

THE STATE OF KANSAS AND THE CITY OF LAWRENCE  
COMMENDED BY A SPECIAL COMMITTEE

TO THE PEOPLE

OF THE UNITED STATES

THE STATE OF KANSAS AND THE CITY OF LAWRENCE

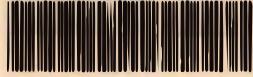
COMMENDED BY A SPECIAL COMMITTEE

CCST

1100051073

3 Perdustakaan  
Universiti Malaysia Terengganu (UMT)

LP 5 FST 1 2007



1100051073

## The removal of iron and manganese in groundwater by asymmetric nanofiltration membrane / Bazlin Hasbullah.



PERPUSTAKAAN  
UNIVERSITI MALAYSIA TERENGGANU (UMT)  
21030 KUALA TERENGGANU

100051073

1100051073

Lihat sebelah



THE REMOVAL OF IRON AND MANGANESE IN  
GROUNDWATER BY ASYMMETRIC NANOFILTRATION  
MEMBRANE

By

Bazlin Hasbullah

Research Report submitted in partial fulfillment  
of the requirements for the degree of  
Bachelor of Science (Environmental Technology)

Department of Engineering Science  
Faculty of Science and Technology  
UNIVERSITI MALAYSIA TERENGGANU

2007

1100051073

## **ACKNOWLEDGEMENT**

First of all, I would like to thank God for HIS endless blessings in my life and for providing me the strength, patience and wisdom all the way especially in accomplishing this thesis.

I would like to extend my deepest gratitude and appreciation to my supervisor, Dr Nora'aini, for all the invaluable support and guidance throughout this research. Her enthusiasm and optimism for research and her confidence in her students certainly make her a unique supervisor. Besides that, my sincere thanks are also to Mr Asmadi, Dr Edlic, Mr Rahman and other lecturers. They had been very warmth and had given me helpful discussion, cooperation, assistance, and advice all the time when needed.

I am also grateful to all my colleagues especially Farhanah, Azham Afrina and Siti Zaidah who have helped and supported me a lot and always there for me through ups and downs. Not to forget, all the master students (Ms Dayah, Ms Shaza, Mrs Nurud, Mr Brian, Ms Khadija), thanks for the advice, support and assistance throughout this research. I would also like to acknowledge all the lab assistants, Ms Najmu, Ms Mazalina, Mrs Siti Zulaikha and Mr Razman for their cooperation and help during laboratory work and also not forgotten to Mr Razali who has provided his expertise during the SEM session.

Lastly, I'm extremely grateful to my parents and siblings who provided me immense encouragement, endless love and a great deal of patience throughout. Lots of obstacles that I've to face during this research and I couldn't have made it through without them. They certainly are the greatest motivation for completion of this thesis. Thank you.

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

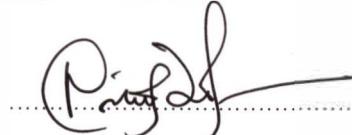
**PENGAKUAN DAN PENGESAHAN LAPORAN  
PROJEK PENYELIDIKAN I DAN II**

Adalah ini diakui dan disahkan bahawa laporan bertajuk:

The Removal of Iron and Manganese in Groundwater by Asymmetric Nanofiltration Membrane.

Oleh Bazlin bt Hasbullah No. Matrik UK 8046 telah diperiksa dan semua pembetulan yang disarankan telah dilakukan. Laporan ini dikemukakan kepada Jabatan Sains Kejuruteraan sebagai mematuhi sebahagian daripada keperluan memperolehi Ijazah Sarjana Muda Teknologi (Alam Sekitar), Fakulti Sains dan Teknologi, Universiti Malaysia Terengganu.

Disahkan oleh:



Penyelia Utama

Nama: Dr. Nora'aini bt 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**

Penyelia Kedua (jika ada)

Nama: En. Asmadi b. Ali

Cop Rasmi:



**24/5/07**

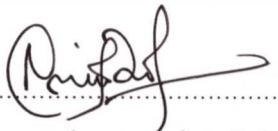
Penyelia Ketiga (jika ada)

Nama: Dr. Edlic Sathiamurthy

Cop Rasmi:

**DR. EDLIC SATHIAMURTHY**  
Penyayang  
Jabatan Sains Kejuruteraan  
Fakulti Sains dan Teknologi  
Universiti Malaysia Terengganu  
21030 Kuala Terengganu.

Tarikh: **31 / 7 / 07**



Ketua Jabatan Sains Kejuruteraan

Nama: Dr. Nora'aini Bt. Ali

Cop Rasmi: DR. NORA'AINI BINTI ALI  
Ketua

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

Tarikh:.....

## LIST OF CONTENT

	PAGE
<b>CONTENT</b>	<b>iv</b>
<b>LIST OF TABLES</b>	<b>ix</b>
<b>LIST OF FIGURES</b>	<b>xi</b>
<b>LIST OF ABBREVIATIONS/SYMBOLS</b>	<b>xiii</b>
<b>LIST OF APPENDICES</b>	<b>xv</b>
<b>ABSTRACT</b>	<b>xvi</b>
<b>ABSTRAK</b>	<b>xvii</b>
<b>CHAPTER 1 INTRODUCTION</b>	
1.1    Water and the public health	1
1.2    Groundwater as a source of water supplies	2
1.2.1 <i>Groundwater quality</i>	3
1.2.1 <i>Overview of Groundwater Utilization in Malaysia</i>	6
1.3    Membrane technology	7
1.4    Problem statement	10
1.5    Research objectives	13
1.6    Scopes of research	14

## **CHAPTER 2 LITERATURE REVIEW**

2.1	Groundwater characteristics	15
2.2	Groundwater treatment	18
2.3	Iron and its chemistry in natural environment	20
2.4	Effects of iron to the environment and human health	21
2.5	Manganese and its chemistry in natural environment	22
2.6	Effects of manganese to the environment and human health	23
2.7	Conventional treatment tecnologies	24
	2.7.1 <i>Adsorption – Activated carbon</i>	24
	2.7.2 <i>Ion Exchange</i>	25
	2.7.3 <i>Oxidation</i>	26
2.8	Membrane approach	28
	2.8.1 <i>Asymmetrif Polysulfone NF Membrane</i>	28
	2.8.2 <i>Effects of Evaporation Time on Membrane Structure and Performance</i>	30
	2.8.3 <i>Steric Hindrance Pore (SHP) Model</i>	32
2.9	Critique-of-State-of-the-Art	35

## **CHAPTER 3 METHODOLOGY**

3.1	Materials	37
	3.1.1 <i>Polysulfone</i>	38
	3.1.2 <i>N-Methyl-2-Pyrrolidone (NMP)</i>	38
	3.1.3 <i>Water</i>	39
3.2	Membrane preparation	39

3.2.1	<i>Preparation of Dope</i>	40
3.2.2	<i>Fabrication of PSF Flatsheet Membrane</i>	41
3.3	Scanning electron microscope (SEM)	43
3.4	Membrane performance measurement	44
3.4.1	<i>Pure Water Permeation</i>	44
3.4.2	<i>NaCl Permeation</i>	46
3.4.3	<i>Preparation for Iron and Manganese</i>	51
3.4.4	<i>Steric Pore Hindrance (SHP) Model</i>	54
<b>CHAPTER 4 RESULTS AND DISCUSSION</b>		
4.1	Membrane characterization	56
4.1.1	<i>Pure Water Permeability</i>	57
4.1.2	<i>Sodium Chloride (NaCl) Rejection</i>	59
4.1.3	<i>Theoretical Approach – SHP Model</i>	62
4.1.4	<i>Membrane Morphology</i>	69
4.2	Membrane Performance : Application on Iron and Manganese Removal	70
4.2.1	<i>Effects of Applied Pressure</i>	70
4.2.2	<i>Separation Mechanism</i>	75
<b>CHAPTER 5 CONCLUSION AND RECOMMENDATION</b>		
5.1	Conclusion	84
5.2	Recommendation	86

**REFERENCES**

89

**APPENDICES**

92

**VITAE**

105

## LIST OF TABLES

<b>NO. TABLE</b>		<b>PAGE</b>
1.1	International Standard For Drinking Water Supplies	5
1.2	Water Resources in Malaysia	7
2.1	Groundwater as share of drinking water by region	16
2.2	Raw water resources in Malaysia, 2001.	17
2.3	The Physical Data of Iron	20
2.4	The Physical Data of Manganese	23
3.1	Volume of salt solution and distilled water for making 500 ml of salt solution at different concentration ranging from 0 to 0.01 M.	47
3.2	Linear equation for calibration curve of conductivity versus Concentration	48
3.3	The solute radius and diffusivity of each ions of NaCl	51
4.1	Pure Water Fluxes	58
4.2	Flux and percentage of rejection of electrolytes (0.01M NaCl)	60
4.3	NaCl rejection by commercial membrane	62
4.4	The modelling results	63
4.5	Relation between reflection coefficient and pore radius	65
4.6	Summary of the characteristic of 29 commercial NF	66
4.7	Diffusivities and Stokes radii of ions	76
4.8	Average pore radius for each type of membrane	76
4.9	The relation between membrane pore radius for each membrane and ions rejections.	77
4.10	The molecular weight and diffusion coefficient of ion	79

4.11	Rejection values and hydration energy of ions	80
4.12	Ion valence for iron and manganese	81
4.13	Percentage of Fe and Mn removals by conventional treatments	83

## LIST OF FIGURES

<b>NO. FIGURE</b>		<b>PAGE</b>
1.1	Groundwater Contamination Routes	4
1.2	The filtration Spectrum	9
2.1	Flow diagram of a softening plant (groundwater)	19
3.1	Molecular structure of Polysulfone (PSF)	38
3.2	Molecule structure of <i>N</i> -methyl-2-pyrrolidone	38
3.3	A schematic diagram of membrane preparation flow	40
3.4	Apparatus set up for dope solution preparation	41
3.5	The electrical casting machine	42
3.6	Autocoater (Model JFC 1600) apparatus	43
3.7	Scanning Electron Microscopy (SEM)	44
3.8	Dead-End Cell Filtration (Sterlitech HP4750 Stirred Cell)	45
4.1	Pure water flux vs. pressure at different evaporation time	58
4.2	Influence of applied pressure on the rejection of sodium chloride	61
4.3	Pore radius and membrane thickness vs. different evaporation time at 10 bars	64
4.4	Pore radius and porosity vs. different evaporation time at 10 bars	64
4.5	Scanning electron micrographs of membrane cross section for NF-PSF 18.3% at evaporation time 0s, 5s, 10s and 15s	69
4.6a.	Influence of applied pressure on the flux of iron	70
4.6b.	Influence of applied pressure on the rejection of iron	71
4.6c.	Influence of applied pressure on the flux of manganese	71
4.6d.	Influence of applied pressure on the rejection of manganese	72
4.7.	Iron flux and rejection vs. different evaporation time at 10 bars	74

4.8	Manganese flux and rejection vs. different evaporation time at 10 bars	74
4.9	Molecular Structure of Polysulfone (PSF)	82

## **LIST OF ABBREVIATION / SYMBOLS**

H <sub>3</sub> PO <sub>4</sub>	-	Phosphoric acid
INOS	-	Institute of Oceanography
KMnO <sub>4</sub>	-	Potassium permanganate
MF	-	Microfiltration
MW	-	Molecular Weight
MWCO	-	Molecular weight cut off
NaCl	-	Sodium chloride
NF	-	Nanofiltration
NMP	-	N-methyl-2-pyrrolidone
PA	-	Polyamide
PES	-	Polyethersulfone
PSF	-	Polysulfone
PWD	-	Public Works Department
PWP	-	Pure water permeation
RO	-	Reverse osmosis
SEM	-	Scanning Electron Microscope
SHP	-	Steric Hindrance Pore
THM	-	Trihalomethane
TMS	-	Teorell-Meyer-Sievers
UF	-	Ultrafiltration

WHO	-	World Health Organization
WSB	-	Water Supply Board
WSC	-	Water Supply Company
WSD	-	Water Supply Department
$ZnCl_2$	-	zinc chloride
$r_p$	-	pore radius
$A_k/\Delta x$	-	ratio of membrane porosity to membrane thickness
$\sigma$	-	reflection coefficient
$P_s$	-	solute permeability
$J_v$	-	flux
$P_m$	-	water permeability
$C_p$	-	concentration in permeate (mol/liter)
$C_b$	-	concentration in bulk (for dead end filtration) (mol/liter)
$C_w$	-	concentration in wall (mol/liter)
$r$	-	radius of stirred cell
$\nu$	-	kinematic viscosity
$D_{l\infty}$	-	bulk diffusivity
$k_B$	-	Boltzmann's constant
$H_F, H_D, S_F, S_D$	-	steric and hindrance factors
$\eta$	-	ratio of solute radius to pore radius

## **LIST OF APPENDICES**

<b>APPENDIX</b>		<b>PAGE</b>
A	Salt Calibration Curve	92
B	Calculation of Preparation of 500 mL of 0.01 M NaCl	93
C	Dilution of 0.01 M NaCl	94
D	Pure Water and Sodium Chloride Data	95
E	Iron and Manganese Data	101

## **ABSTRACT**

Iron and manganese are common elements in groundwater. Excessive content of both metals in the groundwater will cause aesthetical and operational problems to human. Oxidation, ion exchange and adsorption are some of the conventional methods used to remove the iron and manganese in groundwater. However, these methods have their own merits and limitations and could not remove this metal effectively. The efficiency of iron and manganese removal from groundwater was investigated in this research by means of asymmetric nanofiltration (NF) membrane separation technology. DR/2500 Laboratory Spectrophotometer was used to analyze the concentrations of samples obtained. The effects of evaporation time in the formation of asymmetric nanofiltration membrane using a simple dry/wet phase inversion technique were also determined. Employing the combination of solution-diffusion model (Spiegler-Kedem equation) and steric-hindrance pore (SHP) model, the membrane structural properties were determined and have been characterized for different cases of the formation parameter. The experimental and modeling showed very promising results in terms of membrane performance with interesting structural details. The best evaporation time for the removal of iron and manganese was determined to be in the range of 5 seconds to 7.5 seconds. The iron was found to be 90% successfully removed while the manganese was 75% removed in which these removals were observed to comply with the WHO standard guidelines for drinking water.

## **ABSTRAK**

Ferum dan mangan merupakan unsur yang biasa ditemui dalam air bawah tanah. Kandungan kedua-dua elemen ini yang berebihan di dalam air akan menimbulkan banyak masalah sehingga menyebabkan nilai estetika air berubah. Terdapat beberapa kaedah rawatan untuk menyingkirkan ferum dan mangan ini. Contohnya pengoksidaan, pertukaran ion dan penjerapan. Walaubagaimanapun, terdapat beberapa kekurangan pada kaedah-kaedah ini dan ianya didapati tidak begitu berkesan. Kajian ini dijalankan untuk mengkaji keberkesanan membran penuras nano dalam menyingkirkan logam-logam berat ini. Alat *DR/2500 Spectrophotometer* digunakan untuk menganalisis sample-sampel yg diperolehi. Kesan jangkamasa evaporasi ketika formasi membran penuras nano ini turut dikaji. *Spiegler-Kedem Equation and Steric-Hindrance Pore (SHP) Model* telah digunakan dalam mengkaji struktur membran yang digunakan dan ciri-ciri membran untuk setiap parameter juga dikenalpasti. Sebanyak 90 peratus ferum dan 75 peratus mangan yang berjaya disingkirkan yang mana masa evaporasi yang terbaik ialah pada julat antara 5 saat hingga 7.5 saat. Penyingiran ferum dan mangan ini didapati telah memenuhi garis panduan yang ditetapkan oleh *WHO*.