

SUBMERGED MEMBRANE PHOTOCATALYTIC REACTOR USING
POLYVINYLDENE FLUORIDE-POLYVINYLPIRROLIDONE-TITANIUM
DIOXIDE FOR OILY WASTEWATER TREATMENT

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UNIVERSITI TEKNOLOGI MALAYSIA

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TITANIUM DIOXIDE FOR OILY WASTEWATER TREATMENT

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I would like to dedicate this thesis to my parents for their endless support and encouragement.

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ABSTRACT

The objective of this study is to develop submerged polyvinylidene fluoride (PVDF) based hollow fiber ultrafiltration (UF) membranes with improved separation properties for oily wastewater treatment in which the membranes can also act as photocatalysis medium. The prepared membranes were characterized with respect to their morphological structure, surface roughness, hydrophilicity and separation performances. In the first stage of this study, PVDF based hollow fiber membranes incorporated with different titanium dioxide (TiO_2) loading (0-4 wt%) were fabricated. The results indicated that when 2 wt.% TiO_2 was incorporated into PVDF membranes, the permeate flux and oil rejection of 70.48 $\text{L/m}^2\cdot\text{h}$ and 99.7 %, respectively, could be obtained when tested using 250 ppm synthesized oily solution under vacuum condition. With increasing feed oil concentration from 250 to 1000 ppm, the permeate flux was declined but oil rejection was improved. In the second stage of study, PVDF membrane consists of 2 wt.% TiO_2 was further investigated by incorporating different molecular weight (M_w) of polyvinylpyrrolidone (PVP) (10, 24, 40, 360 kDa) and the membrane filtration performance and water flux recovery were performed. The obtained results revealed that PVDF- TiO_2 composite membrane prepared from PVP 40kDa was the best performing membrane owing to its promising water flux (72.2 $\text{L/m}^2\cdot\text{h}$) coupled with good rejection of oil (94 %). It is also found that with increasing PVP M_w , membrane tended to exhibit higher PVP and protein rejection, greater mechanical strength, smaller porosity and smoother surface layer. Regarding to the effect of pH, the permeate flux of the PVDF-PVP40k membrane was reported to increase with increasing pH from 4 to 7, however, showed a decrease when pH was further increased to 10. A simple backflushing process could retrieve approximately 60 % of the membrane original flux without affecting the oil separation efficiency. The membranes were further studied by integrating with photocatalysis process. The investigation of various operating parameters such as TiO_2 catalyst loading, membrane module packing density, feed oil concentration and air bubble flow rates (ABFR) on the permeate flux, oil rejection and total organic carbon (TOC) degradation (in the bulk feed solution) were conducted. The average flux was reported to be around 73.04 $\text{L/m}^2\cdot\text{h}$ using PVDF membrane incorporated with 2 wt.% TiO_2 at 250 ppm oil concentration with module packing density of 35.3 % and ABFR of 5 L/min. A remarkable TOC degradation and oil rejection as high as 80 % and > 90 %, respectively, could be reached under these operating conditions. In the final stage, an attempt was made to evaluate the effects of UV irradiation period on the membrane (2 wt.% TiO_2) by exposing the membrane to UV light for up to 250 h. It was observed that permeate flux was increased and some cracks and fractures were formed on the membrane outer surface when it was exposed to 120 h UV light. Furthermore, the mechanical strength and thermal stability of irradiated membrane were also reported to decrease with increasing UV exposure time, suggesting a membrane made of excellent UV resistant polymer is highly required. The overall findings shown in this study provide useful information for the research of separation and degradation of oily wastewater and facilitate the development of hybrid submerged membrane photocatalytic reactor (SMPR).

ABSTRAK

Objektif kajian ini adalah membangunkan membran turasan-ultra (UF) bergentian geronggang terendam berasaskan poliviniliden fluorida (PVDF) dengan sifat pemisahan yang meningkat untuk rawatan air sisa berminyak di mana membran ini juga boleh bertindak sebagai medium fotopemangkinan. Membran yang disediakan dianalisa dari segi struktur morfologi, kekasaran permukaan, kehidrofilikan dan prestasi pemisahan. Pada fasa pertama kajian ini, membran gentian geronggang berasaskan PVDF digabung dengan titanium dioksida (TiO_2) yang mempunyai berat bebanan yang berbeza-beza (0-4% berat) telah dihasilkan. Hasil kajian mendapati bahawa membran PVDF dengan 2% berat TiO_2 menunjukkan prestasi dengan kadar fluks air tulen sebanyak $70.48 \text{ L/m}^2\cdot\text{jam}$ dan penyingkiran minyak sebanyak 99.7 % apabila diuji dengan larutan sintetik berminyak berkepekatan 250 ppm dalam keadaan vakum. Dalam mengkaji kesan kepekatan minyak terhadap prestasi membran, didapati fluks air tulen membran menurun tetapi penyingkiran minyak meningkat dengan peningkatan kepekatan minyak dari 250 hingga 1000 ppm. Pada fasa kedua kajian, membran PVDF berkepekatan 2% berat TiO_2 telah digunakan untuk mengkaji secara lanjut kesan penambahan polivinilpirolidone (PVP) yang mempunyai berat molekul yang berbeza-beza (10, 24, 40, 360 kDa) ke dalam larutan dop membran tersebut terhadap prestasi penapisan dan pemulihan fluks air. Keputusan kajian ini menunjukkan bahawa membran komposit PVDF- TiO_2 dengan penambahan PVP 40kDa dalam larutan dop membran memperolehi prestasi yang paling baik dengan kadar fluks air tulen yang memberangsangkan ($72.2 \text{ L/m}^2\cdot\text{jam}$) dan penyingkiran minyak yang baik (94 %). Kajian ini juga mendapati bahawa membran menunjukkan peningkatan dalam kadar penyingkiran PVP dan protein, dan kekuatan mekanikal, penurunan keliangan membran dan lapisan permukaan yang semakin licin sejajar dengan peningkatan berat molekul PVP. Dalam mengkaji kesan pH terhadap prestasi membran, didapati fluks air tulen membran PVDF-PVP40k meningkat dengan peningkatan pH dari 4 hingga 7, namun menunjukkan penurunan apabila pH terus meningkat kepada 10. Proses pancuran balik yang mudah boleh mengembalikan kira-kira 60% fluks asal membran tanpa menjejaskan kecekapan pemisahan minyak. Seterusnya, membran tersebut dikaji lebih lanjut dengan mengintegrasikan proses fotopemangkinan. Siasatan kesan pelbagai operasi parameter seperti kandungan pemangkin TiO_2 , kepadatan membran modul, kepekatan minyak dalam larutan suapan dan kadar aliran gelembung udara (ABFR) terhadap fluks air tulen, penyingkiran minyak dan degradasi jumlah karbon organik (TOC) (dalam larutan suapan) telah dijalankan. Purata fluks membran PVDF berkepekatan 2% berat TiO_2 adalah dalam lingkungan $73.04 \text{ L/m}^2\cdot\text{jam}$ apabila diuji dengan larutan berminyak yang berkepekatan 250 ppm dengan kepadatan modul sebanyak 35.3 % dan ABFR sebanyak 5 L/min. Pada keadaan operasi ini juga, degradasi TOC setinggi 80 % dan penyingkiran minyak melebihi 90 % mampu diperolehi. Pada fasa akhir kajian ini, kesan masa penyinaran UV ke atas membran (2% berat TiO_2) telah dijalankan dengan mendedahkan sinaran cahaya UV sehingga 250 jam. Selepas 120 jam, kadar fluks resapan didapati meningkat dan beberapa keretakan terbentuk pada permukaan luar membran tersebut. Tambahan pula, kekuatan mekanikal dan kestabilan terma membran yang terdedah kepada sinaran UV didapati merosot seiring dengan peningkatan masa penyinaran UV. Hal ini menunjukkan bahawa membran diperbuat daripada polimer berketahanan cahaya UV yang tinggi sangat diperlukan. Keseluruhan hasil kajian ini dapat memberi maklumat yang berguna dalam penyelidikan pemisahan dan degradasi air sisa berminyak dan memudahkan pembangunan hibrid membran tenggelam bersama reaktor fotopemangkinan (SMPR).

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LIST OF ABBREVIATIONS

ABFR	-	Air bubble flow rate
AFM	-	Atomic force microscopy
AOPs	-	Advanced oxidation processes
BOD	-	Biological oxygen demand
BPA	-	Bisphenol-A
BSA	-	Bovine serum albumin
BTSE	-	Biologically treated sewage effluent
CA	-	Cellulose acetate
CFR	-	Cross-flow rate
COD	-	Chemical oxygen demand
DP-AC	-	Date-pit activated carbon
EA	-	Egg albumin
FESEM	-	Field emission scanning electron microscopy
FTIR	-	Fourier transform infrared spectroscopy
GC-MS	-	Gas chromatography-mass spectrometry
GO	-	Graphene oxide
HA	-	Humic acid
HAP	-	Hydroxyapatite
HCl	-	Hydrochloric acid
HMO	-	Hydrous manganese dioxide
HRT	-	Hydraulic retention time
KCl	-	Potassium chloride
LPGC	-	Liquefied petroleum gas condensate
MEK	-	Methyl ethyl ketone
MF	-	Microfiltration
MW	-	Molecular weight

NaOH	-	Sodium hydroxide
NF	-	Nanofiltration
NIST	-	National Institute of Standards and Technology
NOM	-	Natural organic matter
PAN	-	Polyacrylonitrile
PBIE	-	Poly(2,2'-ethylene-5,5'-bibenzimidazole)
PCD	-	Photocatalytic degradation
PEG	-	Polyethylene glycol
PEI	-	Polyethylenimine
PEO	-	Poly(ethylene oxide)
PES	-	Polyethersulfone
PI	-	Polyimide
PP	-	Polypropylene
PPESK	-	Poly(pthalazine ether sulfone ketone)
PPM	-	Part per million
PSF	-	Polysulfone
PTS	-	Phosphorylated TiO ₂ -SiO ₂
PVA	-	Polyvinyl alcohol
PVC	-	Polyvinyl chloride
PVDF	-	Polyvinylidene fluoride
PVP	-	Polyvinylpyrrolidone
RB5	-	Reactive black 5
RH	-	Hydrocarbon compound
RO	-	Reverse osmosis
SEM	-	Scanning electron microscopy
SiO ₂	-	Silicon dioxide
SMPR	-	Submerged membrane photocatalytic reactor
SPE	-	Solid phase extraction
SPES	-	Sulfonated polyethersulfone
SZP	-	Phosphorylated Zr-doped hybrid silica
SZY	-	Sulfated Y-doped zirconia
TGA	-	Thermal gravimetric analysis
TiO ₂	-	Titanium dioxide
TMP	-	Transmembrane pressure

TOC	-	Total organic carbon
TrOC	-	Trace organic compound
UF	-	Ultrafiltration
USEPA	-	United States Department of Energy
UV	-	Ultraviolet
VB	-	Valence band
XRD	-	X-ray diffraction
ZnO	-	Zinc oxide
ZnS	-	Zinc sulfide

LIST OF SYMBOLS

A	-	Effective membrane area (m^2)
C_0	-	Initial concentration of organic pollutant (ppm)
C	-	Final concentration of the pollutant (ppm)
C_f	-	Feed concentration (ppm)
$C_{f,i}$	-	Concentration of oil in the feed (ppm)
C_p	-	Permeate concentration (ppm)
$C_{p,i}$	-	Concentration of oil in the permeate (ppm)
d_p	-	Pore size of membrane (μm)
E_g	-	Band gap energy (eV)
I	-	Intensity of UV lamp (mW/cm^2)
J	-	Flux ($L/m^2.h$)
J_{w1}	-	Pure water flux ($L/m^2.h$)
J_{w2}	-	Permeate flux ($L/m^2.h$)
K_{ad}	-	Adsorption equilibrium constant (L/mg)
K_{app}	-	Apparent rate constant (min^{-1})
k_r	-	Intrinsic rate constant (ppm)
r	-	Degradation rate (mg/L.min)
R	-	Rejection (%)
R^2	-	Correlation coefficient (dimensionless)
R_a	-	Mean roughness (nm)
R_q	-	Root mean square of Z data (nm)
R_z	-	Mean difference between five highest peaks and five lowest valleys (nm)
TOC_0	-	TOC concentration of the permeate (ppm)
TOC_t	-	TOC concentration of the initial feed (ppm)
w_{dry}	-	Weight of dry membrane (g)

W_{t_f}	-	Final weight of the hollow fiber (g)
W_{t_i}	-	Initial weight of the hollow fiber (g)
$W_{t_{loss}}$	-	Weight loss (%)
w_{wet}	-	Weight of wet membrane (g)
ρ_p	-	Density of the polymer (g/cm ³)
ρ_w	-	Density of water (g/cm ³)
t	-	Time (h)

Greek letters

σ_p	-	Geometric standard deviation (dimensionless)
μ_p	-	Mean pore size (μm)
ε	-	Membrane porosity (%)
λ	-	Wavelength of UV lamp (nm)

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Oil contaminated wastewater has been recognized as one of the most concerned pollution sources. This kind of wastewater comes from variety of sources such as crude oil production, oil refinery, petrochemical industry, metal processing, compressor condensates, car washing, lubricant and cooling agents. According to statistics, every year at least 500 to 1000 million tons of oil is discharged into the water through a variety of ways (USEPA, 2015). The oily wastewater is considered as hazardous industrial wastewater because it contains toxic substances such as phenols, petroleum hydrocarbons, polyaromatic hydrocarbons which are inhibitory to plant and animal growth and possess mutagenic and carcinogenic risk to human being. In this regard, considerable efforts have been focused on the removal of oil from effluent using many kinds of technologies, such as electrocoagulation, adsorption, cyclone, evaporation, membrane technologies as well as other chemical and biological treatment methods.

Nevertheless, most of these conventional methods face energy and environmental barriers when dealing with finely emulsified oily wastewater streams because oil in these stable emulsions is stabilized by surfactants and its droplet size is normally less than 20 μm in diameter (Chakrabarty *et al.*, 2010; Li *et al.*, 2014; Miller *et al.*, 2013). Therefore, advanced separation technologies must be employed in order to enhance the oil and water separation efficiency and maximize the water reuse. Ultrafiltration (UF) membranes with pore sizes between 0.002 and 0.05 μm have been

used to remove stable oil particles from wastewater, owing to its high water oil separation efficiency and permeability under low operating pressure (Bevis, 1992; Chakrabarty *et al.*, 2010; Li *et al.*, 2014; Miller *et al.*, 2013; Ohya *et al.*, 1998; Scott *et al.*, 1994; Um *et al.*, 2001). However, the filtration performance was found to vary with pore diameter of the membranes, and decreasing oil rejection was observed as the pore size was enlarged (Ohya *et al.*, 1998). In addition, typical oil rejection of UF ranges from 80% to less than 99%, hence, the UF membrane surface is tended to be easily fouled at high oil concentration and additional surface modification procedures must be conducted to decrease the fouling tendency (Xu *et al.*, 1999; Ju *et al.*, 2008; Li *et al.*, 2006b).

Submerged membrane photocatalytic reactor (SMPR) is a hybrid system coupling photocatalysis and membrane process in a single unit. Photocatalysis allows the organic pollutants to be decomposed and mineralized to water (H₂O), carbon dioxide (CO₂) and mineral salts. Additionally, the membrane could serve as a barrier for the molecules present in the solution, both initial compounds and products or by-products formed during the decomposition. However, the traditional SMPR is limited by the large amount of residual pollutants and the catalyst retained in the process requires additional treatments to eliminate them (Araújo *et al.*, 2006; Painmanakul *et al.*, 2013; Seo *et al.*, 2007).

Therefore, this study aims to enhance the membrane filtration performance and provide a better understanding on the effects of different SMPR operating parameters such as TiO₂ catalyst loadings, feed concentration, air bubble flow rate (ABFR), fiber packing density in order to achieve desired separation and degradation performance. Although great deals of studies have been reported so far in fundamental and practical manners, material development of UF separation process and detailed discussion in maximizing SMPR operating condition are still inadequate. In addition, the impacts of long term exposure of UV irradiation on polymer membrane is also needed to be investigated to facilitate the development of SMPR for wastewater treatment process.

1.2 Problem Statements

The presence of various recalcitrant, toxic and non-biodegradable constituents in the oily wastewater has led to the searching of new and innovative methods to produce quality-complied and safely dischargeable oily wastewater. UF membrane has been widely applied in various separation processes. However, high fouling tendency remains one of the most challenging issues in membrane separation processes which hinders wider applications of UF in wastewater treatment system.

Polyvinylidene fluoride (PVDF) is one of the popular membrane materials due to its outstanding properties including thermal stability, chemical resistance and excellent mechanical strength. Due to the easy dissolution of PVDF in common organic solvents such as N,N-dimethylacetamide (DMAc), N,N-dimethylformamide (DMF) and N-methyl-2-pyrrolidone (NMP), porous PVDF membranes can be produced via a simple phase inversion method. However, its hydrophobic nature, which often results in severe membrane fouling and decline of permeability, has been a barrier to its application in water treatment (Lang *et al.*, 2007). Many studies have attempted to improve the hydrophilicity of PVDF membranes using various techniques, including physical blending, chemical grafting, and surface modifications (Lu *et al.*, 2006). Among these methods, blending with inorganic materials is the simplest modification method, yet efficient, to enhance a membrane morphological properties as well as its filtration performance (Li *et al.*, 2009).

Titanium dioxide (TiO₂) is the most common anti-fouling material and photocatalyst that used to enhance the membrane flux performance and providing high degradation rate in mineralizing organic pollutants, as well as to enhance the biodegradability of oily wastewater for further downstream treatments (Chong and Jin, 2012). When the TiO₂ surfaces are photon-activated, the reactive hydroxyl radicals will react, degrade or even mineralize the organic pollutants without creating a secondary pollution (Chong *et al.*, 2010). However, when higher amount of TiO₂ is presented in the membrane matrix, it will inhibit the photocatalytic activity and membrane performance, due to the agglomeration of TiO₂ nanoparticles on the

membrane surface. Thus, it is necessary to study the impact of the different amount of TiO₂ nanoparticles in order to optimize the membrane filtration performance.

Polyvinylpyrrolidone (PVP) is a hydrophilic polymer commonly used in membrane fabrication. It possesses excellent pore forming ability, and is highly miscible with polymer material as well as soluble in organic solvent (Jung *et al.*, 2004, Basri *et al.*, 2011, Xu *et al.*, 1999). However, considering the importance of both thermodynamic and kinetic effects during phase inversion process, it is necessary to fully understand the impact of different PVP M_w on UF membrane properties and filtration performance.

Despite the excellent oil separation efficiency of UF membranes, there are several persistent problems that ravage this system from gaining complete reliance to substitute conventional treatment methods, particularly in dealing with those recalcitrant and non-biodegradable contaminants. The potential advantages of SMPR has been utilized to further improve the limitation of UF membrane, however, an in-depth understanding of the theory behind the common reactor operational parameters and their interactions is inadequate and presents a difficult task for maximizing the treatment performance. Other technical challenges are also required to be considered such as possible deterioration of the polymeric membrane material when membrane is directly exposed to UV light for a long period of time during treatment process. This is because the immobilized photocatalysts (in membrane matrix) might absorb UV light energy, causing membrane ageing and further altering its surface morphology and separation performance.

Thus, the ultimate goal is to understand the performance of the UF membranes and also the oil separation efficiency under low pressure submerged condition. It is also essential to understand the correlation between the membrane properties (i.e. morphological structure, surface roughness, and hydrophilicity) and system operating conditions towards the filtration performance and photodegradation efficiency. In addition, present study is to provide greater understanding and highlight underlying problems associated with photocatalytic membrane system which will contribute

important insight towards the development of effective solution for oily wastewater treatment.

1.3 Objectives of the Study

Based on the aforementioned problem statements, the objectives of the current study are outlined as follows:

- (i) To study the effect of titanium dioxide (TiO_2) concentration on the properties and performance of PVDF based hollow fiber membrane.
- (ii) To investigate the effect of molecular weight (M_w) of polyvinylpyrrolidone (PVP) on the properties and performance of PVDF based hollow fiber membrane.
- (iii) To evaluate performances of SMPR in oily wastewater process under various operating conditions.
- (iv) To evaluate the long term effect of UV irradiation on polymer-based membrane in SMPR for oily wastewater treatment.

1.4 Scopes of the Study

In order to achieve the listed objectives, the following scopes of studies have been identified as follows:

- (i) Formulating dope solution of hollow fiber UF membranes using different concentrations of TiO_2 (0-4 wt.%) at fixed PVDF polymer weight of 18 wt.%.

- (ii) Formulating dope solution of hollow fiber UF membranes using different M_w of polyvinylpyrrolidone (PVP) (10, 24, 40 and 360 kDa) at fixed PVDF polymer weight (18 wt.%) and TiO_2 concentration (2 wt.%).
- (iii) Fabricating hollow fiber UF membranes by dry-wet spinning process at fixed spinning conditions.
- (iv) Characterizing the surface morphological structure and its properties, thermal stability, membrane chemical composition, surface hydrophilicity and charge properties using techniques/methods such as scanning electron microscopy (SEM), field emission scanning electron microscopy (FESEM), atomic force microscopy (AFM), X-ray diffraction (XRD), thermal gravimetric analysis (TGA), attenuated total reflection-fourier transform infrared spectroscopy (ATR-FTIR), contact angle, mechanical strength, zeta potential, porosity and viscosity measurement.
- (v) Preparing the oily solution by mixing distilled water with commercial cutting oil.
- (vi) Evaluating performance of the prepared membranes (with various TiO_2 concentrations) in terms of water permeation flux, oil separation efficiency, protein rejection (i.e. Bovine serum albumin (BSA), egg albumin (EA) and trypsin) and also anti-fouling properties by varying oil concentration from 250 to 1000 ppm.
- (vii) Setting up submerged membrane photocatalytic reactor (SMPR) with single 8W UVA lamp immersed in the middle of the tank.
- (viii) Comparing the photocatalytic degradation of direct photolysis, neat PVDF UF membrane and PVDF- TiO_2 UF membrane under UV irradiation.
- (ix) Evaluating the performance of SMPR in terms of water permeation flux, oil separation efficiency and TOC degradation by varying operating parameters such as TiO_2 catalyst loadings (0-4 wt.%), feed concentration

(250, 1,000, 5,000 and 10,000 ppm), air bubble flow rate (ABFR) (0, 1, 3 and 5 L/min) and module packing density (17.6, 35.3 and 52.9 %).

- (x) Investigating the intrinsic properties and performance stability of prepared membrane by exposing the membrane to UV light for up to 250 h.

1.5 Limitation of the Study

In order to accomplish the listed objectives and scopes, some constraints of this study must be clearly defined and identified as follows: 1) The resulting membrane performance and photocatalytic degradation are only applicable for SMPR system with that specific dimension, operating condition, targeted pollutants, membrane configuration, UV wavelength and its intensity as used in this study. 2) The outcomes of the polymer degradation study are only applied to that specifically designed UV exposure chamber as used in this study.

1.6 Rationale and Significance of the Study

This study aims to optimize the membrane performance and operation of SMPR to treat oily wastewater. It is acknowledged that the membrane properties (i.e. surface roughness, hydrophilicity and pore structure) are fundamentally responsible for membrane performance. In order to improve the membrane properties, blending with hydrophilic additives could offer a possible route to produce highly effective membranes with high water permeation flux and excellent separation performance. Thus, efforts have been made to investigate the impacts of direct blending of TiO₂ and PVP on UF membrane properties and performance.

Additionally, heterogeneous photocatalysis has great potential to be used in degrading those hazardous and non-biodegradable compounds from oily wastewater, mainly due to generation of hydroxyl radicals that can act as strong oxidizing agent to react with the targeted pollutants and eventually mineralize them to innocuous carbon dioxide and water. Therefore, efforts have also been dedicated to identify the impact of different operating conditions on the separation performance and degradation efficiency. To date, no relevant study has been conducted to investigate the performance of SMPR in treating oily wastewater with combination of various operating parameters.

Realizing the important roles of heterogeneous photocatalyst integrated with membrane process as hybrid process, particularly for wastewater treatment, efforts are made to investigate how the long-term exposure of UV irradiation on polymer membrane would affect membrane structural morphologies and further its separation performance. It is then expected that outcomes from this study would be beneficial to further understand the suitability and sustainability of polymeric membrane that is widely considered as the host for photocatalysts, providing useful information for the research of simultaneous separation and degradation of oily wastewater and facilitate the development of hybrid SMPR.

1.7 Organization of the Thesis

The thesis consists of 8 chapters. Chapter 1 gives a general and brief introduction of the research undertaken. The problem statements of this study are defined and the objectives as well as the scopes of study are further elaborated to provide the research direction of this study. The significance of the study is also provided.

Chapter 2 provides a general information of the current oil demand and its severe impact to the receiving water bodies system. A comparison of the maximum oil

discharged standard among different countries is made to give a clear understanding of the urgent need to deal with the increasing amount of oily wastewater. A general overview of conventional treatment process for oily wastewater treatment is provided by comparing each different method with its own pros and cons. After that, detailed discussion on UF membranes and its modification methods followed by the UF limitation for treating the oily wastewater are elaborated. A brief information on SMPR and a summary on recent SMPR studies is provided. After that, a comparison of catalyst suspended and immobilized reactor is made followed by the selection criteria of photocatalyst and the photocatalysis mechanism. Then, review on the impacts of various operating parameters on the performance of SMPR is provided followed by some challenges facing in the development of current SMPR are highlighted in the end of the chapter. Chapter 3 will focus on the experimental methods and characterizations that were used in this study. The analytical methods of membrane properties and SMPR performance are also discussed in detail.

Chapter 4 discusses the characterization and performances of PVDF-based UF membrane incorporated with different concentration of TiO_2 . The fabricated hollow fiber membranes were investigated in terms of their morphological structure, surface properties and filtration performance. The structural morphologies and surface properties of the membranes were characterized by FESEM/SEM, AFM and contact angle analyzer. The filtration performance by means of water permeation flux and oil rejection are presented and discussed in detail. In addition, detailed discussion on the anti-fouling performance of the membranes by varying oil concentration is also addressed.

Chapter 5 discusses on the fabrication, characterization and anti-fouling performance of PVDF hollow fiber membranes incorporated with various M_w of PVP. The properties of the membranes are characterized by using FESEM/SEM, AFM, contact angle and mechanical strength analysis. Then, the hollow fiber membranes are discussed in great detail in terms of water permeation flux, oil rejection and anti-fouling performance. Additionally, separation performances of protein (BSA, EA and trypsin) and PVP are also included. Discussion on the impact of different pH and cleaning efficiency are also presented in this chapter. On the other hand, the impacts

of various operating parameters, i.e. TiO₂ catalyst loadings, feed concentration, ABFR and module packing density, on the SMPR filtration and degradation performance are elaborated in detail in Chapter 6.

Chapter 7 presents the long-term effect of UV irradiation on the optimized membrane with respect to its structural morphologies and separation performance. The impacts of UV irradiation on membrane structural morphologies were characterized using FESEM and EDX. In addition, the UV impacts on chemical composition of the membrane was investigated using FTIR. The filtration performances of both pristine and irradiated membranes were also compared in the end of chapter. Finally, the general conclusions of this study and recommendations for future research works in this field are drawn in Chapter 8.

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