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

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MASTER OF SCIENCE
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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."

This thesis is dedicated to

My parents (Hj Abdull bin Said and Hjh Zamaliah 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.

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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-phenelyne 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^3/m^2.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 believes 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 demonstrates 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

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

Antara permasalahan utama membran NF ialah penurunan fluks terhadap masa. Oleh itu, pengaruh kepekatan bahan pencelup (100 mg/L, 200 mg/L, 300 mg/L dan 400 mg/L) dan kepekatan campuran bahan pencelup - garam (0.1 g/L, 1.0 g/L dan 10.0 g/L dengan kepekatan bahan pencelup yang tetap pada 100 mg/L) terhadap kelakuan penurunan fluks air sisa bahan pencelup 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 pencelup dan campuran bahan pencelup – 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 (mekanisma penyumbatan liang dan penjerutan liang). Apabila lebih banyak bahan pencelup termendak pada permukaan membran, mekanisma penurunan fluks bertukar kepada mekanisma pembentukan kek (penyumbatan boleh balikan). Pada peringkat ini, keadaan stabil dicapai. Maka, ini membuktikan bahawa hampir keseluruhan proses penurusan 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 Load is the Most Generous. Who has tought (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.

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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.

APPROVAL

I certify that an Examination Committee has met on 25th 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:

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Date: 07 JUL 2009

APPROVAL

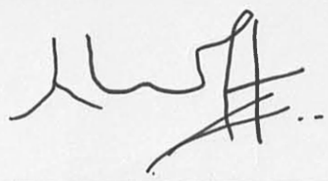
This thesis submitted to the Senate of University Malaysia Terengganu and has been accepted as fulfillment of the requirement for the degree of Master of Science.

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

Date: 07 JUL 2009

DECLARATION

I hereby declare that the thesis is based on my original work except for quotation and citations which have been duly acknowledgement. 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

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A_k	Membrane porosity
c	Concentration, mol/m^3
C_i	Concentration in the bulk solution, mol/m^3
c_i	Concentration of component *i*, mol/m^3
$ci_{,p}$	Concentration of component *I* in the permeate, mol/m^3
C_{total}	Total charge concentration in bulk solution (of –ve or =ve solutes) permeate, mol/m^3
D_i	Diffusivity of ion *i* in free solution, m^2/s
D_s	Solute diffusivity for neutral molecule, or generalized diffusivity for 1–1 type of electrolyte defined as $D_s = 2\,(D1/D2) / (D1+D2)$, m^2/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/m3s
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^3
z_i	Valence of ion

GREEK LETTER

Δx	Effective membrane thickness, m
ε	Membrane porosity (dimensionless)
η	Ratio of solute radius to membrane pore radius
σ	Reflection coefficient, %
τ	Tortuosity (dimensioneless
ξ	Ratio of fixed charge