# TITANIUM DIOXIDE INCORPORATED POLYAMIDE THIN FILM COMPOSITE MEMBRANE FOR BISPHENOL A SEPARATION AND DEGRADATION

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A thesis submitted in fulfilment of the
requirements for the award of the degree of
Master of Philosophy

Faculty of Engineering
Universiti Teknologi Malaysia

JANUARY 2021

**DEDICATION**

Dedicated to my parents,

(Mat Anan Muda and Zainab Ismail)

my beloved siblings,

(Syamim Alia, Syifa Elmi and Nor Shahuri)

my husband,

(Muhammad Hafiz Zulkarnain)

my beloved daughter

(Nur Humaira Raissa)

family and friends who gave me inspiration, encouragement and endless support throughout the success of my study.

May this thesis be an inspiration and guidance in the future.

## ACKNOWLEDGEMENT

Foremost, I would first like to express special appreciation to my supervisor, Asc. Prof. Dr Juhana binti Jaafar, for the continuous support, for her patience and motivation during my study. I am extremely thankful and indebted to her for sharing expertise and valuable guidance and encouragement extended to me throughout the time. Thank you for willingly to accept and trusted me to work with you.

I am also grateful to all staff of Advanced Membrane Technology Research Centre (AMTEC) for the help and guidance provided. I also wish to express my sincere thanks to all fellow friends especially Nurafidah Arsat, Nur Atiqah Zulariffin, Roziana Kamaluddin and others comrade for their continuous advice and support. May our journey in completing our Masters and phD will be eased.

Last but not least, I take this opportunity to express my deepest gratitude to my beloved parents; Mr. Anan and Mrs. Zainab and also to my brothers and sisters for their endless love, prayers, attention and encouragement. To those who indirectly contributed in this research especially my husband, Hafiz zulkarnain whose has been helped me a lot, your kindness means a lot to me. Thank you very much.

# ABSTRACT

Endocrine disrupting compounds (EDC) that exist in plastic waste is a real problem in wastewater management system nowadays since there is no exact way to treat it due to its low molecular weight. The estrogenic properties of bisphenol A (BPA), a ubiquitous synthetic monomer that can leach into the food and water supply, have prompted considerable research into exposure-associated health risks in humans. Photocatalytic process is one of the advanced oxidation processes that has been widely applied in wastewater treatment system due to its low cost and environmentally friendly. In addition, this process has huge ability to remove persistent pollutant like EDC in water. The main part of photocatalytic process is the photocatalyst itself and the immobilization of this photocatalyst in thin film membrane can make the resultant membrane acts as both photocatalytic site and selective layer for filtration. This approach also can reduce membrane fouling and avoid post treatment which is recovery of photocatalyst from treated water. Titanium dioxide ($TiO_2$) was chosen as photocatalyst for degrades BPA particle due to its low in cost and high performance in degradation of pollutants. The main goal of this project is to fabricate and characterize a hybrid photocatalytic thin film composite membrane that consists of PSF support membrane and polyamide (PA)/$TiO_2$ thin film layer for BPA removal. This hybrid membrane was fabricated through interfacial polymerization method using trimesoyl chloride (TMC) and m-phenylenediamine (MPD). Besides that, the effect of $TiO_2$ loading (0-0.5%) on the photocatalytic membrane performances in term of photocatalytic degradation and BPA rejection were also studied. These hybrid membranes were analysed for several characterization using field emission scanning electron microscopy (FESEM), Fourier-transform Infrared spectroscopy (FTIR), energy-dispersive X-ray spextroscopy (EDX) and contact angle analyzer. A 100 ppm of BPA synthetic wastewater was prepared and used for membrane performance test. The performance of fabricated PA/$TiO_2$ photocatalytic membrane in BPA degradation and rejection was tested using photocatalytic flat sheet membrane reactor. According to the results obtained this type of hybrid membranes show promising performance in BPA rejection but do not effective for BPA degradation. The fabrication of PA layer was contributed to higher rejection of BPA compare to PSF membrane. For PA/$TiO_2$ TFC membrane, the highest rejection recorded is performed by 0.4 PA/$TiO_2$ TFC membrane with 99.9 % BPA rejection while the lowest is given by 0.1 PA/$TiO_2$ TFC membrane with 91.7% BPA rejection. Meanwhile, in terms of BPA degradation, the highest degradation achieve is 14% which performed by 0.4 PA/$TiO_2$ TFC membrane and the lowest degradation is 4.5% which is performed by 0.1 PA/$TiO_2$ TFC membrane. Based on the results obtained, PA/$TiO_2$ TFC membrane is only suitable for BPA separation but not effective for its degradation.

# ABSTRAK

Sebatian pengganggu endokrin yang wujud dalam sisa plastik telah menjadi satu masalah dalam sistem rawatan air sisa kebelakangan ini berikutan tiada cara yang tepat untuk merawatnya kerana sebatian tersebut mempunyai berat molekul yang rendah. Sifat estrogenik bisphenol A (BPA), sejenis sintetik monomer yang didapati di mana mana boleh meresap ke dalam makanan dan bekalan air, telah menggesa kajian yang menyeluruh tentang pendedahan nya terhadap risiko kepada kesihatan manusia. Proses fotopemangkinan adalah salah satu proses pengoksidaan yang maju dan telah digunakan secara meluas dalam sistem rawatan air sisa berikutan kos yang rendah dan mesra alam dan proses ini mempunyai keupayaan untuk membuang bahan pencemar yang tegar seperti sebatian pengganggu endokrin di dalam air. Komponen asas dalam proses fotopemangkinan ini adalah fotopemangkin itu sendiri dan imobilisasi fotopemangkin ini di dalam membran selaput nipis akan menjadikan selaput nipis itu bertindak sebagai tapak fotopemangkin dan juga lapisan memilih. Pendekatan ini juga boleh mengurangkan halangan membran dan mengelakkan daripada rawatan selepas proses iaitu pengambilan semula pemangkin daripada air yang telah dirawat. Titanium dioxide ($TiO_2$) telah dipilih sebagai pemangkin yang akan menghapuskan zarah BPA memandangkan ianya berkos rendah dan mempunyai prestasi yang tinggi dalam penghapusan bahan pencemar. Tujuan projek ini adalah untuk menghasilkan dan mencirikan membran komposit selaput nipis hibrid fotopemangkin yang terdiri daripada PSF membran sokongan dan polyamide (PA) $TiO_2$ lapisan selaput nipis untuk pembuangan BPA. Hibrid membran ini akan dihasilkan melalui proses mempolimerkan antara dua permukaan menggunakan trimesoyl chloride (TMC) dan m-phenylenediamine MPD. Selain itu, kesan kuantiti pemangkin, $TiO_2$ (0-0.5%) pada keupayaan membran fotopemangkin dari segi penghapusan fotopemangkin dan pemisahan BPA. Membran hibrid ini juga dianalisa untuk beberapa ciri menggunakan mikroskop elektron imbasan (FESEM), transformasi Fourier spektroskopi inframerah (FTIR), Spektroskopi sinar-X penyebaran tenaga (EDX) dan analisa sudut sentuhan air. 100ppm air kumbahan BPA sintetik disediakan dan digunakan untuk uji prestasi membran. Prestasi fotopemangkin hibrid membrane dalam penghapusan dan pemisahan BPA telah diuji menggunakan reaktor fotopemangkin lembaran rata. Berdasarkan keputusan yang diperoleh, hibrid membran jenis ini menunjukkan prestasi yang memuaskan dalam penghapusan BPA dari segi pemisahan tapi kurang berkesan dari segi penghapusan menggunakan proses fotopemangkinan. Penghasilan lapisan PA yang padat membawa kepada peratusan pemisahan BPA yang lebih tinggi berbanding membrane PSF. Bagi membran PA/$TiO_2$ TFC, peratusan pemisahan BPA yang tertinggi adalah 99.9% dimana menggunakan membrane 0.4 PA/$TiO_2$ TFC manakala yang terendah adalah 91.7% yang dilakukan oleh membrane 0.1 PA/$TiO_2$ TFC. Manakala dari segi penghapusan BPA, peratusan penghapusan BPA yang tertinggi tercapai adalah 14% yang dihasilkan oleh membran 0.4 PA/$TiO_2$ TFC dan yang terendah adalah 4.5% yang dihasilkan oleh membran 0.1 PA/$TiO_2$ TFC. Berdasarkan data eksperimen berikut, membrane PA/$TiO_2$ TFC sesuai untuk diaplikasikan untuk memisahkan BPA tapi tidak begitu sesuai untuk penghapusan BPA.

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## LIST OF ABBREVIATIONS

| | | |
|---|---|---|
| AOP | - | Advance Oxidation Process |
| ATR | - | Attenuated Total Reflectance |
| BPA | - | Bisphenol A |
| CAO | - | Chemical Advance Oxidation |
| CBZ | - | Carbamazepine |
| CdS | - | Cadmium sulphide |
| COD | - | Chemical oxygen demand |
| DCF | - | Diclofenac |
| DDT | - | Dichlorodiphenyltrichloroethane |
| DI | - | Dionized water |
| $H_2PO_4$ | - | Dihydrogen phosphate |
| EDC | - | Endocrine Disruptive Compunds |
| EDX | - | Energy-dispersive X-ray |
| FESEM | - | Field- emission scanning electron microscope |
| FO | - | Forward osmosis |
| FTIR | - | Fourier transform infrared |
| HPLC | - | High performance liquid chromatography |
| IR | - | Infrared |
| IP | - | Interfacial polymerization |
| MPD | - | M-Phenylenediamine |
| MF | - | Microfiltration |
| NF | - | Nanofiltration |
| $NO_3$ | - | Nitrate |
| OM | - | Organic matter |
| $O_3$ | - | Ozone |
| PA | - | Polyamide |
| PCBs | - | Polychlorinated biphenyls |
| PES | - | Polyethersulfone |
| PI | - | Polyimide |
| $PO_4$ | - | Phosphate |

| | | |
|---|---|---|
| PP | - | Polypropylene |
| PSF | - | Polysulfone |
| PTFE | - | Polytetrafluoroethylene |
| PVA | - | Polyvinyl alcohol |
| PVDF | - | Polyvinylidene fluoride |
| RO | - | Reverse Osmosis |
| RfD | - | Reference dose |
| SEM | - | Scanning electron microscope |
| $TiO_2$ | - | Titanium Dioxide |
| TMC | - | Trimesoyl chloride |
| TFC | - | Thin film composite |
| TFN | - | Thin film nanocomposite |
| UF | - | Ultrafiltration |
| UV | - | Ultraviolet |
| WCA | - | Water contact angle |
| WWTPs | - | Wastewater treatment plant |

# LIST OF SYMBOLS

| | | |
|---|---|---|
| $\theta$ | - | Contact angle |
| $C_f$ | - | Concentration of solute in feed (ppm) |
| $C_p$ | - | Concentration of solute in permeate (ppm) |
| $C_t$ | - | Concentration at time=t |
| *cb* | - | Conduction band |
| $J$ | - | Flux ($Lm^{-2}h^{-1}$) |
| $C_o$ | - | Initial concentration |
| $A$ | - | Membrane surface area ($m^2$) |
| $\Delta t$ | - | time of permeate accumulation (h) |
| *vb* | - | Valence band |
| $V$ | - | Volume (L) |
| *w/v* | - | Weight per volume |

# CHAPTER 1

# INTRODUCTION

## 1.1 Research Background

Bisphenol-A (BPA) is one of the highest volume chemicals produced worldwide. Current estimation indicates that over 6 billion pounds were produced annually in the manufacturing of polymers (such as polycarbonate, epoxy resins, polysulfone, or polyacrylate) and polyvinyl chloride plastics. Polycarbonate is used in materials of foodstuffs (such as baby bottles, reusable plastic bottles, plates, goblets, cups, microwave ovenware, and storage containers) and the epoxy resins are used for internal coating of food and beverage cans. Thus, over 100 t of BPA are released into the atmosphere every year (Rezg et al., 2014). BPA is categorized as one of the Endocrine Disruptive Compound (EDC).

Scientists positively believe that this EDC can initiate detrimental effects on human and animal (Helland, 2006). More than that, real hormones in human endocrine system can be imitated by EDC and it is believed can generate few disturbance to human life, especially to its endocrine system itself (Snyder et al., 2003; Liu et al., 2009). In addition, chemicals that has been categorized under EDC is related in health problem among aquatic life (Snyder et al., 2003). The phrase “endocrine disrupters” means synthetic chemicals and authentic nature compounds that can affect the endocrine system (Helland, 2006). It also means as exogenous medium that conflict with the “creation, secretion, carrier, restraining, behavior, or exclusion of original hormones of living things that are in charge for the continuance of homeostasis, reproduction, growth, and function” (Snyder et al., 2003).

Start from early 1990`s, increment of contamination of such compounds was detected especially in surface waters, agricultural fields, and atmosphere, specifically after the analytical analysis for its discovery have been enhanced (Jagnytsch et al., 2005). The estrogenic features of BPA, a ubiquitous synthetic monomer that possible to extract into the meals and drinks source, have raised awareness among researchers and some study into BPA exposure-related health hazards in humans has been conducted (Seachrist et al., 2016).

Currently, physical treatment, biodegradation and chemical advanced oxidation (CAO) are three categories of methods available to remove EDC (Liu et al., 2009). This study focused on the BPA removal using photocatalysis process along with membrane technology. Photocatalysis can be stated as a "*catalytic reaction involving the yield of a catalyst by preoccupation of light*" (Lazar et al., 2012). In this study, flat sheet membrane is supporting photocatalyst process and consequently improves the effectiveness of the separation system. The capability to eliminate persistent organic compounds and microorganisms in effluent by this enrichment technology has been widely demonstrated. This type of innovation become more interesting due to its advantage in improving the decontamination in treating wastewater compared to others processes (Nor et al., 2013). In fact, removal of both original and synthetic especially destructive organic substances from fresh water can be achieved successfully by photocatalysis process (Le-Clech et al., 2006). The combination of a photocatalytic degradation process with a membrane separation process could produce a very efficient system since it takes benefit of the synergy of both technologies, along with the membrane having double duty of supporting the photocatalyst as well as functioned as a selective barrier for the pollutant to be removed. In this research, the existence of thin film acted as photocatalytic site to provide direct exposure of light for the photocatalyst, hence improving the degradation of BPA through photocatalyst process. The fabrication of polyamide thin film on top of PSF support membrane was done through interfacial polymerization method using M-phenylenediamine (MPD) and 1, 3, 5-benzenetricarboxylic acid chloride (TMC). The well-known photocatalyst, Titanium Dioxide ($TiO_2$), is being used in this research. Over the last decades, a lot of study has been focus on the employment of $TiO_2$ as a photocatalyst in photodegradation of pollutants exist in effluents. $TiO_2$ has been expressed as one the excellent semiconductor photocatalysts usable for photocatalysis, since its exhibits high photoactivity and photodurability owing to chemical and biological inactivity, mechanical toughness, flexibility in its surface function, excellent mechanical strength, large surface area to volume ratio towards the light irradiation and low cost (Doh et al. 2008).

## 1.2 Problem Statement

As good quality drinking water source has been limited, unintended indirect potable water reuse, where wastewater effluent is chosen as a section of a downstream drinking water origin, has initiate a huge attention all around the globe. In this case, many types of organic micro-pollutants existed in wastewater effluent such as EDC could become an issue. Due to fast growth of analytical analysis, it has been recorded that many aquatic environments are contaminated with just a little concentrations of EDCs effluents are normally believed to be a main source of this class of contamination. One of endocrine disrupting compounds that exist in huge amount in wastewater is BPA. BPA is a major raw component in polycarbonate plastics and epoxy resins manufacturing. Large production of this chemicals has bring the issue of effect of BPA to living things.

Application of membrane filtration system has installed rapidly in water treatment system over these past few years. These membranes are functioned primarily to separate the undesirable micro and macro particles. However, the application of ultrafiltration (UF) and microfiltration (MF) membrane in treating EDC is not favorable due to the small particle size of EDC and porous structure of these membranes. Hence, membrane with most fine pores size must has been produced to be used for treating EDC. Other than that, fouling problem has become a great obstacle in membrane filtration system since it is affecting membrane's separation efficiency. This issue has practically and economically limited membrane employment in effluent treatment improvement. Membrane will face fouling problem when some particles stick on the outer layer of the membrane and consequently produced a cake layer. This layer is affecting membrane's system productiveness as it will influence the capability of the membrane. In the development of water treatment system, this issue has clearly destruct membrane installment due to the maintenance cost. The decline in efficiency that originates by membrane fouling can be defined as the reductions in flux with operation duration that cause by grow of hydraulic repellent. Besides that, it can be stated as a necessity for more energy provide for the membrane filtration system in order to preserve the system production. Energy and cost for cleaning processes also included because the system need to be clean to eliminate the unwanted layer from the outer layer of membrane so that it can generate the quantity of permeate as much as it is new one. Basically, several processes to degrade EDC from wastewater effluent efficiently other than membrane treatment have been explored and developed. Among of those methods, photocatalyst have become a great option to degrade these compounds.

Recently, photocatalytic oxidation has been emerged as an important technology for air and water disinfection since it has ability to decompose organic pollutants without applying any chemicals to form safe products. This advanced oxidation process (AOPs) consist of many reactions such as organic synthesis, water splitting, photoreduction, hydrogen transfer, gaseous pollutant removal and others. In photocatalyst process, the immersed photocatalysts exhibits better photocatalytic efficiencies due to all active surface of the photocatalyst are in interaction with the organic contaminants in water/air and straightly absorbed more UV light. However, this type of method needs extra post-treatment in order to remove the catalyst which are the emission of the catalyst with effluent might be dangerous to the environment due to its biological accumulative reaction. Thus, the most common problem that arise with photocatalyst process is addition cost from the post treatment which the photocatalyst used need to be separated from the wastewater treated. Thus, combine membrane separation and photocatalytic process together will overcome the membrane fouling problem and avoid the separation of catalyst. Other than can minimize the fouling membrane issue, combining these two processes together also can avoid the post treatment of common suspension photocatalysis process, which is recovering of catalyst from wastewater since the catalyst is immobilized onto the membrane. There are already many photocatalytic membrane that has been develop but this type of membrane shows low rejection and degradation of BPA due to the large pore size of membrane and the distance of light source with embedded catalyst is quite far. With the fabrication of dense thin film layer, the rejection and degradation of BPA might improve since photocatalyst $TiO_2$ is located on top of the membrane.

In this study, polyamide (PA) thin film will be functioned as selective layer and photocatalyst site since $TiO_2$ will be immobilized into it. The fabrication of PA thin film will produce dense layer of membrane on top of porous substrate membrane which will enhance the separation of EDC and act as site that hold the catalyst in the membrane. In others word, both degradation by photocatalytic and separation by thin film will occur at same time. Generally, this work is mean to identify the capability of a photocatalytic process by $TiO_2$ associate with membrane filtration for the removal of BPA from wastewater effluent.

## 1.3 Objectives of the Study

The purpose of this proposed project is to prepare and characterize a hybrid photocatalytic thin film composite membrane with polyamide (PA) titanium dioxide ($TiO_2$) as selective thin film for Bisphenol A (BPA) rejection. The specific objectives of the project are:

1) To fabricate and characterize hybrid photocatalytic thin film composite membrane with PA titanium dioxide ($TiO_2$) thin film supported by PSF flat sheet membrane
2) To evaluate the efficiency of the hybrid membrane as a function of $TiO_2$ loading under UV irradiation on BPA removal.

## 1.4 Scopes of the Study

In accomplishing the above mentioned objective of the study, the following scopes are outlined:

1) Preparing polyamide (PA) thin films through interfacial polymerization method on top of PSF substrate by varying $TiO_2$ loading (0-0.5%).

2) Conducting characterization study on the PSF photocatalytic PA/doped $TiO_2$ thin film membranes by several characterizations obtained through FESEM image, AFM image, EDX image, FTIR data, mean pore size and contact angle data.
3) Preparing 100ppm BPA solution to be used as synthetic wastewater in the performance of prepared photocatalytic hybrid membrane
4) Examining the photocatalytic performance of these hybrid membranes for BPA removal in terms of photodegradation under UV light by employ high performance liquid chromatography (HPLC, Agilent Technology 1200 Series) coupled with a programmable UV detector.
5) Examining the separation performance of these hybrid membranes for BPA removal in terms of pure water flux and BPA rejection by employ high performance liquid chromatography (HPLC, Agilent Technology 1200 Series) coupled with a programmable UV detector under 5 bar pressure.

## 1.5 Significance of Study

The combination of membrane and photocatalytic technology was nominated as an Advanced Oxidation Process (AOP) owing to its promising ability to degrade trace level environmental pollutants via hybrid technology approach; photodegradation and membrane separation. The immobilization of $TiO_2$ onto PA thin film membrane will make the photocatalyst get the maximum light intensity, thus improving the photocatalytic activity compared to the immobilization of catalyst in support membrane but need higher loading of photocatalyst since current loading leads to low degradation of BPA. Furthermore, the immobilization of $TiO_2$ on the PA thin film membrane can simplify the conventional photocatalytic process by eliminating the post treatment of catalyst separation process thus indicated that this study significant as the photocatalytic membrane is vital to sustain a clean and safer environment. The fabrication of PA/$TiO_2$ TFC on top layer of PSF substrate give significant impact on rejection of BPA which leads to 99% rejection of BPA.

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**(**Anan et al. / Malaysian Journal of Fundamental and Applied Sciences Vol. 15, No. 5 (2019) 755-760)