COPPER OXIDE INCORPORATED POLYVINYLIDENE FLUORIDE DUAL LAYER HOLLOW FIBER PHOTOCATALYTIC MEMBRANE FOR BISPHENOL A REMOVAL

SITI HAWA BINTI MOHAMED NOOR

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

School of Chemical and Energy Engineering Faculty of Engineering Universiti Teknologi Malaysia

MARCH 2022

DEDICATION

This thesis is dedicated to my late father [Mohamed Noor Abdul Kadir], my mother [Siti Jaminah Samian], parents in-law [Ramlan Abu Bakar & Nora Abdul Wahab], my siblings, in-laws, nieces and nephews who taught me that the best kind of knowledge to have been that which is learned for its own sake and encouraged me to further study to the next step. Lastly, dedicated to my beloved husband and daughter [Mohd Hairil Nizam Ramlan & Hayla Yasmin Mohd Hairil Nizam] who supports me in every aspect and always been there through thick and thin.

ACKNOWLEDGEMENT

In preparing this thesis, I was in contact with many people, researchers, academicians, and practitioners. They have contributed towards my understanding and thoughts. In particular, I wish to express my sincere appreciation to my main thesis supervisor, Professor Dr. Ts. Mohd Hafiz Dzarfan Othman, for encouragement, guidance, critics, guidance, advice and motivation. Without his continued support and interest, this thesis would not have been the same as presented here.

I am also indebted to Universiti Teknologi Malaysia (UTM) for funding my Masters study. Librarians at UTM also deserve special thanks for their assistance in supplying the relevant literatures. Other than that, Advanced Membrane Technology Research Centre (AMTEC) staffs also deserve special thanks for guiding me in handling chemicals and laboratory works.

My fellow postgraduate student should also be recognised for their support. My sincere appreciation also extends to all my colleagues and others who have provided assistance at various occasions. Their views and tips are useful indeed. Unfortunately, it is not possible to list all of them in this limited space. I am grateful to all my family member.

ABSTRACT

Bisphenol A (BPA) is grouped under endocrine disrupting compound (EDC), which accumulating in most Southeast Asia rivers from 8 ng/L to 36.9 ng/L. It is a common plasticizer have been in plastic bottles, water pipes, and toys and enters our household water after being exposed to heat, acid, or base. Continuous exposure to BPA may lead to myocardial infraction, cardiac hypertrophy, preterm birth, and neurobehavioral disturbances. This study developed a novel photocatalytic membrane to remove BPA from water body efficiently. The photocatalysis process was chosen to be a hybrid with membrane in this work as it is safe and has no secondary by-product. Copper (I) oxide (Cu₂O), also known as cuprous oxide, is a type of semiconductor which is nontoxic and able to work under visible light with its low band gap of 2.2 eV. In this study, Cu₂O was incorporated into polyvinylidene fluoride (PVDF) based duallayer hollow fiber membrane at different Cu₂O to PVDF ratios, namely 0.25, 0.50, and 0.75. The outer dope layer flowrate was also varied at 3, 6, and 9 ml/min. The membranes were analyzed for scanning electron microscope, contact angle, porosity, tensile strength test, atomic force microscopy, X-ray diffraction, dispersive energy Xray, Fourier-transform infrared spectroscopy, and water flux measurement. Based on the finding, a higher outer dope flowrate increased the outer layer finger like structure and thickness. 6 ml/min outer dope flowrate had the highest porosity ($63.13\% \pm 5.09$), and water flux (4919.02 \pm 42.52 L/m²h). Meanwhile, the increase in photocatalyst loading had increased the Cu₂O agglomeration in the outer layer membrane, copper mapping in the outer layer membrane, and surface roughness. The DLHF membrane with a Cu₂O/PVDF ratio of 0.5 possessed the highest water flux (13890.99 \pm 164.96 $L/m^{2}h$) and the lowest contact angle (58.90° ± 1.72). Thus, the selected membranes were observed for their performance to degrade BPA with 10, 20, and 30 mg/L concentrations under visible light irradiation for 360 minutes. The treated water sample was analysed for the leaching test. The best membrane configuration as photocatalytic membrane is 0.50 Cu₂O/PVDF ratio with 6 ml/min outer dope flowrate with the ability to remove 75 % of 10 mg/L BPA, 69.23 % of 20 mg/L BPA and 68.42 % of 30 mg/L BPA in 360 minutes under visible light irradiation. In conclusion, Cu₂O/PVDF DLHF membrane is able to remove BPA under visible light irradiation.

ABSTRAK

Bisphenol A (BPA) tergolong di dalam kumpulan sebatian yang mengganggu endokrin (EDC) yang semakin terkumpul di kebanyakan sungai di Asia Tenggara dari 8 ng/L ke 36.9 ng/L. Ia merupakan pemplastik lazim dalam botol plastik, paip air dan permainan kanak-kanak dan berupaya memasuki sumber air rumah selepas terdedah pada haba, asid dan alkali. Pendedahan berterusan terhadap BPA boleh menyebabkan infraksi miokardium, hipertrofi jantung, kelahiran pramatang dan gangguan tingkahlaku neuro. Dalam kajian ini, satu membran fotomangkin novel telah dibangunkan untuk menyingkirkan BPA dari sumber air secara efisien. Proses fotomangkin telah dipilih untuk dihibridkan bersama membran kerana ianya selamat dan tiada hasil sampingan sekunder terhasil. Kuprum (I) oksida (Cu₂O) atau dikenali sebagai kuprus oksida adalah sejenis semikonduktor yang tidak bertoksik dan berupaya bekerja di bawah cahaya tampak dengan sela jalurnya yang rendah, 2.2 eV. Melalui kajian ini, Cu₂O telah digabungkan bersama membran dua lapis gentian berongga polivinilidena flourida (PVDF) dengan nisbah Cu₂O kepada PVDF yang berbeza, 0.25, 0.50 dan 0.75. Kadar aliran lapisan luar juga telah divariasikan pada 3, 6 dan 9 ml/min. Membran telah dianalisa menggunakan mikroskop elektron imbasan, sudut sentuh, keliangan, ujian kekuatan tegangan, mikroskopi daya atom, pembelauan sinar-X, sinar-X sebaran tenaga, spektroskopi inframerah transformasi Fourier dan pengukuran fluks air. Berdasarkan keputusan kajian, struktur kadar air dop luar tinggi meningkatkan struktur jari lapisan luar dan ketebalan. Kadar aliran lapisan luar 6 ml/min mempunyai keliangan paling tinggi (63.13% \pm 5.09) dan fluks air (4919.02 \pm 42.52 L/m²h). Manakala, peningkatan muatan fotomangkin meningkatkan pengaglomeratan Cu₂O pada lapis luar membran, pemetaan kuprum pada lapis luar membran dan kekasaran permukaan membran. Membran DLHF dengan nisbah Cu₂O/PVDF 0.5 mempunyai fluks air paling tinggi (13890.99 \pm 164.96 L/m²h) dan sudut sentuh paling rendah $(58.90^{\circ} \pm 1.72)$. Membran terpilih telah dicerap untuk prestasinya untuk penurunan BPA dengan kepekatan 10, 20 dan 30 mg/L dibawah sinaran cahaya tampak selama 360 minit. Sampel air terawat telah dianalisa untuk ujian larut lesap. Konfigurasi membran fotomangkin terbaik adalah nisbah Cu₂O/PVDF 0.5 dengan kadar aliran lapisan luar 6 ml/min berupaya mendegradasi 75% BPA 10 mg/L, 69.23% BPA 20 mg/L dan 68.42% BPA 30 mg/L dalam 360 minit dibawah sinaran cahaya tampak. Kesimpulannya, membran DLHF Cu₂O/PVDF berjaya menyingkirkan BPA di bawah sinaran cahaya tampak.

TABLE OF CONTENTS

TITLE

DI	ECLARATION	iii
DF	EDICATION	iv
AC	CKNOWLEDGEMENT	v
AF	STRACT	vii
AI	STRAK	viii
TABLE OF CONTENTS		viii
LI	ST OF TABLES	xii
LI	ST OF FIGURES	xii
LIST OF ABBREVIATIONS		xivv
LIST OF SYMBOLS		XV
LI	ST OF APPENDICES	xvii
CHAPTER 1	INTRODUCTION	1
1.1	Background of study	1
1.2	Problem statement	4
1.3	Research objectives	6
1.4	Scope of study	6
1.5	Significance of study	8
1.6	Thesis organization	9
CHAPTER 2	LITERATURE REVIEW	11

2.	Introduction	11
2.	2 Endocrine Disrupting Compound	12
2.	Bisphenol A	14
2.	Conventional Methods to Remove Bisphenol A	17
2.	5 Photocatalysis	23
2.	5 Visible Light Photocatalyst	25
2.	7 Membrane Technology	31

	2.7.1 Polyvinylidene fluoride Membrane	32	
	2.7.2 Dual Layer Hollow Fibre Membrane	33	
	2.7.3 Photocatalytic Membrane	35	
2.8	Research Gap		
CHAPTER 3	METHODOLOGY		
3.1	Research Design	39	
3.2	Materials		
3.3	Fabrication of Photocatalytic Dual Layer Hollow Fiber Membrane		
	3.3.1 Polymer Dope Materials	41	
	3.3.1.1 Inner Layer Dope	41	
	3.3.1.2 Outer Layer Dope	42	
	3.3.2 Dry/Wet Co Extrusion Technique	43	
	3.3.3 Post Treatment	43	
3.4	Characterization Methods	44	
	3.4.1 Morphological Structure	44	
	3.4.2 Crystallinity Properties	44	
	3.4.3 Elemental Mapping	44	
	3.4.4 Functional Group	45	
	3.4.5 Surface Roughness	45	
	3.4.6 Tensile Strength and Elongation at Break	45	
	3.4.7 Hydrophilicity	46	
	3.4.8 Porosity	46	
	3.4.9 Water Flux	47	
3.5	Photocatalytic Performance	48	
	3.5.1 Preparation of BPA Solution	48	
	3.5.2 Photocatalytic Performance of DLHF Membrane	48	
	3.5.3 Leaching Compound Detection	50	
CHAPTER 4	RESULTS AND DISCUSSION	51	
4.1	Introduction	51	

4.2	The Effect of Outer Layer Extrusion Flowrate on the DLHF's Properties	51
	4.2.1 Morphology	52
	4.2.2 Porosity	55
	4.2.3 Water Flux	56
	4.2.4 Crystalline Property	57
	4.2.5 Functional Group	58
4.3	Effect of Cu ₂ O/PVDF Ratio on the Membrane's Characteristics	60
	4.3.1 Morphology	60
	4.3.2 Hydrophilicity	64
	4.3.3 Porosity	66
	4.3.4 Water flux	66
	4.3.5 Surface Roughness	68
	4.3.6 Tensile Strength and Elongation at Break	69
4.4	Photocatalytic Performance	
4.5	Leaching Compound Detection	
CHAPTER 5	CONCLUSIONS AND RECOMMENDATIONS	79
5.1	Conclusions	79
5.2	Recommendation for Future Direction	80
REFERENCE		83
LIST OF PUBLICATION		102

LIST OF TABLES

TABLE NO.	TITLE	PAGE
Table 2.1	Advantages and disadvantages of conventional method to remove BPA	22
Table 2.2	Summary of visible light photocatalyst activity	30
Table 2.3	Application of DLHF membrane in photocatalysis process	36
Table 3.1	List of materials for membrane fabrication	41
Table 3.2	Polymer dope solutions compositions	42
Table 3.3	Condition in dry/wet co-extrusion technique	43
Table 4.1	Pore size for 0.25 $Cu_2O/PVDF$ DLHF membranes with 3 ml/min, 6 ml/min and 9 ml/min outer dope flowrate	53
Table 4.2	Outer layer layer thickness of 0.25 $Cu_2O/PVDF$ DLHF membranes for different outer layer dope flowrate 3 ml/min, 6 ml/min and 9 ml/min	54
Table 4.3	Pore size of 0.25, 0.50 and 0.75 $Cu_2O/PVDF$ DLHF membranes	61
Table 4.4	EDX mapping of $Cu_2O/PVDF$ DLHF membrane with 6 ml/min outer dope flowrate	63
Table 4.5	Outer layer thickness of 0.25, 0.50 and 0.75 $Cu_2O/PVDF$ DLHF membrane	63
Table 4.6	AFM analysis of Cu ₂ O/PVDF DLHF membrane	68
Table 4.7	Summary of Cu ₂ O/PVDF DLHF membrane photocatalytic performance in removing BPA.	75
Table 4.8	Comparison between Cu ₂ O/PVDF DLHF and other photocatalysts and BPA photodegradation	77
Table 4.9	Copper element detection in degraded BPA water sample.	78

LIST OF FIGURES

FIGURE NO	. TITLE	PAGE
Figure 2.1	Summary of sources of EDC enters the environment (Wan Ismail and Mokhtar, 2020).	13
Figure 2.2	Molecular structure of BPA.	15
Figure 2.3	Scenario of adsorption process (Sharma and Saini, 2016).	17
Figure 2.4	Photocatalysis mechanism schematic diagram (Saravanan et al., 2017).	24
Figure 2.5	Dry/Wet Co-extrusion schematic diagram (Khan et al., 2018).	34
Figure 2.6	Schematic diagram of dual layer hollow fibre membrane (Kamaludin <i>et al.</i> , 2019).	35
Figure 3.1	Schematic diagram of the research design.	40
Figure 3.2	Experimental set up for inner layer and outer layer dope preparation.	42
Figure 3.3	Loop of membrane module, DLHF membrane.	49
Figure 3.4	Schematic diagram of pilot-scale submerged photocatalytic membrane reactor.	49
Figure 4.1	SEM images of 0.25 Cu ₂ O/PVDF DLHF membranes with different outer dope flowrate (a) 3 ml/min (b) 6 ml/min (c) 9 ml/min.	53
Figure 4.2	Porosity of 0.25 Cu ₂ O/PVDF DLHF membranes with outer dope flowrate 3 ml/min, 6 ml/min and 9 ml/min.	55
Figure 4.3	Water flux of 0.25 Cu ₂ O/PVDF DLHF membranes with outer dope flowrate 3 ml/min, 6 ml/min and 9 ml/min.	56
Figure 4.4	XRD graph of Cu ₂ O/PVDF DLHF membrane.	58
Figure 4.5	FTIR spectrum of (a) PVDF single layer hollow fibre membrane (b) $0.25 \text{ Cu}_2\text{O}/\text{PVDF}$ DLHF membrane with 6 ml/min outer dope flowrate.	59
Figure 4.6	SEM images of (a) 0.25, (b) 0.50 and (c) 0.75 $Cu_2O/PVDF$ DLHF membranes with different outer dope flowrate 6 ml/min.	61
Figure 4.7	Contact angle of 0.25, 0.5 and 0.75 $Cu_2O/PVDF$ DLHF membranes with outer dope flowrate 6 ml/min.	65

Figure 4.8	Porosity of 0.25, 0.5 and 0.75 $Cu_2O/PVDF$ DLHF membranes with outer dope flowrate 6 ml/min.	66
Figure 4.9	Water flux of 0.25, 0.5 and 0.75 $Cu_2O/PVDF$ DLHF membranes with outer dope flowrate 6 ml/min.	67
Figure 4.10	Tensile strength of 0.25, 0.5 and 0.75 $Cu_2O/PVDF$ DLHF membrane	70
Figure 4.11	Elongation of 0.25, 0.5 and 0.75 $Cu_2O/PVDF$ DLHF membrane	71
Figure 4.12	Adsorption desorption equilibrium graph of Cu ₂ O/PVDF DLHF membranes on BPA	72
Figure 4.13	10 mg/L of BPA removal by $Cu_2O/PVDF$ DLHF membranes at different $Cu_2O/PDVF$ ratio under visible light irradiation	73
Figure 4.14	20 mg/L of BPA removal by $Cu_2O/PVDF$ DLHF membranes at different $Cu_2O/PDVF$ ratio under visible light irradiation	74
Figure 4.15	30 mg/L of BPA removal by Cu ₂ O/PVDF DLHF membranes at different Cu ₂ O/PDVF ratio under visible light irradiation	75

LIST OF ABBREVIATIONS

SEM	-	Scanning Electron Microscopy
XRD	-	X-ray Diffraction
FTIR	-	Fourier-transform Infrared Spectroscopy
AFM	-	Atomic Force Microscopy
EDX	-	Energy Dispersive X-ray
DLHF	-	Dual Layer Hollow Fibre
PVDF	-	Polyvinylidene fluoride
DMAc	-	Dimethylacetamide
PEG	-	Polyethylene glycol
Cu ₂ O	-	Copper (I) oxide
PVC	-	Polyvinyl chloride
EDC	-	Endocrine Disrupting Compound
BPA	-	Bisphenol A
WWTP	-	Wastewater Treatment Plant
MSN-	-	Hexadecyltrimetgylammonium
CTAB		
ANMWC	-	Antimony Nanoparticle Multi-Walled Carbon
MWCNT	-	Multi-Walled Carbon Nanotube
NF	-	Nanofiltration
TiO ₂	-	Titanium dioxide
WO ₃	-	Tungsten trioxide
Ag ₃ PO ₄	-	Silver phosphate
UV	-	Ultraviolet
CdS	-	Cadmium sulfide
BiVO ₄	-	Bismuth vanadate
g-C ₃ N ₄	-	Graphitic carbon nitride
PPCP	-	Pharmaceuticals and Personal Care Products
CuO	-	Copper (II) oxide
ZnO	-	Zinc Oxide

LIST OF SYMBOLS

kV	-	Kilo Volt
mA	-	Milli Ampere
Ν	-	Newton
pa	-	Pascal
3	-	Porosity
ρр	-	Polymer Density
ρw	-	Water Density

LIST OF APPENDICES

APPENDIX

TITLE

PAGE

Appendix A Calibration Curve

101

CHAPTER 1

INTRODUCTION

1.1 Background of study

According to the World Health Organization (2019), by 2025, half of the world's population will face significant challenges with access to safe drinking water. Even now, 2 billion people use faeces-contaminated water as drinking water (Shakya *et al.*, 2021). Contaminated water transmits diseases such cholera, hepatitis A, polio, diarrhea and dysentery. According to Environmental Protection Agency (2016), compounds that labelled as contaminants in water are nitrogen, salts, metals, toxins, bleach, microorganisms, uranium, cesium, human drugs, animal drugs and endocrine disrupting compounds (EDCs). Thus, more efforts need to start from now to prepare the world for water crisis in 2025. Contaminants from water need to remove so it can be use as drinking water.

Because of estrogenic effect, toxicity, durability, and bioaccumulation, EDCs, a collection of organic compounds, have garnered worldwide interest. Humans' exposure to EDC through drinking water and tap water leads to the risk of health issues (Wee and Aris, 2017). Bisphenol A (BPA) is a member of EDCs found in each house, as it is one of food and beverages packaging composition. It demands also increasing annually worldwide (Corrales *et al.*, 2015). BPA can be detected in municipal and industrial wastewater due to leaching, domestic waste combustion, or plastic degradation (Santhi *et al.*, 2012). It affects not only human health but also animals. Reproduction problems such as fertility, miscarriage, and premature deliveries, human development problems such as neurodevelopment and birth weight, and metabolic problems such as cardiovascular disease, obesity, and hypertension are the main target of BPA as it is an endocrine disruptor compound (Rochester, 2013). BPA also disturbs animals' reproduction systems and hormone signals (Larsen, 2015).

BPA is widely used in various industries. The concentration of BPA found in the environment is also quite high, but there is less concern to remove it extensively (Rochester, 2013). Surface water in Asia itself exceeded 80 % of Canadian Predicted No Effect Concentrations of BPA, which is 750 ng/L. Meanwhile, Europe exceeded 63.4 %, North America exceeded 56.3 %, and Asia exceeded 52.4 % for effluent water (Corrales *et al.*, 2015). BPA has been removed by several methods, including adsorption, nanofiltration, biological method, and emulsion liquid membrane (A Boukhelkhal *et al.*, 2016; Abdel-Fatah, 2018; Iosob *et al.*, 2016; Kumar *et al.*, 2019). However, these methods still have limitations to remove BPA optimally without producing secondary compounds, green process, less fouling, short time duration of treatment, and good stability.

The Photocatalysis concept was first discovered in 1911 by Dr Alexander Eibner, originally from Germany (Coronado *et al.*, 2013). He found that zinc oxide could bleach Prussian blue, a dark blue pigment, under the presence of illumination (Nawaz *et al.*, 2021). The photocatalysis process is low in cost, but it is also reusable, eco-friendly, and able to degrade completely compared to other treatment processes (Kumar *et al.*, 2014). This process can activate when the photocatalyst is irradiated with visible light or UV light, depending on its bandgap energy. Few factors affect the photocatalysis process; light intensity, amount of catalyst, temperature, structure, size, pH, surface area, and pollutants concentration. This process has been used in organic pollutant degradation, especially in wastewater, hydrogen production, air purification, and disinfectant (Saravanan *et al.*, 2017). It removed contaminants in water, including organic compounds, textile dyes, EDCs, and pharmaceutical drugs (Ismail *et al.*, 2019; Kamaludin *et al.*, 2018; Wang *et al.*, 2018).

A chemically stable, photocorrosion stable, low cost, safe, and can get activated when exposed under visible light irradiation photocatalyst is needed. Copper (I) oxide (Cu₂O) is chosen because of its narrow band gap semiconductor. It has a 2.0 -2.4 eV of band gap value, which can get activated after being exposed under visible light, which is cost effective as solar light is also considered as a visible light source (Koiki and Arotiba, 2020). Besides, it also has a lower recombination rate (Imtiaz *et al.*, 2019). It is chemically stable and can be found abundant naturally. Cu₂O is also

applied in various areas such as sensor application, solar cells, photocatalysis, and water splitting (Koiki and Arotiba, 2020). Cu₂O also has a high affinity towards organic contaminants (Jing *et al.*, 2014). Based on a previous study, Cu₂O is capable of removing up to 95% of 45 mg/L of BPA (Losada-Garcia *et al.*, 2020). A visible light photocatalyst is needed as it can fully utilized 45% of the visible light solar spectrum rather than only 5% of the UV solar spectrum. Visible light photocatalysis advantages on its clean, use low-cost visible light as driving force, and renewable (Chen *et al.*, 2016).

Cooperating photocatalytic technology and membrane technology maintains the advantages of photocatalytic technology to degrade high concentrations of organic pollutants in wastewater and benefits from rapid reaction speed and extensive degradation (Wang, 2018). Other than that, the photocatalytic membrane is the hybrid of the filtration and photocatalysis process, no recovery treatment is needed for the photocatalyst as it is immobilized on the membrane and has a longer membrane lifetime as it has self-cleaning properties (Nascimbén Santos *et al.*, 2020).

DLHF membrane is a hollow fiber membrane that consists of two-layer, the inner layer, and the outer layer. DLHF have been applied in various kinds of field, such as forwarding osmosis, nanofiltration, separation of gas and liquid, and protein separation (Kamaludin *et al.*, 2017). Besides, it also has been applied in pervaporation and membrane distillation (Setiawan *et al.*, 2012). DLHF membrane has good flexibility as two different polymer dope solutions are used in fabrication, and each layer integrated together makes the membrane reduce certain individual materials weakness (Setiawan *et al.*, 2012). DLHF membrane also has a larger area per unit volume and has its mechanical support than other membrane types (Khan *et al.*, 2018). Once it is integrated with photocatalyst become photocatalytic DLHF membrane, outer layer acts as degradation site, and inner layer plays its role as a separation layer. Thus, DLHF membrane is among the most suitable membrane configurations to cooperate with photocatalyst and form a photocatalytic DLHF membrane.

1.2 Problem statement

Several methods have been attempted to remove BPA, which are adsorption (Boukhelkhal *et al.*, 2016), nanofiltration (Abdel-Fatah, 2018), biological agents (Alin *et al.*, 2016), and emulsion liquid membrane (Mondal *et al.*, 2018). Membrane fouling, limited to a certain particle size of pollutants, longer duration, and bad membrane stability are among the limitations of these conventional methods (Boukhelkhal *et al.*, 2016; Abdel-Fatah, 2018; Alin *et al.*, 2016; Mondal *et al.*, 2018). Meanwhile, the current development on the photocatalytic membrane is mainly on UV light. Various studies reported on the photocatalytic membrane, but it emphasizes utilizing UV light as a source of light rather than using visible light, as reported by Argurio *et al.* (2018) and Nyamutswa *et al.* (2020). Other than that, there is no study reported on using Cu₂O as a visible light photocatalyst in the membrane, not to mention in the DLHF membrane. Thus, this becomes a novelty of this study.

In this study, Cu₂O was chosen as a visible light photocatalyst because of its narrow bandgap, which lies between 2.0 - 2.4 eV, as it is a good potential in harvesting solar energy. This compound is abundant, non-toxic, can be synthesised easily, has a good visible light absorber, and is cheap (Koiki and Arotiba, 2020). Moreover, this compound can be found abundant naturally and also chemically stable (Muthukumaran *et al.*, 2019). Cu_2O was incorporated in the DLHF membrane to produce a simultaneous filtration and photocatalytic process. Other than that, the incorporation is to immobilize the Cu₂O thus, no secondary treatment is required to separate photocatalyst from BPA solution. The Cu₂O also has a longer lifetime and can be recycled compared to in suspension form (Teixeira et al., 2016). Immobilization of Cu₂O also could prevent any suspension left in the BPA solution after the treatment process compared to the suspended photocatalyst. Deposition of Cu₂O into the DLHF membrane structure by co-extrusion method is preferred as it can prevent fouling, and the hydrophilicity can be controlled (Zakria et al., 2021). Co-extrusion technique is more favourable compared to other spinning techniques due to it could reduce the risk of the inducing defect, adhesion between layers also improved, able to make structures of multifunction in a single process, and each layer provides a specific feature (Ullah Khan, Othman, A F Ismail, et al., 2018). Photocatalytic membrane exists in a few

configurations, such as hollow fiber membrane, flat sheet membrane, and tubular membrane. A hollow fiber membrane is a preferable configuration as its module processing is very easy, less expensive, and stable compared to the others (Wang, 2018). Hollow fiber membrane has two configurations: single-layer hollow fiber (SLHF) membrane and dual-layer hollow fiber (DLHF) membrane. However, the DLHF membrane has more advantages in comparison to the SLHF membrane when it comes to the amount and specific location of the nanoparticles that can be loaded into the membrane matrix (Kamaludin *et al.*, 2017). The membrane's lifetime could also be enhanced as photocatalyst has self-cleaning properties (Wan *et al.*, 2020). Moreover, this method could prevent photocatalyst leaching and low energy use (Zakria *et al.*, 2021).

As Cu_2O needs the presence of visible light irradiation, the Cu_2O was in the outer layer of the DLHF membrane as it was mixed up with PVDF during dope preparation and co-extruded together with an inner layer of the membrane. There is no study incorporating Cu₂O with PVDF in the DLHF membrane yet for BPA removal application. Outer dope flowrate 3 ml/min, 6 ml/min, and 9 ml/min were chosen based on research by Kamaludin et al. (2018) with some alterations to study the effect of outer dope flowrate on the outer layer thickness, membrane morphology, and membrane permeability. The ratio of Cu₂O to PVDF, 0.25, 0.5, and 0.75 also was chosen based on research by Kamaludin et al. (2019) with some modifications. The different ratio of Cu₂O to PVDF was varied to study the effect of photocatalyst amount on the photocatalytic performance to remove BPA. The optimum outer dope flowrate and optimum ratio of Cu₂O to PVDF resulting the best membrane in terms of morphology, permeability, hydrophilicity, water flux, and photocatalytic performance. On the other hand, the BPA concentration varied to analyse the membrane capability to remove BPA. The photocatalyst amount and amount of pollutants affect the photocatalytic membrane performance (Saravanan et al., 2017). Meanwhile, the outer layer thickness affects membrane morphology and permeability (Marino et al., 2018). Overall, integrating Cu₂O into the DLHF membrane will produce a visible light photocatalytic membrane with good morphology and degradation activity of BPA.

1.3 Research objectives

The aim of the present study is to develop a PVDF/Cu₂O based photocatalytic DLHF membrane for the efficient removal of BPA from contaminated water under visible light irradiation.

The specific objectives for this study are:

- To examine the influence of outer layer dope flowrate on the physical and chemical characteristics of the DLHF membrane fabricated via co-extrusion technique.
- 2. To investigate the effect of Cu₂O loading in the outer layer on physicochemical properties of the DLHF membrane.
- 3. To evaluate the photocatalytic performance of the $Cu_2O/PVDF$ dual layer hollow fiber membrane in removing Bisphenol A at various concentrations and analyse the treated water for leaching copper element from the membrane.

1.4 Scope of study

The present study is conducted to investigate the removal of BPA from water by photocatalytic DLHF membrane. In order to achieve the objectives of this research, the following scopes are outlined:

Scope of objective 1:

 Preparing 0.25 ratio of Cu₂O/PVDF DLHF dope solutions. 3.75 wt.% of copper oxide (Cu₂O) as the photocatalyst, 15 wt.% of polyvinylidene fluoride (PVDF) as the polymer with 81.25 wt.% of dimethylacetamide (DMAc) as a solvent for outer layer dope solution and 15 wt.% for PVDF, 3 wt.% for polyethylene glycol (PEG) which act as pore former and 82 wt.% for DMAc for inner layer dope solution

- 2. Fabricating photocatalytic dual layer hollow fiber membrane which can work under visible light by using dry/wet phase inversion co-extrusion technique with different outer layer dope extrusion flow rate 3 ml/min, 6 ml/min, and 9 ml/min and fixed other spinning condition. The fabricated membrane was subjected to post-treatment, dried at room temperature, and stored until further used.
- Characterizing the 0.25 Cu₂O/PVDF dual layer hollow fiber membrane with different outer dope flowrate physico-chemical characteristics by scanning electron microscopy (SEM) under several magnifications, contact angle, membrane porosity, flux measurement, and Fourier-transform infrared spectroscopy (FTIR).

Scope of objective 2:

- Preparing inner and outer dope solution with varied ratios, polyethylene glycol (PEG) as pore former and dimethylacetamide (DMAc) as solvent. Inner dope suspension solution consists of PVDF/PEG/DMAc with the concentration of 15/3/82 wt.%. While PVDF/Cu₂O/DMAc as outer dope suspension solution with different ratio concentration 15/3.75/81.25 wt.% (0.25), 15/7.5/77.5 wt.% (0.5) and 15/11.25/73.75 wt.% (0.75).
- 2. Fabricating photocatalytic dual-layer hollow fiber membrane which can work under visible light by using dry/wet phase inversion co-extrusion technique with the optimum outer layer dope extrusion from objective 1 and fixed other spinning conditions. The fabricated membrane was subjected to posttreatment, dried at room temperature, and stored until further used.
- 3. Characterizing the Cu₂O/PVDF dual layer hollow fiber membrane with different loading ratio Cu₂O/PVDF 0.25, 0.50, and 0.75 physico-chemical properties using atomic force microscopy (AFM), contact angle, membrane porosity, tensile strength and elongation at break, energy dispersive X-ray (EDX) and Fourier-transform infrared spectroscopy (FTIR).

Scope of objective 3:

- Evaluating the removal of BPA with the concentration of 10 mg/L, 20 mg/L, and 30 mg/L by using Cu₂O/PVDF visible light photocatalytic dual layer hollow fiber membrane using the submerged photocatalytic system which consists of 23 cm length membrane in U-shape membrane module under visible light irradiation and assisted with UV-Vis spectrophotometer.
- Analysing the treated sample to detect the leaching of Cu₂O from the Cu₂O/PVDF dual layer hollow fiber membrane into the water body using ICP-OES analysis.

1.5 Significance of study

DLHF membrane has been widely studied and well published in recent years, but for visible light photocatalytic membrane, removing EDC is quite unexplored. Using semiconductor Cu₂O, which has narrow bandgap, is chemically stable, and is widely applied in various industries, are good characteristics for it to function as an excellent photocatalyst. BPA exists in our drinking water and causes various health problems to humans and animals as it is an endocrine-disrupting compound. Few studies reported on the removal of BPA using photocatalytic membrane but need the presence of ultraviolet light. Photocatalytic Cu₂O/PVDF DLHF membrane eventually saves the electricity cost as it just needs visible light and can be operated in the night with a visible lamp or under sunlight irradiation. BPA can be removed using this photocatalytic Cu₂O/PVDF DLHF membrane without producing side effects or secondary compounds towards the environment as the photocatalytic process will totally degrade contaminants. This membrane can be used in wastewater treatment plants to remove the BPA totally. Thus, preparing the environment with BPA-free will improve the household water quality in Malaysia. Moreover, this study will contribute to society's prolonging healthiness with free from various health problems, especially related to the endocrine system. As a result, there will be significant enhancement in fulfilling the Environmental Protection Act (2012) and 6th and 7th Sustainable

Development Goal (SDG), which provide clean water and sanitation and affordable and clean energy, respectively.

1.6 Thesis organization

This thesis is organized into five chapters that describe original works on the fabrication of visible light photocatalytic DLHF membrane with different loading of Cu₂O nanoparticles and different outer dope flowrate for application towards degradation and separation process of BPA in contaminated water.

Chapter 1 briefly introduces the issues that lead to the current study. Three objectives of the study were identified, followed by the scopes of study to attain these objectives. **Chapter 2** describes the literature review on the occurrence and side effects of BPA exposure and conventional methods to remove BPA. Other than that, a comprehensive review was presented on the photocatalytic mechanism, factors affecting the photocatalysis process, and visible light photocatalyst. Besides, the review also describes membrane technology and dual-layer hollow fiber membrane configuration and development. **Chapter 3** provides the research frameworks. All the materials, experimental setups, working procedures and analytical methods for synthesized nanoparticles, fabrication of membrane, characterization techniques, and membrane performance evaluations were described.

Chapter 4 explains the fabrication of Cu₂O/PVDF DLHF membrane using the dry wet phase inversion co-extrusion technique. Different outer dope flowrate also applied on the membrane. The different ratio between Cu₂O and PVDF was varied in the outer dope solution. The effect of different outer dope flowrate in DLHF membrane was investigated on morphological analysis and permeability. The chemical properties of the membrane also well investigated. The membrane performances on BPA degradation were evaluated using a submerged membrane photoreactor. The degradation result compared with the previous study. The treated water sample was analysed to detect the leaching of copper components from the

membrane into the water sample. **Chapter 5** is to conclude this thesis, the general conclusion of this study, and some recommendations for future works have been listed.

REFERENCE

Abdel-Fatah, M.A., 2018. Nanofiltration systems and applications in wastewater treatment: Review article. *Ain Shams Engineering Journal*, 9(4), pp.3077–3092. Available at: https://doi.org/10.1016/j.asej.2018.08.001.

Abo, R., Kummer, N.A. and Merkel, B.J., 2016. Optimized photodegradation of Bisphenol A in water using ZnO, TiO2 and SnO2 photocatalysts under UV radiation as a decontamination procedure. *Drinking Water Engineering and Science*, 9(2), pp.27–35.

Ahmad, A.L., Ramli, M.R.M. and Esham, M.I.M., 2019. Effect of additives on hydrophobicity of PVDF membrane in two-stage coagulation baths for desalination. *Journal of Physical Science*, 30(3), pp.207–221.

Ahmad, A.L., Sugumaran, J. and Shoparwe, N.F., 2018. Antifouling Properties of PES Membranes by Blending with ZnO Nanoparticles and NMP – Acetone Mixture as Solvent.

Ahmad, S. and Mushir Ahmed, S., 2014. Membrane technology in food processing. *Food Composition and Analysis: Methods and Strategies*, pp.49–94.

Akbari, R., Mohammadizadeh, M.R., Khajeh Aminian, M. and Abbasnejad, M., 2019. Hydrophobic Cu 2 O surfaces prepared by chemical bath deposition method. *Applied Physics A: Materials Science and Processing*, 125(3), pp.1–7. Available at: http://dx.doi.org/10.1007/s00339-019-2470-7.

Alin, I. et al., 2016. Biological Remediation of Soil Polluted With Oil Products : An Overview of Available Technologies. *Studii Si Cercetari Stiintifice Universitatea Bacau Seria Biologie*, 25(2), pp.89–101. Available at: https://www.researchgate.net/publication/309901995_BIOLOGICAL_REMEDIATI ON_OF_SOIL_POLLUTED_WITH_OIL_PRODUCTS_AN_OVERVIEW_OF_AV AILABLE_TECHNOLOGIES.

Amiri, M., Etemadifar, Z., Daneshkazemi, A. and Nateghi, M., 2017. Antimicrobial

Effect of Copper Oxide Nanoparticles on Some Oral Bacteria and Candida Species. *Journal of dental biomaterials*, 4(1), pp.347–352. Available at: http://www.ncbi.nlm.nih.gov/pubmed/28959764%0Ahttp://www.pubmedcentral.nih.gov/articlerender.fcgi?artid=PMC5608049.

An, J. and Zhou, Q., 2012. Degradation of some typical pharmaceuticals and personal care products with copper-plating iron doped Cu2O under visible light irradiation. *Journal of Environmental Sciences*, 24(5), pp.827–833. Available at: http://dx.doi.org/10.1016/S1001-0742(11)60847-4.

Argurio, P., Fontananova, E., Molinari, R. and Drioli, E., 2018. Photocatalytic membranes in photocatalytic membrane reactors. *Processes*, 6(9).

Artioli, Y., 2008. The Chemistry of Adsorption. *Ecological Processes*, pp.60–65.

Ashtiani, S. et al., 2020. Co0·5Ni0·5FeCrO4 spinel nanoparticles decorated with UiO-66-based metal-organic frameworks grafted onto GO and O-SWCNT for gas adsorption and water purification. *Chemosphere*, 255.

Bai, H., Wang, X., Zhou, Y. and Zhang, L., 2012. Preparation and characterization of poly(vinylidene fluoride) composite membranes blended with nano-crystalline cellulose. *Progress in Natural Science: Materials International*, 22(3), pp.250–257. Available at: http://dx.doi.org/10.1016/j.pnsc.2012.04.011.

Bensouici, F. et al., 2015. Effect of Thickness on Photocatalytic Activity of TiO2 Thin Films. In: *Progress in Clean Energy, Volume 1*. Springer International Publishing, Cham, pp. 763–776.

Berg, T. Van Den and Ulbricht, M., 2020. Polymer Nanocomposite Ultrafiltration Membranes : The Influence of Polymeric Additive, Dispersion Quality and Particle Modification on the Integration of Zinc Oxide Nanoparticles into Polyvinylidene Difluoride Membranes.

Bilal, M. et al., 2019. Emerging contaminants of high concern and their enzymeassisted biodegradation – A review. *Environment International*, 124(January), pp.336–353. Boukhelkhal, A. et al., 2016. Adsorptive removal of amoxicillin from wastewater using wheat grains : equilibrium , kinetic , thermodynamic studies and mass transfer. *Desalination and Water Treatment*, 3994(November 2017), pp.1–13. Available at: http://dx.doi.org/10.1080/19443994.2016.1166991.

Busscher, H.J. et al., 1984. The effect of surface roughening of polymers on measured contact angles of liquids. *Colloids and Surfaces*, 9(4), pp.319–331.

Camacho-Espinosa, E. et al., 2018. Stability of sputter deposited cuprous oxide (Cu2O) subjected to ageing conditions for photovoltaic applications. *Journal of Applied Physics*, 123(8). Available at: http://dx.doi.org/10.1063/1.5017538.

Carwile, J.L. et al., 2011. Canned soup consumption and urinary bisphenol A: A randomized crossover trial. *JAMA - Journal of the American Medical Association*, 306(20), pp.2218–2220.

Chakraborty, M., Bhattacharya, C. and Datta, S., 2010. Emulsion liquid membranes: Definitions and classification, theories, module design, applications, new directions and perspectives. In: *Liquid Membranes*. Elsevier B.V., pp. 141–199.

Chan, M. and Ng, S., 2018. Effect of membrane properties on contact angle. *AIP Conference Proceedings*, 2016(September).

Chen, J., Cen, J., Xu, X. and Li, X., 2016. The application of heterogeneous visible light photocatalysts in organic synthesis. *Catalysis Science and Technology*, 6(2), pp.349–362. Available at: http://dx.doi.org/10.1039/C5CY01289A.

Chinnaiyan, P., Thampi, S.G., Kumar, M. and Balachandran, M., 2019. Photocatalytic degradation of metformin and amoxicillin in synthetic hospital wastewater: effect of classical parameters. *International Journal of Environmental Science and Technology*, 16(10), pp.5463–5474. Available at: https://doi.org/10.1007/s13762-018-1935-0.

Chisty, A.H. et al., 2019. Enhanced Epoxy/GO Composites Mechanical and Thermal Properties by Removing Air Bubbles with Shear Mixing and Ultrasonication. *ChemistrySelect*, 4(38), pp.11417–11425.

Chung, H.H., Mireles, M., Kwarta, B.J. and Gaborski, T.R., 2018. Use of porous

membranes in tissue barrier and co-culture models. *Lab on a Chip*, 18(12), pp.1671–1689.

Coronado, J.M., Fresno, F., Hernández-Alonso, M.D. and Portela, R., 2013. Design of advanced photocatalytic materials for energy and environmental applications. *Green Energy and Technology*, 71, pp.1–4.

Corrales, J. et al., 2015. Global assessment of bisphenol a in the environment: Review and analysis of its occurrence and bioaccumulation. *Dose-Response*, 13(3), pp.1–29. Available at: https://doi.org/10.1177/1559325815598308.

Cydzik-kwiatkowska, A. and Zielińska, M., 2017. Toxic / Hazardous Substances and Environmental Engineering Microbial composition of biofilm treating wastewater rich in bisphenol A. , 4529(November), pp.0–8. Available at: https://doi.org/10.1080/10934529.2017.1404326.

Dahman, Y., Javaheri, H., Chen, J. and Sulaiman., B.A.-C., 2017. Nanoparticles. In: *Nanotechnology and Functional Materials for Engineers*. Elsevier, pp. 93–119.

Daramola, M.O., Aransiola, E.F. and Ojumu, T. V., 2012. Potential applications of zeolite membranes in reaction coupling separation processes. *Materials*, 5(11), pp.2101–2136.

David, R. et al., 2019. Review of "The Role of Contact Angle and Pore Width on Pore Condensation and Freezing," by R.O. David et al. 2019. *Atmospheric Chemistry and Physics Discussions*, (3), pp.1–33.

Dong, P. et al., 2017. WO 3 -based photocatalysts: morphology control, activity enhancement and multifunctional applications. *Environmental Science: Nano*, 4(3), pp.539–557. Available at: http://xlink.rsc.org/?DOI=C6EN00478D.

Dulmaa, A., Vrielinck, H., Khelifi, S. and Depla, D., 2019. Sputter deposition of copper oxide films. *Applied Surface Science*, 492(June), pp.711–717.

Dumbrava, A., Badea, C., Prodan, G. and Ciupina, V., 2010. Synthesis and characterization of cadmium sulfide obtained at room temperature. *Chalcogenide Letters*, 7(2), pp.111–118.

Dzinun, H., Othman, M.H.D., Ismail, A F, et al., 2015. Fabrication of Dual Layer Hollow Fibre Membranes for Photocatalytic Degradation of Organic Pollutants. *International Journal of Chemical Engineering and Applications*, 6(4), pp.289–292.

Dzinun, H., Othman, M.H.D., Ismail, A. F., et al., 2015. Morphological study of coextruded dual-layer hollow fiber membranes incorporated with different TiO2 loadings. *Journal of Membrane Science*, 479, pp.123–131. Available at: http://dx.doi.org/10.1016/j.memsci.2014.12.052.

Dzinun, H., Hafiz, M., et al., 2015. Photocatalytic degradation of nonylphenol by immobilized TiO 2 in dual layer hollow fibre membranes. *CHEMICAL ENGINEERING JOURNAL*, 269, pp.255–261. Available at: http://dx.doi.org/10.1016/j.cej.2015.01.114.

Dzinun, H., Othman, M.H.D., Ismail, Ahmad Fauzi, et al., 2015. Photocatalytic degradation of nonylphenol by immobilized TiO2 in dual layer hollow fibre membranes. *Chemical Engineering Journal*, 269, pp.255–261.

Dzinun, H. et al., 2018. Stability study of extruded dual layer hollow fibre membranes in a long operation photocatalysis process. *Polymer Testing*, 68, pp.53–60. Available at: https://doi.org/10.1016/j.polymertesting.2018.03.048.

Ezugbe, E.O. and Rathilal, S., 2020. Membrane technologies in wastewater treatment: A review. *Membranes*, 10(5).

Galiano, F. et al., 2018. Novel photocatalytic PVDF/Nano-TiO2 hollow fibers for Environmental remediation. *Polymers*, 10(10), pp.1–20.

Gao, X., Kang, S., Xiong, R. and Chen, M., 2020. Environment-friendly removal methods for endocrine disrupting chemicals. *Sustainability (Switzerland)*, 12(18), pp.1–16.

Geens, T. et al., 2012. A review of dietary and non-dietary exposure to bisphenol-A. *Food and Chemical Toxicology*, 50(10), pp.3725–3740. Available at: http://dx.doi.org/10.1016/j.fct.2012.07.059.

Gnanaprakasam, A., Sivakumar, V.M. and Thirumarimurugan, M., 2015. Influencing

Parameters in the Photocatalytic Degradation of Organic Effluent via Nanometal Oxide Catalyst: A Review. *Indian Journal of Materials Science*, 2015, pp.1–16.

Gonzales, R.R. et al., 2018. Modification of nanofiber support layer for thin film composite forward osmosis membranes via layer-by-layer polyelectrolyte deposition. *Membranes*, 8(3), pp.1–15.

González-Borrero, P.P. et al., 2010. Optical band-gap determination of nanostructured WO3 film. *Applied Physics Letters*, 96(6), pp.4–6.

Gonzalez-Martinez, A. et al., 2014. Effect of ciprofloxacin antibiotic on the partialnitritation process and bacterial community structure of a submerged biofilter. *Science of the Total Environment*, 476–477, pp.276–287. Available at: http://dx.doi.org/10.1016/j.scitotenv.2014.01.012.

Goulart, L.A., Alves, S.A. and Mascaro, L.H., 2019. Photoelectrochemical degradation of bisphenol A using Cu doped WO 3 electrodes. *Journal of Electroanalytical Chemistry*, 839(February), pp.123–133. Available at: https://doi.org/10.1016/j.jelechem.2019.03.027.

Hamdaoui, O., 2017. Extraction of organic pollutants from water by emulsion liquid membrane Sonochemical degradation of organic pollutants in water View project Extraction of organic pollutants from water by emulsion liquid membrane. *Process Engineering Journal*, 1(May), pp.19–28. Available at: http://process-eng-j.webs.com/.

He, M. et al., 2018. Manipulating membrane surface porosity and pore size by in-situ assembly of Pluronic F127 and tannin. *Journal of Membrane Science*, 556(January), pp.285–292. Available at: https://doi.org/10.1016/j.memsci.2018.03.087.

He, T., 2016. Spongelike Structure. In: Drioli, E. and Giorno, L., (eds.) *Encyclopedia of Membranes*. Springer Berlin Heidelberg, Berlin, Heidelberg, pp. 1814–1815.

Hoepner, L.A. et al., 2013. Urinary concentrations of bisphenol A in an urban minority birth cohort in New York City, prenatal through age 7 years. *Environmental Research*, 122, pp.38–44. Available at: http://dx.doi.org/10.1016/j.envres.2012.12.003.

Houis, S., Engelhardt, E.M., Wurm, F. and Gries, T., 2010. Application of

Polyvinylidene Fluoride (PVDF) as a Biomaterial in Medical Textiles. *Medical and Healthcare Textiles*, pp.342–352.

Hssi, A.A. et al., 2018. Growth and characterization of Cu2O for solar cells applications. *AIP Conference Proceedings*, 2056(December), pp.2–8.

Imtiaz, F., Rashid, J. and Xu, M., 2019. Semiconductor Nanocomposites for Visible Light Photocatalysis of Water Pollutants. In: *Concepts of Semiconductor Photocatalysis*. IntechOpen, p. 13.

Ismail, A.F., Ibrahim, S.M. and Nasri, N.S.N., 2002. Effects of dope extrusion rate on the morphology and gas separation performance of asymmetric polysulfone hollow fiber membranes for O2/N2 separation. *Journal of Science Technology*, 24(July 2003), pp.833–842.

Ismail, N.J., Othman, M.H.D., Kamaludin, R. and Mohamad, I., 2019. Characterization of Bauxite as a Potential Natural Photocatalyst for Photodegradation of Textile Dye. *Arabian Journal for Science and Engineering*, 44(12), pp.10031– 10040. Available at: https://doi.org/10.1007/s13369-019-04029-9.

Jiao, H., Peng, W., Zhao, J. and Xu, C., 2013. Extraction performance of bisphenol A from aqueous solutions by emulsion liquid membrane using response surface methodology. *Desalination*, 313, pp.36–43. Available at: http://dx.doi.org/10.1016/j.desal.2012.12.002.

Jing, H.Y. et al., 2014. Efficient adsorption/photodegradation of organic pollutants from aqueous systems using Cu2O nanocrystals as a novel integrated photocatalytic adsorbent. *Journal of Materials Chemistry A*, 2(35), pp.14563–14570.

José, É. et al., 2017. BRAZILIAN ARCHIVES OF BIOLOGY AND TECHNOLOGY ICP OES Determination of Contaminant Elements Leached from Food Packaging Films. *Arch. Biol. Technol. v*, 60(December), p.17160465.

Junkar, I., 2016. Interaction of cells and platelets with biomaterial surfaces treated with gaseous plasma 1st ed., Elsevier Inc.

Kamaludin, R., Syarifuddin, A., et al., 2019. Incorporation of N-doped TiO 2 into dual

layer hollow fi ber (DLHF) membrane for visible light-driven photocatalytic removal of reactive black 5., 78(June).

Kamaludin, R., Mohamad Puad, A.S., et al., 2019. Incorporation of N-doped TiO2 into dual layer hollow fiber (DLHF) membrane for visible light-driven photocatalytic removal of reactive black 5. *Polymer Testing*, 78(February).

Kamaludin, R. et al., 2017. THE MORPHOLOGICAL PROPERTIES STUDY OF PHOTOCATALYTIC TIO2/PVDF DUAL LAYER HOLLOW FIBER MEMBRANE FOR ENDOCRINE DISRUPTING COMPOUNDS DEGRADATION. *Malaysian Journal of Analytical Science*, 21(2), pp.426–434.

Kamaludin, R. et al., 2018. Visible-Light-Driven Photocatalytic N-Doped TiO2 for Degradation of Bisphenol A (BPA) and Reactive Black 5 (RB5) Dye. *Water, Air, and Soil Pollution*, 229(11).

Kamaludin, R. et al., 2020. Visible-light active photocatalytic dual layer hollow fiber (DLHF) membrane and its potential in mitigating the detrimental effects of bisphenol A in water. *Membranes*, 10(2).

Kang, G. dong and Cao, Y. ming, 2014. Application and modification of poly(vinylidene fluoride) (PVDF) membranes - A review. *Journal of Membrane Science*, 463, pp.145–165.

Keskinkan, O. and Behzat Balci, 2018. Removal of Bisphenol-A from Aqueous Solutions by Pseudomonas aeruginosa in Batch Reactors : Effect of Carbon Source, Temperature and Abstract : , pp.1–9.

Khiavi, N.D. et al., 2019. Visible light driven heterojunction photocatalyst of cuo-cu20 thin films for photocatalytic degradation of organic pollutants. *Nanomaterials*, 9(7).

Koiki, B.A. and Arotiba, O.A., 2020. Cu2O as an emerging semiconductor in photocatalytic and photoelectrocatalytic treatment of water contaminated with organic substances: A review. *RSC Advances*, 10(60), pp.36514–36525.

Kotsilkova, R. et al., 2018. Tensile and Surface Mechanical Properties of Polyethersulphone (PES) and Polyvinylidene Fluoride (PVDF) Membranes. *Journal*

of Theoretical and Applied Mechanics (Bulgaria), 48(3), pp.85–99.

Kumar, A., Thakur, A. and Panesar, P.S., 2019. A review on emulsion liquid membrane (ELM) for the treatment of various industrial effluent streams. *Reviews in Environmental Science and Biotechnology*, 18(1), pp.153–182. Available at: https://doi.org/10.1007/s11157-019-09492-2.

Kumar, S. et al., 2014. Nanotechnology-based water treatment strategies. *Journal of Nanoscience and Nanotechnology*, 14(2), pp.1838–1858.

Kuo, C.Y., Wu, C.H., Wu, J.T. and Chen, Y.C., 2014. Preparation of immobilized Cu2O using microwave irradiation and its catalytic activity for bisphenol A: Comparisons of Cu2O/H2O2 and visible-light/Cu2O/H2O2 systems. *Water Science and Technology*, 70(8), pp.1428–1433.

Kuvarega, A.T. and Mamba, B.B., 2016. Photocatalytic Membranes for Efficient Water Treatment. In: *Semiconductor Photocatalysis - Materials, Mechanisms and Applications*. pp. 116–124.

Lang, D. et al., 2014. Synthesis and visible-light photocatalytic performance of cadmium sulfide and oxide hexagonal nanoplates. *ChemPlusChem*, 79(12), pp.1726–1732.

Larsen, G.D., 2015. Refining HDAC inhibition to restore memory. *Nature Publishing Group*, 44(6), p.2015.

Lazim, Z.M., Hadibarata, T., Puteh, M.H. and Yusop, Z., 2015. Adsorption characteristics of bisphenol a onto low-cost modified phyto-waste material in aqueous solution. *Water, Air, and Soil Pollution*, 226(3).

Li, X. et al., 2019. Application of silver phosphate-based photocatalysts: Barriers and solutions. *Chemical Engineering Journal*, 366, pp.339–357. Available at: https://doi.org/10.1016/j.cej.2019.02.083.

Liu, X. et al., 2016. A P/N type compounded Cu2O/TiO2 photo-catalytic membrane for organic pollutant degradation. *Research on Chemical Intermediates*, 42(7), pp.6289–6300.

Losada-Garcia, N., Rodriguez-Otero, A. and Palomo, J.M., 2020. Fast degradation of bisphenol a in water by nanostructured cunps@calb biohybrid catalysts. *Nanomaterials*, 10(1).

Luo, J.Y. et al., 2015. Anodic deposition-assisted photoelectrocatalytic degradation of bisphenol A at a cadmium sulfide modified electrode based on visible light-driven fuel cells. *Electrochimica Acta*, 186, pp.420–426. Available at: http://dx.doi.org/10.1016/j.electacta.2015.10.193.

Mahmoudi, E. et al., 2019. Enhancing Morphology and Separation Performance of Polyamide 6, 6 Membranes By Minimal Incorporation of Silver Decorated Graphene Oxide Nanoparticles. *Scientific Reports*, (August 2018), pp.1–16. Available at: http://dx.doi.org/10.1038/s41598-018-38060-x.

Marino, T., Russo, F. and Figoli, A., 2018. The formation of polyvinylidene fluoride membranes with tailored properties via vapour/non-solvent induced phase separation. *Membranes*, 8(3), pp.1–17.

Martín-Lara, M.A. et al., 2020. Adsorptive behavior of an activated carbon for bisphenol A removal in single and binary (bisphenol A-heavy metal) solutions. *Water* (*Switzerland*), 12(8).

Martins, P.M. et al., 2019. Photocatalytic microporous membrane against the increasing problem of water emerging pollutants. *Materials*, 12(10).

Mataram, A., Rizal, S. and Pujiono, E., 2018. Physical and mechanical properties of membrane polyvinilidene flouride with the addition of silver nitrate. *MATEC Web of Conferences*, 156, pp.10–13.

Mohammad, A.W. et al., 2007. Modelling the effects of nanofiltration membrane properties on system cost assessment for desalination applications. *Desalination*, 206(1–3), pp.215–225.

Mondal, S., Purkait, M.K. and De, S., 2018. Emulsion Liquid Membrane. In: *Advances in Dye Removal Technologies*. pp. 313–323.

Mu, C. et al., 2017. Removal of bisphenol A over a separation free 3D Ag3PO4-

graphene hydrogel via an adsorption-photocatalysis synergy. *Applied Catalysis B: Environmental*, 212, pp.41–49. Available at: http://dx.doi.org/10.1016/j.apcatb.2017.04.018.

Munusamy, Y. and Fun, T.Y., 2019. Effect of graphene oxide (GO) on water flux of polyvinylidene difluoride (PVDF) membrane in oily wastewater. *AIP Conference Proceedings*, 2124(July).

Muthukumaran, M. et al., 2019. Enhanced photocatalytic activity of Cuprous Oxide nanoparticles for malachite green degradation under the visible light radiation. *Materials Research Express*, 7(1).

Nascimbén Santos, É. et al., 2020. Photocatalytic membrane filtration and its advantages over conventional approaches in the treatment of oily wastewater: A review. *Asia-Pacific Journal of Chemical Engineering*, 15(5), pp.1–29. Available at: https://onlinelibrary.wiley.com/doi/10.1002/apj.2533.

Nawaz, A. et al., 2021. Challenges and implication of full solar spectrum-driven photocatalyst. *Reviews in Chemical Engineering*, 37(4), pp.533–560.

Ndimele, P.E. et al., 2018. Remediation of Crude Oil Spillage, Elsevier Inc.

Nguyen, H.T.V. et al., 2019. Preparation and characterization of a hydrophilic polysulfone membrane using graphene oxide. *Journal of Chemistry*, 2019, pp.15–20.

Niu, F., Huang, M., Cai, T. and Meng, L., 2018. Effect of Membrane Thickness on Properties of FO Membranes with Nanofibrous Substrate. *IOP Conference Series: Earth and Environmental Science*, 170(5).

Nqombolo, A., Mpupa, A., Moutloali, R.M. and Nomngongo, P.N., 2018. Wastewater Treatment Using Membrane Technology. In: *Wastewater and Water Quality*. InTech, pp. 116–124.

Nyamutswa, L.T. et al., 2020. Light conducting photocatalytic membrane for chemical-free fouling control in water treatment. *Journal of Membrane Science*, 604(March), p.118018. Available at: https://doi.org/10.1016/j.memsci.2020.118018.

Oh, S. and Choi, D., 2019. Microbial Community Enhances Biodegradation of

Bisphenol A Through Selection of Sphingomonadaceae. , pp.631–639.

Paredes, L. et al., 2019. Application of immobilized TiO 2 on PVDF dual layer hollow fibre membrane to improve the photocatalytic removal of pharmaceuticals in different water matrices. *Applied Catalysis B: Environmental*, 240(April 2018), pp.9–18.

Peeva, L.G., Marchetti, P. and Livingston, A.G., 2010. Nanofiltration operations in nonaqueous systems. In: *Comprehensive Membrane Science and Engineering: Second Edition*. pp. 36–78.

Raship, N.A. et al., 2017. Effect of annealing temperature on the properties of copper oxide films prepared by dip coating technique. *AIP Conference Proceedings*, 1788(Dc), pp.1–7.

Renuga, D., Jeyasundari, J., Shakthi Athithan, A.S. and Brightson Arul Jacob, Y., 2020. Synthesis and characterization of copper oxide nanoparticles using Brassica oleracea var. italic extract for its antifungal application. *Materials Research Express*, 7(4).

Rochester, J.R., 2013. Bisphenol A and human health: A review of the literature. *Reproductive Toxicology*, 42, pp.132–155. Available at: http://dx.doi.org/10.1016/j.reprotox.2013.08.008.

Rongwong, W. et al., 2018. Membrane-based technologies for post-treatment of anaerobic effluents. *npj Clean Water*, 1(1).

Rovani, S. et al., 2020. Fast, efficient and clean adsorption of bisphenol-A using renewable mesoporous silica nanoparticles from sugarcane waste ash. *RSC Advances*, 10(46), pp.27706–27712.

Sahare, P., 2018. Synthesis and Characterization of CdS Nanoparticles. *International Journal of Engineering Research & Technology (IJERT)*, Volume 6(Issue 1). Available at: https://www.ijert.org/synthesis-and-characterization-of-cds-nanoparticle.

Sai Guru Srinivasan, S. et al., 2019. Effect of oxygen partial pressure on the tuning of copper oxide thin films by reactive sputtering for solar light driven photocatalysis.

Solar Energy, 187(May), pp.368–378. Available at: https://doi.org/10.1016/j.solener.2019.05.057.

Saleh, T.A. and Gupta, V.K., 2016. An Overview of Membrane Science and Technology. In: *Nanomaterial and Polymer Membranes*. pp. 1–23.

Salehi, F., 2013. Food and Bioproducts Processing Current and future applications for nanofiltration technology in the food processing. *Food and Bioproducts Processing*, 92(2), pp.161–177. Available at: http://dx.doi.org/10.1016/j.fbp.2013.09.005.

Salim, N.E. et al., 2018. Performance of PES/LSMM-OGCN photocatalytic membrane for phenol removal: Effect of OGCN loading. *Membranes*, 8(3).

Samadi, M.T. et al., 2016. Removal of bisphenol, using antimony nanoparticle multiwalled carbon nanotubes composite from aqueous solutions. *Oriental Journal of Chemistry*, 32(2), pp.1015–1024.

Santhi, V.A., Sakai, N., Ahmad, E.D. and Mustafa, A.M., 2012. Occurrence of bisphenol A in surface water, drinking water and plasma from Malaysia with exposure assessment from consumption of drinking water. *Science of the Total Environment*, 427–428, pp.332–338. Available at: http://dx.doi.org/10.1016/j.scitotenv.2012.04.041.

Saravanan, R., Gracia, F. and Stephen, A., 2017. Basic Principles, Mechanism, and Challenges of Photocatalysis. In: *Nanocomposites for Visible Light-induced Photocatalysis*. pp. 19–40.

Sathe, P. et al., 2017. Bioinspired nanocoatings for biofouling prevention by photocatalytic redox reactions. *Scientific Reports*, 7(1), pp.1–12.

Setiawan, L. et al., 2012. Novel dual-layer hollow fiber membranes applied for forward osmosis process. *Journal of Membrane Science*, 421–422, pp.238–246.

Shakya, B., Shrestha, S.R. and Silvanus, V., 2021. Bacteriological Examination of Water supply and Drinking Water at Household level in Makalbari Area by the Most Probable Number Method. *Nepal Medical College Journal*, 23(2), pp.146–152. Available at: https://www.nepjol.info/index.php/nmcj/article/view/38525.

Shareef, U. and Waqas, M., 2020. Bisphenol A Removal through Low-Cost Kaolin-Based Ag @ TiO 2 Photocatalytic Hollow Fiber Membrane from the Liquid Media under Visible Light Irradiation. , 2020.

Sharma, R. and Saini, P., 2016. Graphene-Based Composites and Hybrids for Water Purification Applications. *Diamond and Carbon Composites and Nanocomposites*.

Shehab, Z.N., Jamil, N.R. and Aris, A.Z., 2020. Occurrence, environmental implications and risk assessment of Bisphenol A in association with colloidal particles in an urban tropical river in Malaysia. *Scientific Reports*, 10(1), pp.1–16. Available at: https://doi.org/10.1038/s41598-020-77454-8.

Shi, Y. et al., 2019. Photocatalytic membrane in water purification: is it stepping closer to be driven by visible light? *Journal of Membrane Science*, 584(January), pp.364–392.

Siddique, S., Kubwabo, C. and Harris, S.A., 2016. A review of the role of emerging environmental contaminants in the development of breast cancer in women. *Emerging Contaminants*, 2(4), pp.204–219. Available at: http://dx.doi.org/10.1016/j.emcon.2016.12.003.

Singh, R., Yadav, V.S.K. and Purkait, M.K., 2019. Cu2O photocatalyst modified antifouling polysulfone mixed matrix membrane for ultrafiltration of protein and visible light driven photocatalytic pharmaceutical removal. *Separation and Purification Technology*, 212, pp.191–204. Available at: https://doi.org/10.1016/j.seppur.2018.11.029.

Song, Y. and Jiang, L.Y., 2017. Fabrication and characterization of dual-layer hollowfiber ultrafiltration membranes. *Journal of Polymer Research*, 24(8).

Teixeira, S. et al., 2016. Reusability of photocatalytic TiO2 and ZnO nanoparticles immobilized in poly(vinylidene difluoride)-co-trifluoroethylene. *Applied Surface Science*, 384, pp.497–504. Available at: http://dx.doi.org/10.1016/j.apsusc.2016.05.073.

Tolu, H., Iren, E. and Altinbas, M., 2021. Full scale sanitary landfill leachate treatment by MBR: Flat sheet vs. hollow fiber membrane. *Journal of Membrane Science and* *Research*, 7(2), pp.118–124.

Ullah Khan, I., Othman, M.H.D., Ismail, A. F., et al., 2018. Status and improvement of dual-layer hollow fiber membranes via co-extrusion process for gas separation: A review. *Journal of Natural Gas Science and Engineering*, 52(July 2017), pp.215–234.

Ullah Khan, I., Othman, M.H.D., Ismail, A F, et al., 2018. Status and improvement of dual-layer hollow fiber membranes via co-extrusion process for gas separation: A review. *Journal of Natural Gas Science and Engineering*, 52(December 2017), pp.215–234.

Wan Ismail, W.N. and Mokhtar, S.U., 2020. Various Methods for Removal, Treatment, and Detection of Emerging Water Contaminants. In: *Emerging Contaminants [Working Title]*. IntechOpen, pp. 1–28.

Wan, P. et al., 2020. Self-cleaning and antifouling polyvinylidene difluoride hollow fiber membrane enabled by visible light irradiation for water treatment. *Desalination and Water Treatment*, 187, pp.370–377.

Wang, J. et al., 2018. Antibiotic removal from water: A highly efficient silver phosphate-based Z-scheme photocatalytic system under natural solar light. *Science of the Total Environment*, 639(January 2019), pp.1462–1470.

Wang, J. et al., 2020. Influence of surface roughness on contact angle hysteresis and spreading work. *Colloid and Polymer Science*, 298(8), pp.1107–1112.

Wang, L., 2018. Configurations and Membranes of Photocatalytic Membrane Reactors for Water and Wastewater Treatment. *IOP Conference Series: Earth and Environmental Science*. 2018

Wee, S.Y. and Aris, A.Z., 2017. Endocrine disrupting compounds in drinking water supply system and human health risk implication. *Environment International*, 106(May), pp.207–233. Available at: http://dx.doi.org/10.1016/j.envint.2017.05.004.

Wu, T. et al., 2015. Facile and low-cost approach towards a PVDF ultrafiltration membrane with enhanced hydrophilicity and antifouling performance via graphene oxide/water-bath coagulation. *RSC Advances*, 5(11), pp.7880–7889. Available at:

http://dx.doi.org/10.1039/C4RA13476A.

Xiong, L. et al., 2014. Fast and simplified synthesis of cuprous oxide nanoparticles: Annealing studies and photocatalytic activity. *RSC Advances*, 4(107), pp.62115–62122.

Yap, C.K., Peng, S.H.T. and Leow, C.S., 2019. Contamination in Pasir Gudang Area, Peninsular Malaysia: What can we learn from Kim Kim River chemical waste contamination? *Journal of Humanities and Education Development*, 1(2), pp.82–87.

Yue, Y. et al., 2020a. Enhanced dark adsorption and visible-light-driven photocatalytic properties of narrower-band-gap Cu 2 S decorated Cu 2 O nanocomposites for efficient removal of organic pollutants. , 384(September 2019).

Yue, Y. et al., 2020b. Enhanced dark adsorption and visible-light-driven photocatalytic properties of narrower-band-gap Cu2S decorated Cu2O nanocomposites for efficient removal of organic pollutants. *Journal of Hazardous Materials*, 384(May 2019), p.121302. Available at: https://doi.org/10.1016/j.jhazmat.2019.121302.

Yüksel, S., Kabay, N. and Yüksel, M., 2013. Removal of bisphenol A (BPA) from water by various nanofiltration (NF) and reverse osmosis (RO) membranes. *Journal of Hazardous Materials*, 263, pp.307–310. Available at: http://dx.doi.org/10.1016/j.jhazmat.2013.05.020.

Yunus, N.N., Hamzah, F., So'Aib, M.S. and Krishnan, J., 2017. Effect of Catalyst Loading on Photocatalytic Degradation of Phenol by Using N, S Co-doped TiO2. *IOP Conference Series: Materials Science and Engineering*, 206(1).

Zainol Abidin, M.N., Mahmoud Nasef, M. and Matsuura, T., 2022. Fouling Prevention in Polymeric Membranes by Radiation Induced Graft Copolymerization. *Polymers*, 14(1).

Zakria, H.S. et al., 2021. Immobilization techniques of a photocatalyst into and onto a polymer membrane for photocatalytic activity. *RSC Advances*, 11(12), pp.6985–7014.

Zeng, Y. et al., 2019. Degradation of bisphenol a using peroxymonosulfate activated by WO3@MoS2/Ag hollow nanotubes photocatalyst. *Chemosphere*, 227, pp.589–

597. Available at: https://doi.org/10.1016/j.chemosphere.2019.04.067.

Zhang, D. et al., 2020. Construction of Cu2O-reduced graphene oxide composites with enhanced photoelectric and photocatalytic properties. *Optical Materials*, 100(December 2019), p.109612. Available at: https://doi.org/10.1016/j.optmat.2019.109612.

Zhang, L.-Z., 2013. Heat and Mass Transfer in Hollow Fiber Membrane Bundles with Randomly Distributed Fibers. *Conjugate Heat and Mass Transfer in Heat Mass Exchanger Ducts*, pp.233–254.

Zhao, C., Xu, X., Chen, J. and Yang, F., 2013. Effect of graphene oxide concentration on the morphologies and antifouling properties of PVDF ultrafiltration membranes. *Journal of Environmental Chemical Engineering*, 1(3), pp.349–354. Available at: http://dx.doi.org/10.1016/j.jece.2013.05.014.

Zhu, S. and Wang, D., 2017. Photocatalysis: Basic principles, diverse forms of implementations and emerging scientific opportunities. *Advanced Energy Materials*, 7(23), pp.1–24.

Zielińska, M. et al., 2016. Removal of bisphenol A (BPA) from biologically treated wastewater by microfiltration and nanofiltration. *International Journal of Environmental Science and Technology*, 13(9), pp.2239–2248.

LIST OF PUBLICATION

Article paper

 Siti Hawa Mohamed Noor, Mohd Hafiz Dzarfan Othman, Watsa Khongnakorn, Oulavanh Sinsamphanh, Huda Abdullah, Mohd Hafiz Puteh, Tonni Agustiono Kurniawan, Hazirah Syahirah Zakria, Tijjani El-badawy, Ahmad Fauzi Ismail, Mukhlis A. Rahman, Juhana Jaafar. Bisphenol A Removal Using Visible Light Driven Cu2O/PVDF Photocatalytic Dual Layer Hollow Fiber Membrane. Membranes. 2022 Feb 10;12(2):208. Available from: https://www.mdpi.com/2077-0375/12/2/208

Conference proceeding

- Siti Hawa Mohamed Noor, Mohd Hafiz Dzarfan Othman, Juhana Jaafar, Mukhlis A Rahman, A F Ismail (2021). Textile dye Reactive Black 5 (RB5) removal by visible light photocatalyst and its characterization. *IOP Conference Series: Materials Science and Engineering*, 1142(1), p.012017.
- Siti Hawa Mohamed Noor, Mohd Hafiz Dzarfan Othman, Mukhlis A Rahman, Juhana Jaafar, Ahmad Fauzi Ismail. (2019). Cadmium sulfide as High Potential Visible Light Driven Photocatalyst: Investigation on its Characteristics and Performances for Textile Dye Reactive Black 5 (RB5) Removal. International Conference of Sustainable Environmental Technology 2019.

Book chapter

 Nurul Jannah Ismail, Hazirah Syahirah Zakria, Siti Hawa Mohamed Noor, Mohd Hafiz Dzarfan Othman, Mukhlis A Rahman, Juhana Jaafar, Ahmad Fauzi Ismail. (2021). Photocatalytic Nanocomposites for Environmental Remediation. (In review of Royal Society of Chemistry)