

CHARGED SURFACE MODIFYING MACROMOLECULES HOLLOW FIBER
NANOFILTRATION MEMBRANE FOR THE REMOVAL OF BISPHENOL-A
IN DOMESTIC WASTEWATER

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IN DOMESTIC WASTEWATER

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A thesis submitted in fulfilment of the
requirements for the award of the degree of
Doctor of Philosophy (Civil Engineering)

Faculty of Civil Engineering
Universiti Teknologi Malaysia

AUGUST 2009

ACKNOWLEDGEMENT

First and foremost, *Alhamdulillah* and thank to Allah S.W.T, the Most Gracious, the Most Merciful for giving me direction in my life that brought me to the level of successful completion of this PhD study.

No task of this magnitude is accomplished alone, and therefore I would like to place on record deepest gratitude and indebtedness to my supervisors, Professor Ahmad Fauzi Ismail and Professor Mohd Razman Salim for their constant encouragement and inspiration they has unhesitatingly given, financial support for this project, for the keen interest they have taken in the progress of the project, and the learned guidance they have provide at every stage of the project and the preparation of the thesis.

I also thank Professor Takeshi Matsuura and Dr. Dipak Rana from Industrial Membrane Research Laboratory, University of Ottawa, Canada for their committed research collaboration and also for their insightful comments and suggestions during the period of this work. My thanks also goes to Professor Zeng Hua Chun and his team from the Department of chemical and biomolecular engineering, National university of Singapore (NUS), Singapore, who allowed me to undertake a visiting scholar programme at NUS.

Many thanks to my team-mate or research associates, whose have taught me so much and help me to get through my work in the lab: Anam, Be Cheer, Hatijah, Hong Heng, Jay Chee, Juhana, Lau, Mimi, Pei Sean, Sohaimi, Suhaila, Zularisham, and all people in the Advanced Membrane Technology Research Centre (AMTeC), Faculty of Civil Engineering and Faculty of Science UTM for their assistance and friendship during my study. Thanks for the fun you shared with me.

I gratefully acknowledge Universiti Malaysia Sabah for giving me the study leave and scholarship to complete my PhD study. Also to the Ministry of Higher Education (MOHE) and the Ministry of Science, Technology and Industry (MOSTI) that provided funds for which I stay grateful.

I wish to thank my other half and also my life partner, Ismail Saad, who has been a part of my spirit and soul. In spite of being fully involved in his PhD work, he had given me priority in every possible ways. His constant encouragement and emotional support kept me vigor and alive in the process of completing my PhD research. The partnership and sharing the responsibility of this life journey with me and both our two lovely children had given me the strength, love and support throughout the years.

ABSTRACT

The substances that cause endocrine disruption are massive; nevertheless estrogenic hormones as Bisphenol-A (BPA) can produce disrupting potency several thousand times higher than other chemicals. Furthermore, BPA was selected as the focus of this study due to its widespread applications and large possible abundance in wastewater. Hollow fiber polyethersulfone (PES) nanofiltration (NF) membrane has been fabricated, characterized and applied for the removal of BPA from wastewater. The fabricated PES hollow fiber NF membranes are spun by phase inversion method formulated with water and charged surface modifying macromolecule (cSMM) as additives and *N*-methyl pyrrolidinone as solvent. The synthesized cSMM comprised of Poly(ethylene glycol) (PEG), end-capped with Hydroxybenzene-sulfonate (HBS). The study reveals that the sulfonic charge modification produces higher flux and improves the removal of ionic solutes when compared to the unmodified PES. The elemental modification of PES hollow fiber NF membrane surface is demonstrated through Energy Dispersive X-Ray (EDX), Fourier Transforms Infrared (FTIR) and X-ray Photoelectron (XPS) analysis. A small increase in the thickness of the hollow fiber outer layer is observed from the Field Emission Scanning Electron Microscopy (FESEM). Additionally, Differential Scanning Calorimetry (DSC) and FTIR analysis verify the miscibility of cSMM with PES and the presence of cSMM's functional group. The fabricated PES hollow fiber NF membrane performs 90% removal under BPA concentration as much as 10 ppm in the wastewater of pH 8 condition. This is due to charge properties of the membrane and the negatively-charged solute under the influence of higher pH feed water matrix. Furthermore, the fabricated PES NF membrane has a high electrical characteristic of negative charge of 3.10 ± 0.03 and a nano size pores of 1.2 ± 4.1 nm.

ABSTRAK

Bahan yang menyebabkan gangguan endokrin adalah banyak; namun hormon estrogenik seperti Bisfenol-A (BPA) boleh mengakibatkan gangguan beribu lebih tinggi berbanding bahan kimia yang lain. Tambahan pula, BPA dipilih sebagai tumpuan kajian disebabkan oleh aplikasinya yang meluas dan kemungkinan kewujudannya yang tinggi dalam air sisa. Membran turasan-nano gentian geronggang polietersulfona (PES) telah difabrikasi, dicirikan dan digunakan untuk penyahan BPA dari air sisa. Membran turasan-nano gentian geronggang PES yang difabrikasi melalui kaedah penukaran fasa yang terdiri daripada air dan makromolekul pengubah permukaan bercas (cSMM) sebagai bahan tambah dan N-metil polivinilpirolidona sebagai pelarut. cSMM yang disintesis terdiri daripada poli(etilena-glikol) (PEG) yang ditutup-hujung dengan hidrosibenzena-sulfona (HBS). Kajian ini mendapati modifikasi cas sulfonik menghasilkan penyahan bahan terlarut ionik dan fluks yang tinggi berbanding PES yang tak diubahsuai. Modifikasi asas membran gentian geronggang PES dibuktikan melalui analisis x-ray penyerak tenaga (EDX), inframerah pengubah fourier (FTIR) and fotoelektron x-ray (XPS). Penambahan kecil pada ketebalan lapisan luar gentian geronggang diperhatikan melalui pemancar medan imbasan mikroskopi (FESEM). Tambahan pula, kalorimetri pengimbas pembeza (DSC) dan analisis FTIR mengesahkan kebolehcampuran cSMM dengan PES dan kewujudan kumpulan berfungsi cSMM. Membran gentian geronggang PES turasan-nano yang difabrikasi menghasilkan 90% penyahan BPA dalam air sisa semasa keadaan pH 8 apabila kepekatan sebanyak 10 ppm. Hal ini disebabkan oleh sifat cas membran dan bahan terlarut bercas negatif kesan suapan pH air yang tinggi. Tambahan lagi, PES turasan-nano mempunyai sifat elektrik yang tinggi iaitu cas negatif 3.10 ± 0.03 dan keporosan saiz nano 1.2 ± 4.1 nm.

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LIST OF ABBREVIATIONS

ATR	-	Attenuated Total Reflection
BOD	-	Biological Oxygen Demand
BPA	-	Bisphenol-A
CA	-	Cellulose acetate
COD	-	Chemical oxygen demand
cSMM	-	Charge surface-modifying macromolecule
Da	-	Dalton
DER	-	Dope extrusion rate
DI	-	De-ionized
DIPS	-	Diffusion Induced Phase Separation
DOC	-	Dissolved Organic Carbon
DSC	-	Differential scanning calorimetry
DDT	-	Dichloro-Diphenyl-Trichloroethane
ED	-	Endocrine Disruptor
EDC	-	Endocrine disrupting chemicals/compounds
FTIR	-	Fourier transform spectroscopy
FESEM	-	Field emission scanning electron microscopy
GCFID	-	Gas chromatography-flame ionization detector
IEH	-	Institute of Environment and Health
JS	-	Jet stretch

MF	-	Microfiltration
MW	-	Molecular weight
MWCO	-	Molecular weight cut-off
NF	-	Nanofiltration
NOM	-	Natural organic matter
NMP	-	1-methyl-2-pyrrolidon
PEG	-	Polyethylene glycol
HBS	-	Hydroxybenzene sulfonate
PES	-	Polyethersulfone
POPs	-	Persistent organic pollutants
PPCPs	-	Pharmaceuticals and Personal care products
PVC	-	Polyvinylchloride
PVP	-	Polyvinylpyrrolidones
PWP	-	Pure water permeation
RO	-	Reverse osmosis
rpm	-	Rotation per minutes
SEM	-	Scanning electron microscopy
SPE	-	Solid phase extraction
TBT	-	Tributyltin
TFC	-	Thin film composite
TMP	-	Transmembrane pressure
TOC	-	Total organic carbon
TDS	-	Total dissolved solid
TSS	-	Total suspended solid
UF	-	Ultrafiltration
VTG	-	Vitellogenin

v/v	-	Volume solute per volume solution
WWTP	-	Wastewater treatment plant
XPS	-	X-ray photoelectron spectroscopy

LIST OF SYMBOLS

$\frac{A_k}{\Delta x}$	-	Ratio of membrane porosity to thickness of membrane (m^{-1})
A	-	Cross sectional area in m^2
A_{sp}	-	The spinneret cross section (m^2)
C	-	Concentration of solute over the thickness of membrane ($mol\ m^{-3}$)
C_f	-	Concentration of feed or bulk solution
C_i	-	Concentration of an ion in the bulk solution ($mol\ m^{-3}$)
C_m	-	Concentration of solute in the fluid at the feed (membrane interface ($mol\ m^{-3}$))
C_p	-	Concentration of permeate
C_p	-	Concentration of solute in the fluid at the permeate solution ($mol\ m^{-3}$)
$D_{i,p}$	-	The diffusivity of an ion i in fre solution ($m^2\ s^{-1}$)
D_i	-	Inside diameter of the hollow fiber membrane m
D_o	-	Outside diameter of the hollow fiber membrane m
D_s	-	Diffusivity of solute molecule in a dilute solution ($m^2\ s^{-1}$)
F	-	Faraday constant ($F=96,487\ C\ mol^{-1}$)
G	-	Gas constant
J	-	Flux, or flow rate through the membrane ($m^3\ m^2\ s^{-1}$)
J_v	-	Averaged volume flux over membrane surface ($m\ s^{-1}$)

J_s	-	Averaged solute flux over a membrane surface ($\text{mol m}^{-2} \text{s}^{-1}$)
J_{si}	-	Flux of an ion i over membrane surface ($\text{mol m}^{-2} \text{s}^{-1}$)
k	-	Boltzmann's constant ($2.38 \times 10^{-23} \text{ J K}^{-1}$)
$K_{i,c}$	-	Convective hindrance factor in the membrane
K_{ow}	-	Octanol-water partitioning coefficient (dimensionless)
P	-	Applied pressure (Pa)
pKa	-	Logarithmic value of dissociation constant, Ka (dimensionless)
R	-	Rejection (%)
r_i	-	Ion radius respectively
r_s	-	Stokes radius (nm)
T	-	Absolute temperature (Kelvin)
X_d	-	Effective membrane charge density (mol m^{-3})
Z_i	-	Valence of ion
Δx	-	Effective membrane 'skin' thickness (m)
V_f	-	Spin line final velocity (ms^{-1})
V_0	-	Spin line initial velocity (ms^{-1})
V	-	Permeate volume (m^3)

Greek letters

μ	-	Solvent viscosity (water viscosity at 25°C is used as $8.937 \times 10^{-2} \text{ kg m}^{-1} \text{ s}^{-1}$)
σ	-	Reflection coefficient (dimensionless)
ξ	-	Ratio of effective volume charge density of membrane to ionic salt concentration

λ	-	Ratio of solute radius to pore radius (dimensionless)
ψ	-	Electrical potential (dimensionless)
μ_p	-	Mean effective pore radius (nm)
σ_p	-	Mean effective about pore radius of μ_p (dimensionless)

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CHAPTER 1

INTRODUCTION

1.1 Research Background

The revolution and development of resources, technologies and human needs had contributed more compounds identified to be possessing environmental threat to the livings. The numbers of the contaminants keep on increasing and generate a long list of compounds found in the natural environment comprises products such as human and veterinary pharmaceuticals, personal care products, surfactants and its residues, plasticizers and various industrial chemicals and additives.

These compounds have been related to the presence of Endocrine Disrupting Chemicals (EDCs) specifically in the aquatic environment. As the name stated, Endocrine Disrupting Chemicals (EDCs) are groups of chemicals or substances that interfere the endocrine system by mimicking, blocking or also disrupting function of hormone system.

The pollution of EDC in the aquatic environment have become major concern due to growing evidence of the exposure towards reproductive and health effects in humans and wildlife. Concerns regarding to exposure to EDCs are primarily due to 1) adverse effect in certain wildlife, fish and ecosystem; 2) the increased incidence of

certain endocrine-related human diseases; and 3) endocrine disruption resulting from exposure to certain environmental chemicals observed in laboratory experimental animals (Damstra *et al.*, 2002).

The adverse effects of EDCs have been shown by reported cases such as sexual abnormalities in fish living near wastewater treatment plant (WWTP) outfalls, where male fish producing female yolk precursor protein vitellogenin (VTG) as a result of exposure to the natural hormone 17 β -estradiol (Purdom *et al.*, 1994), reproductive impairment and teratogenic effects in colonial fish-eating birds and immune dysfunction among Baltic seals due to exposure to Polychlorinated dibenzodioxins/ Polychlorinated dibenzofurans (PCDDs/PCDFs) and dioxin-like Polychlorinated biphenyls (PCBs) (IPCS, 2002), intersex in white suckers fish downstream of a WWTP effluent (Vajda, 2006). The risk to human especially through drinking water consumption is currently not much evidence and unknown, yet there is a concern about the possible carcinogenic and threat they pose to humans and biota in general.

The existence of these compound are due to excretes and discharges from human via sewers, entries from industrial effluents, livestock sewage, agricultural runoff and landfill operations. The main pathway of these compounds enters the environment primarily comes from wastewater treatment plants (WWTP) (Urase and Kikuta, 2005). Certainly, the existing WWTP have been designed at its best in treating and removing contaminants and eutrophication pollution loads. However, the occurrence of the new 'unregulated' micro-contaminants such as EDCs requires advanced treatment. This is due to most current WWTPs were not designed to treat these types of substance, in other word not all compounds were completely broken down or converted to biomass, and thus a high portion of emerging compounds and their metabolites can escape and enter the environment via sewage effluents (Petrovic *et al.*, 2003). So, the compounds have been continually discharged to aquatic environment by a number of routes primarily via wastewater effluents. Additionally, the removals of EDCs in water and wastewater treatment have been limited due to the low concentration of these components in water and the associated difficulties in analysis (Snyder *et al.*, 2003), which lead to difficulties in their detections. The conventional WWTP are or not able to eliminate EDCs to a

satisfactory level, thus an advanced treatment processes are needed (Wintgens *et al.*, 2002; Petrovic *et al.*, 2003). Thus, it is obvious that more advanced technologies may be crucial to fulfill the requirements.

Among all water treatment technologies, one of the most promising options for pollutants separation and purification mentioned by Thomas (1991) is membrane technology. Furthermore, membrane processes are becoming more popular in water treatment because the processes can disinfect water without chemical additions and avoid the formation of toxic disinfection byproducts (Rana *et al.*, 2005). Not only that, membrane technology has received more interest in recent years due to stringent standard for water supply and effluent discharge. The benefits of membrane treatment processes has been highlighted (Rachwal *et al.*, 1994; Cartwright, 1992) as; compact, modular construction, minimum of moving parts with low maintenance requirements, no chemical addition requirements and minimal chemical sludge disposal, absolute barriers to particles and pathogens, constant filtered water quality irrespective of feed water quality, easy system upgrading and suitable to small systems and distributed locations.

In this study, nanofiltration (NF) membrane were tailored and applied for the removal of EDCs. The main advantages of NF is the ability to remove low molecular weight organic micropollutant; particularly EDCs (Nghiem *et al.*, 2004a) and at low operating pressure compared to reverse osmosis processes. Furthermore, the separation and transport in NF are governed by the combination of different mechanism namely; convection, diffusion (sieving) and charge effects, and hence offers numerous advantages as compared to conventional techniques.

The ability of producing own made membrane allows a greater chance to achieve a successful treatment system since during the production process of membrane, the membrane can be tailored to suit the requirements. However, many important factors need to be taken into account in order to allow production of membranes that meet the desired characteristics. To achieve the above challenges, the current studies are conducted for developing new types of hollow fiber NF membranes by emphasizing the removal performance of EDCs using Bisphenol-A from domestic wastewater.

1.2 Problem Statement

Based on the research background, the current conventional wastewater treatment is incapable for treating micropollutants such as EDCs due to the compounds complexity and persistence. Malaysia was also at risk as these EDCs have been detected specifically in the Malaysian river. Therefore, the current research was conducted to explore the possibility and effectiveness of using NF in removing EDCs. Understanding the EDCs rejection by the fabricated NF membranes will be explored. This in turn will provide much better controllability of the membranes characteristics in exploring its interactions towards EDCs rejections.

1.3 Objectives of the Study

The main aim of the study was to develop, fabricate and investigate NF membrane performance and applicability in eliminating EDCs, specifically Bisphenol-A. Therefore, the objectives of this study were to fabricate and design a novel hollow fiber NF PES membrane for the removal of EDCs, to study the removal mechanisms of Bisphenol-A by the fabricated hollow fiber NF membranes and to improve the application of NF membrane processes for the removal of Bisphenol-A.

1.4 Scope of the Study

To achieve the above mentioned objectives, the following scopes of study were designed. These were divided into three stages and briefly elaborated as followed:

1. Development and formation of hollow fiber NF membrane.

The NF membrane preparation and fabrication were conducted by formulating membrane materials and dope preparation (polymer, solvent and additive). The incorporation by blending of synthesized charge-surface-modifying macromolecule (cSMM) to modify and induce charge at membrane surface of the fabricated hollow fiber PES membranes was studied. In order to fabricate tailor-made NF hollow fiber membranes, influences of fabrication and spinning factors were also explored.

2. Membrane filtration measurement and characterization.

This task involved preparation of hollow fiber module and setting up the NF membrane testing rigs to determine membrane flux rate and solute rejection. The characteristics as well as their physico-chemical properties of the fabricated hollow fiber membranes were examined to understand the relationship in designing the NF performance. NF membrane was characterized using Field emission scanning electron microscopy (FESEM), contact angles, Differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FTIR), Energy Dispersive X-ray (EDX), X-ray photoelectron spectroscopy (XPS), and as well as solute separation: Polyethylene glycol (represent non-ionic solute) and Sodium Chloride (NaCl) (as ionic solute).

3. Removal performance of Bisphenol-A.

The detection and quantification method was developed and improved to get a reliable determination and quantification method of Bisphenol-A. This involves detection analysis using Gas chromatography (GC) and Flame ionization detector (FID). The characteristic of wastewater and its relation with Bisphenol-A properties and interactions with respect to the tailored NF separations was studied.

1.5 Rationale and Significance

The overall rationale and significance of the current research is to explore the formation and development of hollow fiber polyethersulfone NF membrane. Configuration of hollow fiber membranes has an extra advantage in the higher packing density whereas selection of synthetic polymer of polyethersulfone has a good processibility in the formation of hollow fiber membranes. To date, no study has involved the synthesis and testing of a membrane designed specifically for removal of EDCs. Most of the current work explores the commercial fabricated membranes. Not only that, most of the membrane related studies on EDCs are flat type configuration membranes.

1.6 Thesis Outline

The body of the dissertation was divided into six main chapters. Chapter one presents brief description of the research background, including the objectives, the scope of work, and the significant of research. Chapter two provides the comprehensive literature review and the environmental issues and effects of EDCs with their potential technology removal processes. Removal mechanisms together with the development and fabrication factors of NF were also emphasized. Detailed descriptions of the research methodology carried out in this work were then presented in Chapter three. This is subsequently followed by the exploration and results of NF development and fabrication in Chapter four. In Chapter five, the designed tailored NF membranes in EDC removal performance (specifically Bisphenol-A) were discussed. The dissertation ends at Chapter six, with the overall concluding remarks and suggestions for future research to further enhance the potential of membrane technology removal regarding to contaminants such as EDC.