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

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UNIVERSITI TEKNOLOGI MALAYSIA
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NURMIN BOLONG

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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 hidroksibenzena-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 penykerak tenaga (EDX), inframerah pengubah fourier (FTIR) and fotoelektron x-ray (XPS). Penambahan kecil pada ketebalan lapisan luar gentian geronggang diperhatikan melalui pemanca meredas 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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<td>ATR</td>
<td>Attenuated Total Reflection</td>
</tr>
<tr>
<td>BOD</td>
<td>Biological Oxygen Demand</td>
</tr>
<tr>
<td>BPA</td>
<td>Bisphenol-A</td>
</tr>
<tr>
<td>CA</td>
<td>Cellulose acetate</td>
</tr>
<tr>
<td>COD</td>
<td>Chemical oxygen demand</td>
</tr>
<tr>
<td>cSMM</td>
<td>Charge surface-modifying macromolecule</td>
</tr>
<tr>
<td>Da</td>
<td>Dalton</td>
</tr>
<tr>
<td>DER</td>
<td>Dope extrusion rate</td>
</tr>
<tr>
<td>DI</td>
<td>De-ionized</td>
</tr>
<tr>
<td>DIPS</td>
<td>Diffusion Induced Phase Separation</td>
</tr>
<tr>
<td>DOC</td>
<td>Dissolved Organic Carbon</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>DDT</td>
<td>Dichloro-Diphenyl-Trichloroethane</td>
</tr>
<tr>
<td>ED</td>
<td>Endocrine Disruptor</td>
</tr>
<tr>
<td>EDC</td>
<td>Endocrine disrupting chemicals/compounds</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform spectroscopy</td>
</tr>
<tr>
<td>FESEM</td>
<td>Field emission scanning electron microscopy</td>
</tr>
<tr>
<td>GCFID</td>
<td>Gas chromatography-flame ionization detector</td>
</tr>
<tr>
<td>IEH</td>
<td>Institute of Environment and Health</td>
</tr>
<tr>
<td>JS</td>
<td>Jet stretch</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
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<td>-------------</td>
</tr>
<tr>
<td>MF</td>
<td>Microfiltration</td>
</tr>
<tr>
<td>MW</td>
<td>Molecular weight</td>
</tr>
<tr>
<td>MWCO</td>
<td>Molecular weight cut-off</td>
</tr>
<tr>
<td>NF</td>
<td>Nanofiltration</td>
</tr>
<tr>
<td>NOM</td>
<td>Natural organic matter</td>
</tr>
<tr>
<td>NMP</td>
<td>1-methyl-2-pyrolidon</td>
</tr>
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<td>PEG</td>
<td>Polyethylene glycol</td>
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<td>HBS</td>
<td>Hydroxybenzene sulfonate</td>
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<td>PES</td>
<td>Polyethersulfone</td>
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<td>POPs</td>
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<td>Pharmaceuticals and Personal care products</td>
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<td>PVC</td>
<td>Polyvinylchloride</td>
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<td>PVP</td>
<td>Polyvinylpyrolidones</td>
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<td>PWP</td>
<td>Pure water permeation</td>
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<td>RO</td>
<td>Reverse osmosis</td>
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<td>Rotation per minutes</td>
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<td>SEM</td>
<td>Scanning electron microscopy</td>
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<td>Solid phase extraction</td>
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<td>Tributyltin</td>
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<tr>
<td>TFC</td>
<td>Thin film composite</td>
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<td>Transmembrane pressure</td>
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<tr>
<td>TOC</td>
<td>Total organic carbon</td>
</tr>
<tr>
<td>TDS</td>
<td>Total dissolved solid</td>
</tr>
<tr>
<td>TSS</td>
<td>Total suspended solid</td>
</tr>
<tr>
<td>UF</td>
<td>Ultrafiltration</td>
</tr>
<tr>
<td>VTG</td>
<td>Vitellogenin</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>--------------------------------------</td>
</tr>
<tr>
<td>v/v</td>
<td>Volume solute per volume solution</td>
</tr>
<tr>
<td>WWTP</td>
<td>Wastewater treatment plant</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
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**LIST OF SYMBOLS**

\[
\frac{A_k}{\Delta x} \quad \text{- Ratio of membrane porosity to thickness of membrane (m}^{-1}\text{)}
\]

\[ A \quad \text{- Cross sectional area in m}^2 \]

\[ A_{sp} \quad \text{- The spinneret cross section (m}^2\text{)} \]

\[ C \quad \text{- Concentration of solute over the thickness of membrane (mol m}^{-3}\text{)} \]

\[ C_f \quad \text{- Concentration of feed or bulk solution} \]

\[ C_i \quad \text{- Concentration of an ion in the bulk solution (mol m}^{-3}\text{)} \]

\[ C_m \quad \text{- Concentration of solute in the fluid at the feed (membrane interface (mol m}^{-3}\text{))} \]

\[ C_p \quad \text{- Concentration of permeate} \]

\[ C_p \quad \text{- Concentration of solute in the fluid at the permeate solution (mol m}^{-3}\text{)} \]

\[ D_{i,p} \quad \text{- The diffusivity of an ion i in fre solution (m}^2\text{ s}^{-1}\text{)} \]

\[ D_i \quad \text{- Inside diameter of the hollow fiber membrane m} \]

\[ D_o \quad \text{- Outside diameter of the hollow fiber membrane m} \]

\[ D_s \quad \text{- Diffusivity of solute molecule in a dilute solution (m}^2\text{ s}^{-1}\text{)} \]

\[ F \quad \text{- Faraday constant (F=96,487 C mol}^{-1}\text{)} \]

\[ G \quad \text{- Gas constant} \]

\[ J \quad \text{- Flux, or flow rate through the membrane (m}^3\text{ m}^2\text{ s}^{-1}\text{)} \]

\[ J_v \quad \text{- Averaged volume flux over membrane surface (m s}^{-1}\text{)} \]
\( \mathbf{J}_s \) - Averaged solute flux over a membrane surface (mol m\(^{-2}\) s\(^{-1}\))

\( \mathbf{J}_{si} \) - Flux of an ion \( i \) over membrane surface (mol m\(^{-2}\) s\(^{-1}\))

\( k \) - Boltzmann’s constant (2.38 x 10\(^{-23} \) J K\(^{-1}\))

\( K_{i,c} \) - Convective hindrance factor in the membrane

\( K_{OW} \) - Octanol-water partitioning coefficient (dimensionless)

\( P \) - Applied pressure (Pa)

\( \text{pKa} \) - Logarithmic value of dissociation constant, \( K_a \) (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

\( \Delta x \) - 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**

\( \mu \) - Solvent viscosity (water viscosity at 25°C is used as 8.937x10\(^{-2} \) kg m\(^{-1}\) s\(^{-1}\))

\( \sigma \) - Reflection coefficient (dimensionless)

\( \xi \) - Ratio of effective volume charge density of membrane to ionic salt concentration
<table>
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<th>Description</th>
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<tr>
<td>$\lambda$</td>
<td>Ratio of solute radius to pore radius (dimensionless)</td>
</tr>
<tr>
<td>$\psi$</td>
<td>Electrical potential (dimensionless)</td>
</tr>
<tr>
<td>$\mu_p$</td>
<td>Mean effective pore radius (nm)</td>
</tr>
<tr>
<td>$\sigma_p$</td>
<td>Mean effective about pore radius of $\mu_p$ (dimensionless)</td>
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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 17β-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 compounds 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 eutrophicating 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 rational 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.