



**JABATAN SAINS KEJURUTERAAN
FAKULTI SAINS DAN TEKNOLOGI
UNIVERSITI MALAYSIA TERENGGANU**

**PENGAKUAN DAN PENGESAHAN LAPORAN
PROJEK PENYELIDIKAN I DAN II**

Adalah ini diakui dan disahkan bahawa laporan penyelidikan bertajuk:

THIN FILM COMPOSITE (TFC) MEMBRANES: EFFECTS OF MONOMER AND SOLVENTS IN INTERFACIAL POLYMERIZATION PROCESS FOR DYE REMOVAL oleh Mashitah Abdullah, No.Matrik UK7709 telah diperiksa dan semua pembetulan yang disarankan telah dilakukan. Laporan ini dikemukakan kepada Jabatan Sains Kejuruteraan sebagai memenuhi sebahagian daripada keperluan memperolehi Ijazah Sarjana Muda Teknologi (Alam Sekitar), Fakulti Sains dan Teknologi , Universiti Malaysia Terengganu.

Disahkan oleh:

.....

Penyelia Utama

Nama: En. Asmadi Ali

Cop Rasmi:

.....

ASMADI ALI @ MAHMUD
Pensyarah
Jabatan Sains Kejuruteraan
Fakulti Sains dan Teknologi
Universiti Malaysia Terengganu
21030 Kuala Terengganu.

Tarikh: 24/5/07

Penyelia Kedua

Nama: Dr. Nora'aini Ali

Cop Rasmi: DR. NORA'AINI BINTI ALI

.....

Ketua
Jabatan Sains Kejuruteraan
Fakulti Sains dan Teknologi
Universiti Malaysia Terengganu
21030 Kuala Terengganu

Tarikh: 24/5/07

Ketua Jabatan Sains Kejuruteraan

Nama: Dr. Nora'aini Ali

Cop Rasmi: DR. NORA'AINI BINTI ALI

.....

Ketua
Jabatan Sains Kejuruteraan
Fakulti Sains dan Teknologi
Universiti Malaysia Terengganu
21030 Kuala Terengganu

Tarikh: 24/5/07

ACKNOWLEDGEMENT

I would like to express my special thanks to my supervisor, Mr. Asmadi Ali and my co-supervisor, Dr. Nora'aini Ali for all their support and guiding me in progressing this final year project. I am particularly grateful to Mr. Rahman who always concern and spend a lot of time to discuss, guide, and advise me in order to complete the task.

Besides that, I would like to thank both of the master's students, Ms. Khadija Yahya and Ms. Norhidayah Abdull who always be as my individual references for supporting me to fulfill this project. My sincere appreciation goes to all the Environmental lab's staffs and Electronic and Instrumentation lab's staff for providing the entire necessary facilities lab work especially to Miss Mazalina, Mr. Razman and Mr. Razali.

My sincere thanks to Mazuin, Julidawati, Norashmah, Nazarul Afida and Ainul Nazrah on their willingness to check my drafts and their comment and also helpful suggestion are deeply appreciated. I am extremely grateful to my family members whose moral and financial supports had helped me so much and not to forget my friends, my housemates and those who had help out and given their support and cooperation to complete my project.

Thank you.

TABLE OF CONTENTS

	Page	
TITLE PAGE	i	
CONFIRMATION AND APPROVAL FORM OF REPORT	ii	
ACKNOWLEDGEMENT	iii	
TABLE OF CONTENTS	iv	
LIST OF FIGURES	viii	
LIST OF TABLES	ix	
LIST OF ABBREVIATIONS	x	
LIST OF SYMBOLS	xii	
LIST OF APPENDICES	xiii	
ABSTRACT	xiv	
ABSTRAK	xv	
CHAPTER 1	INTRODUCTION AND OBJECTIVES	
1.1	Membrane Definition and Development	1
1.2	Membrane Classification	2
1.3	Historical of Thin Film Composite Membrane Developments	4
1.4	The Principle of Membrane Processes	6
1.5	Advantages Of Thin Film Composite Membranes	7
1.6	Problem Statements	7
1.7	Research Objectives	9

1.8	Scopes of Study	9
-----	-----------------	---

CHAPTER 2	LITERATURE REVIEW	
2.1	Development of the porous support layer	10
2.1.1	<i>Polysulfone (PSF)</i>	11
2.1.2	<i>N-Methyl-2-Pyrrolidone (NMP)</i>	12
2.1.3	<i>Distilled Water</i>	12
2.2	Fabrication of thin film composite (TFC) membrane	13
2.3	Interfacial Polymerization (IP) process	14
2.4	Development of the polyamide skin layer	16
2.4.1	<i>Material Selection</i>	16
a.	<i>Monomers of TFC Membranes</i>	17
b.	Solvent of TFC Membranes	19
2.4.2	<i>Effect of Preparation Condition</i>	20
2.4.3	<i>Characterisation of TFC membrane using SHP model</i>	21
2.5	Dyes Removal Using TFC membrane	22
2.5.1	<i>Development of Reactive Dyes</i>	22
2.5.2	<i>Reactive Orange 16</i>	23
2.6	Scanning Electron Microscopy (SEM)	25

CHAPTER 3	METHODOLOGY	
3.1	Materials	26
3.2	<i>Formulation of Membrane Doping Solution</i>	27
3.2.1	<i>Polysulfone (PSF)</i>	27

3.2.2	<i>N-methyl-2-pirrolidon (NMP)</i>	27
3.2.3	<i>Distilled Water</i>	28
3.3	Membrane Fabrication	29
3.4	Preparation of Flat Sheet Membrane	30
3.5	Preparation of the polyamide skin layer	31
3.5.1	<i>Membrane prepared under diamine solution</i>	31
3.5.2	<i>Membrane prepared under different trimesoyl chloride (TMC) content and solvent concentration</i>	32
3.6	Characterization of membrane	33
3.6.1	<i>Membrane Permeation Test for PWP and salt rejection</i>	33
a.	<i>Determination of the pore radius, membrane thickness and porosity</i>	38
3.6.2	Permeation test for Dyes	40
3.6.3	Scanning Electron Microscopy (SEM)	43

CHAPTER 4

RESULT AND DISCUSSION

4.1	Measurement of Pure Water Flux	46
4.2	Analysis NaCl and Modeling Results	48
4.2.1	<i>Flux and Rejection of NaCl</i>	48
4.2.2	<i>Rejection and Membrane Thickness</i>	52
4.2.3	<i>Rejection and Pore Radius</i>	54
4.2.4	<i>Flux and Membrane Thickness</i>	56

	<i>4.2.5 Flux and Pore Radius</i>	59
4.3	Analysis Reactive Orange 16	61
	<i>4.3.1 Flux and Rejection of Reactive Orange 16</i>	61
4.4	Membrane Cross-Sectional Morphology Under SEM	65
CHAPTER 5	CONCLUSION AND RECOMMENDATION	
5.1	Conclusion	69
5.2	Recommendation	71
REFERENCES		72
APPENDIXES		78
VITAE		87

LIST OF FIGURES

No. of Figure		Page
1.1	Asymmetric membranes	3
1.2	TFC membranes	3
1.3	Progress in membrane performance during the past forty years reverse osmosis conditions	5
1.4	Schematic representation of a two-phase system separated by a membrane	6
2.1	Schematic representation of the reaction between MPD and TMC to form an aromatic polyamide	15
2.2	Chemical structure of Reactive Orange	23
3.1	A semi-automated electrical casting machine	29
3.2	Dead end filtration cell	32
3.3	Permeation test equipment	34
3.4	Spectrophotometer	40
3.5	SEM apparatus	42
3.6	Flow chart of preparation and characterization method for TFC membranes	43
4.1.	Pure water flux ($\text{L}/\text{m}^2 \cdot \text{h}$) versus pressure (bar)	45
4.2	Rejection and flux versus TMC content in hexane	48
4.3	Rejection and flux versus TMC content in cyclohexane	49

4.4	Rejection and pore radius versus different monomer concentration	51
4.5 (a)	Rejection and pore radius versus different monomer concentration for hexane	53
4.5 (b)	Rejection and pore radius versus different monomer concentration for cyclohexane	54
4.6	Flux and membrane thickness versus different monomer concentration	56
4.7	Flux and pore radius versus TMC content	58
4.8	Rejection and Flux versus TMC content in hexane	61
4.9	Rejection and Flux versus TMC content in cyclohexane	62
4.10	SEM microphotographs under 500x magnification	64

LIST OF TABLES

No. of Table		Page
2.1	Dye classification	23
2.2	General characteristics of Reactive Orange 16	23
3.1	Characteristics and related value for N-Methyl-2-Pyrrolidone	27
3.2	Formulation of aqueous and organic solution in different solvents	31
3.3	A statistical analysis from the SHP modeling	37
3.4	Ions, molecular weights, ion diffusivities and Stokes radii	37
3.5	Dyes concentration and absorbance	41
4.1	Summarize of the membrane codes	45
4.2 (a)	PWF measurement to applied pressure	46
4.2 (b)	Flux and correlation coefficient for different monomer and solvents	46
4.3	Monomer concentration, flux and rejection for hexane	48
4.4	Monomer concentration,flux and rejection for cyclohexane	50
4.5	Monomer concentration, rejection and membrane thickness	52
4.6	Monomer concentration of rejection and pore radius	54
4.7	Monomer concentration of rejection and pore radius	56
4.8	Monomer concentration, flux and pore radius	59
4.9	Flux and rejection for different monomer in hexane	61
4.10	Flux and rejection for different monomer in cyclohexane	62

LIST OF ABBREVIATIONS

ED	electro dialysis
IP	interfacial polymerization
MF	microfiltration
MPD	<i>m</i> -phenyldiamine
NaCl	Sodium Chloride
NF	nanofiltration
NMP	N-Methyl-2-Pirrolidon
PA	Polyamide
PIP	piperazine
PSF	Polysulfone
RO	reverse osmosis
RO16	Reactive Orange 16
SHP	Steric Hindrance Pore
TFC	Thin Film Composite
TMC	<i>trimesoyl chloride</i>
UF	ultrafiltration

LIST OF SYMBOLS

A_k	Membrane porosity
H_F, H_D	Steric parameters related to wall correction factors under diffusion and convection conditions, respectively
P_s	Solute permeability
S_F, S_D	Distribution coefficient of solute by steric hindrance effect under diffusion and convection condition, respectively
r_p	Pore radius, m
η	Ratio of solute radius to membrane pore radius
σ	Reflection coefficient, %

LIST OF APPENDICES

Appendix	Page
A The operation system of Sterlitech HP4750 Stirred Cell	78
B Calibration Curve NaCl 0.01M	79
C Calibration Curve for RO 16 100 ppm (mg/l)	80
D Pure Water Flux and Rejection Raw Tables for Each Membrane	81

ABSTRACT

Thin film composite (TFC) membrane consists of a very thin film which is formed on top of a porous support and commonly made of polysulfone (PSF) where the active layer is an aromatic crosslinked polyamide (PA) film. Hence, PA TFC membranes cause higher water flux and rejection of ion and organic compared to CA membranes. In this study, the effects of different monomers and solvents towards performance of TFC membranes in salt rejection and dyes removal were investigated. TFC membranes were synthesized directly from interfacial polymerisation aromatic polyamide. The preparation condition of TFC membranes are studied with reference to different monomer of trimesoyl chloride (TMC) and solvents of hexane and cyclohexane. Interpretation of experimental data for the separation of sodium chloride (NaCl) with steric hindrance pore (SHP) model permit an assumption of membrane in terms of effective pore radius and membrane thickness. This study has shown the NaCl and reactive orange 16 (RO 16) rejection increase and flux decrease where the optimum rejection was showed by 0.2% TMC which dissolved in hexane with the rejection until 86.9% for NaCl while 97.2% for RO 16. SEM images exhibited that the membrane synthesized with TMC concentration at 0.2% TMC with hexane has a thicker polymerization layer. This membrane provides a superior performance membrane with respect to excellent rejection either for salt or reactive dyes.

ABSTRAK

Membran komposit lapisan nipis terdiri daripada lapisan yang sangat nipis yang terbentuk di atas membran sokongan yang poros dan selalunya diperbuat daripada polisulfon di mana lapisan aktif ini merupakan lapisan poliamida tindakan silang aromatik. Maka, membran komposit lapisan nipis poliamida ini menyebabkan fluks dan penyingkiran air lebih tinggi terhadap prestasi membran. Dalam kajian ini, kesan perbezaan monomer dan pelarut terhadap prestasi membran komposit lapisan nipis dalam penyingkiran garam dan pewarna dikaji. Membran komposit lapisan nipis yang mempunyai poliamida dihasilkan dengan monomer *m-phenyldiamine* (MPD) dan *trimesoyl chloride* (TMC) yang dilarutkan dalam pelarut heksana dan sikloheksana melalui teknik pempolimeran antara permukaan ke atas polysulfon sebagai lapisan penyokong. Sifat membran dikaji dengan menggunakan air suling, natrium klorida dan pewarna serta melalui pengimbas elektron mikroskopik. Kajian ini menunjukkan penyingkiran garam dan *reactive orange 16* (RO16) meningkat dan fluks menurun dengan peningkatan kepekatan monomer dalam turutan $0.1\% \text{ TMC} > 0.15\% \text{ TMC} > 0.2\% \text{ TMC}$. Penyingkiran optimum ditunjukkan oleh monomer yang berkepekatan $0.20\% \text{ TMC}$ iaitu sehingga 86.9% untuk NaCl manakala 97.2% untuk RO16. Membran komposit lapisan nipis menunjukkan struktur seperti jejari, lompang makro dan span melalui pemerhatian pengimbas elektron mikroskopik. Maka membran komposit lapisan nipis yang dihasilkan ditentukan oleh struktur bahan kimia di dalam lapisan membran di mana monomer yang lebih tinggi mempengaruhi peningkatan penyingkiran samada bagi garam ataupun pewarna teraktif.