STUDIES OF ANTIFOULING PROPERTIES ON ULTRAFILTRATION MEMBRANE FOR OILY WASTEWATER

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STUDIES OF ANTIFOULING PROPERTIES ON ULTRAFILTRATION MEMBRANE FOR OILY WASTEWATER

by

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LIST OF SYMBOL

Symbol		Unit
A	Membrane effective area	m^2
C_f	Oil emulsion concentration in feed	mg/L
C_p	Oil emulsion concentration in permeate	mg/L
J_o	Oil flux	$L/m^2.h$
J_{w1}	Initial pure water flux	$L/m^2.h$
J_{w2}	Pure water flux after washing	$L/m^2.h$
Q	Amount of water collected	L
R	Oil rejection rate	%
R_{ir}	Irreversible resistance	-
R_r	Reversible resistance	-
R_t	Total resistance	-
y	Y-axis value of normal distribution curve	-
Δt	Permeation time	hr
$\bar{x}, \mu$	Mean pore size	μm
σ	Standard deviation	-

LIST OF ABBREVIATIONS

$CaCO_3$	Calcium carbonate
FRR	Flux recovery ratio
FTIR	Fourier Transform Infrared
GO	Graphene oxide
NMP	N-methyl pyrrolidinone
PAN	Polyacrylonitrile
rpm	Rotation per minute
SEM	Scanning electron microscopy
TiO_2	Titanium oxide
UF	Ultrafiltration
ZnO_2	Zinc oxide

KAJIAN SIFAT ANTIFOULING PADA ULTRAFILTRATION MEMBRAN UNTUK AIR SISA BERMINYAK

ABSTRAK

Organik-inorganik komposit membran telah disintesis melalui teknik "phase inversion", dengan zarah bersaiz nano seperti zinc oksida (ZnO), kalsium karbonat (CaCO$_3$) atau titanium oksida (TiO$_2$) seragam tersebar dalam polyacrylonitrile (PAN) cecair. Kesan nanopartikel dan jenis nanopartikel telah dikaji melalui proses ultrafiltration untuk tempoh 360 minit: 30 minit mampatan, 100 minit pertama untuk fluks air tulen, 100 minit kedua untuk fluks air sisa berminyak, 30 minit pembersihan membran dan 100 minit terakhir untuk fluks air tulen. Data fluks direkodkan dan dianalisis dari segi nisbah fluks pemulihan, kadar penolakan minyak dan penilaian rintangan fouling. Pencirian membran seperti sudut kenalan, SEM, FTIR dan Porolux telah dijalankan untuk mengkaji hidrofilik, permukaan morfologi, permukaan kimia dan taburan saiz liang membran masing-masing. Berbanding dengan membran PAN tulen, membran diubahsuai menunjukkan penyerapan air yang lebih tinggi dan sifat-sifat antifouling yang lebih baik. Selain itu, titanium oksida (TiO$_2$) telah dipilih sebagai bahan tambahan terbaik dengan fluks air tulen yang tertinggi pada 225.51 L/m^2.h, FRR sebanyak 78.22% dan kadar penolakan minyak sebanyak 98.96%. Kajian telah mendapati bahawa peningkatan hidrofilik dan pengurangan saiz liang mengakibatkan kenaikan ketara fluks air tulen dan kadar penolakan minyak yang hampir sempurna.

STUDIES OF ANTIFOULING PROPERTIES ON ULTRAFILTRATION MEMBRANE FOR OILY WASTEWATER

ABSTRACT

Organic-inorganic composite membranes were synthesized through phase inversion technique with nano-sized particles such as zinc oxide (ZnO), calcium carbonate ($CaCO_3$) or titanium oxide (TiO_2) uniformly dispersed in the polyacrylonitrile (PAN) solution. The effect of nanoparticles and type of nanoparticles were investigated through ultrafiltration process for duration of 360 minutes: 30 minutes of compression, first 100 minutes for pure water flux, second 100 minutes for oily wastewater flux, 30 minutes of membrane cleaning and last 100 minutes for pure water flux. Flux data was recorded and analyzed in terms of flux recovery ratio (FRR), oil rejection rate and fouling resistance evaluation. Characterization of membranes such as contact angle, SEM, FTIR and Porolux were carried out to examine hydrophilicity, surface morphology, surface chemistry and pore size distribution of membranes respectively. Compared with pure PAN membrane, modified membrane showed higher water permeation and better antifouling properties. Besides, titanium oxide (TiO_2) was selected as best additive with the highest pure water flux of 225.51 $L/m^2.h$, a maximum FRR of 78.22% and oil rejection rate of 98.96%. It was found that increasing hydrophilicity and reduction in mean pore size resulted in significant increment of pure water flux and nearly perfect oil rejection rate.

CHAPTER ONE

INTRODUCTION

1.1 Research background

Produced water, is by far the largest source of waste produced by the oil and gas industry. During oil and gas production, it is brought to the surface from underground formations. About seven to ten barrels of produced water are generated for each barrel of oil. Hence, its management presents significant challenges and costs to operators. The water typically contains oil, grease and other hydrocarbons, as well as high levels of salts, metals and suspended solid elements. Thus, the water is considered highly toxic (ABB, 2010).

With industrial development, there is an increase in the amount of oil used, at the same time, the amount of oily wastewater is skyrocketed. The oily wastewater can affect groundwater, seawater, or drinking water as a result of the percolation of contaminations into water resources beneath the soil (Jamaly et al., 2015). Hence, aquatic resources as well as human health are endangered. Besides, the oily wastewater pollution is manifested in the other aspects such as: (i) atmospheric pollution; (ii) affecting crop production; (iii) destructing the natural landscape probably due to coalescence of the oil burner safety issues that arise (Poulopoulos et al., 2005). Therefore, treatment is necessary so that it can be reused to save water resources as well as protect the environment (Otitoju et al., 2016).

For removal of oil from effluent, conventional technologies such as, gravity separation and skimming, air flotation, coalescence, de-emulsification, centrifugation,

flocculation, coagulation and metal mesh have been employed. Recently, membrane separation has become an attractive alternative due to its intrinsic advantages, such as, requires no chemical additives or thermal input to break the emulsion, relatively lower energy requirements, quite compact and fully automated treatment facilities, as well as high oil separation efficiency (Otitoju et al., 2016).

Although there is considerable interest in membrane separation technology, membrane fouling is still a severe problem limiting its potential. Membrane fouling phenomenon is due to deposition of solute or particles onto the membrane surface or into membrane pores such that membrane performance is deteriorated. It presents major barrier for the wide spread use of this technology. Membrane fouling leads to severe flux decline and affect the quality of the water produced. Severe membrane fouling may require intense chemical cleaning or membrane replacement which causes the increment of operating costs of a treatment plant (Franken, 2009).

To properly address this treat, much effort is being devoted to improve the performance of the existing membranes in terms of anti-fouling properties. The membranes are usually made of some polymeric highly used materials such as: polyvinylidene fluoride (PVDF), polysulfone (PSf), polyethersulfone (PES), cellulose acetate (CA), polyacrylonitrile (PAN), polyvinyl chloride (PVC) and polyether imide (PEI) (Rabiee et al., 2015). The main shortcoming of these polymers is its hydrophobic nature which conversely makes it more susceptible to fouling. Various methodologies have been developed to increase its hydrophilic character such as the addition of hydrophilic additives, thereby becoming a solution to membrane fouling (Nair et al., 2013).

1.2 Problem statement

Membrane separation technology has proven to be less energy consumption, relatively lower operating cost and higher separation efficiency. However, fouling remains a major dilemma to extensive use of membrane separation technology. Fouling can significantly reduce membrane performance, increase operating costs and shorten membrane life. It occurs due to the pore blocking and surface adsorption which leads to the unwanted flux reduction problem. The hydrophobic nature of polymeric membranes facilitates the occurrence of fouling during oily wastewater separation process.

Oil is classified as major contaminants in wastewater. However, due to the improvement in regulations and requirements, great interest have been displayed by many researchers to investigate viable and practical solutions at which hydrophobic polymeric membranes can be modified for effective separation performance hence mitigating the negative impacts of discharging waste streams containing oil. During oil wastewater separations, the oily effluents are strongly accumulated on the surfaces of membranes resulting in severe fouling phenomenon, thereby leading to severe decline in membrane flux and thus results in reduction in separation capacity and increase in the cost of the whole process due to deposit of a new layer on the membrane surface or into the membrane pores.

In order to overcome the fouling phenomenon, the modification of membrane surfaces to increase membrane hydrophilicity becomes the main concern to inhibit the unfavorable hydrophobic interaction in recent times.

In this research, phase inversion technique is adopted for incorporation of hydrophilic additives such as titanium oxide, zinc oxide and calcium carbonate in PAN mixed matric membrane. The effect of additives and type of additives on membrane

performance are evaluated through permeability and antifouling studies. Further, surface hydrophilicity, membrane morphologies, surface chemistry and pore size distribution are investigated in detail.

1.3   Research objectives

This research aims,

 i. To characterize membrane in terms of surface morphology, surface chemistry, hydrophilicity and pore size distribution.

 ii. To compare performance between membranes incorporated with additives and those without additives.

 iii. To study the effect of different additives such as titanium oxide, zinc oxide and calcium carbonate on the membrane performance.

 iv. To evaluate membrane fouling for oily wastewater treatment in terms of permeation and flux recovery ratio (FRR), oil rejection rate and resistance mechanism.

1.4   Organization of thesis

The following are the contents for each chapter in this study:

Chapter 1 introduces membrane separation processes for treatment of oily wastewater, research objectives, problem statement and organization of thesis.

Chapter 2 discusses the literature review of this study which includes the oily wastewater, conventional treatment methods for oily wastewater, membrane separation technology, nature of flux decline, membrane material, membrane modification and nanoparticles achievement.

Chapter 3 covers the materials and details of methodology. It discusses on the description of equipment and materials used, ultrafiltration experiment procedures, description of membrane characterization and equations for water flux, FRR, oil rejection rate and fouling resistance evaluation.

Chapter 4 refers to the experimental results and discussions of the data obtained. The discussions are concentrated on two major parts: characterization of membranes and study of antifouling properties.

Chapter 5 concludes all the findings obtained in this study. Recommendations are also included as well.

CHAPTER TWO

LITERATURE REVIEW

2.1 Oily wastewater

The most common pollutants in a wide range of industries and domestic sewages are oil and grease. Millions of cubic meters of oil containing wastewaters are produced daily during metal working, primary metal operations, petroleum refineries, petrochemical, textile, waste collection and transportation and also by the food industry and restaurants etc. (Karhu, 2015).

The oily wastewater often contains micro meter-sized oil droplets dispersed in water, forming a stable oil-in water emulsion even without any stabilizer. As oil is the major pollutants in aquatic environment, its presence poses a serious threat to the environment and human health (Otitoju et al., 2016). Hence, oily wastewater treatment is urgently needed in today's field of environmental engineering problems.

2.2 Conventional treatment methods for oily wastewater

Conventional treatment methods were developed in the 1800's. However, these methods have several disadvantages such as: large land requirements, labour intensive, chemical intensive and reduced effluent quality (Otitoju et al., 2016). Hence, most studies focused on the use of current membrane technology (Kiss et al., 2013).

2.2.1 Flotation

Water is poured in the form of fine bubbles where the tiny air bubbles in the adhesion of oil particles suspended in the water, because the floating density of oil is less than that of water, the formation of a scum layer is separated from the water. Flotation has 2 different categories: dissolved air flotation (DAF) and jet impeller flotation. Dissolved air flotation stay there a long time, device manufacturing and repairing problems, along with high energy consumption are its drawbacks. Conversely, the jet flotation method can not only save energy, but also have small air bubbles, fixtures, easy installation, operation and safety features, which have good prospects. For improvement of flotation, flocculants are added as breaking and sparkling role, on the other hand there are bridging adsorption, and colloidal particles can gather together while bubbles float (Li et al., 2013). However, chemical addition is a daily if not hourly process and is a significant operating cost.

2.2.2 Biological treatment

Biological treatment uses of microbial metabolism to digest colloidal organic pollutants in the wastewater into harmless substances that are stable (Li et al., 2013). However, the system is extremely temperature and pH sensitive. Besides, large space is required due to the amount of residence time required for the bugs to digest the pollutants.

2.2.3 Coagulation

Coagulation can remove emulsified oil, dissolved oil and some difficult biodegradable organic polymer is characterized by the complex. Nevertheless, due to the complexity of oily wastewater composition, the object selected for treatment

coagulants cannot make predictions in theory; there must be a lot of experiments to screen (Li et al., 2013).

2.3 Membrane separation technology

As mentioned previously, conventional treatment methods were widely known for effectiveness along with several disadvantages. These methods were also limited for oily wastewaters containing stable O/W emulsions formed by very small oil droplets. Thus, there is an enormous demand for the development of advanced, cost-effective as well as environmentally friendly treatment methods for oily wastewaters to meet tighter environmental regulations (Karhu, 2015).

Recently, membrane separation technology has emerged as an advanced separation technology. This technology uses of a special porous material manufactured for the interception role in the physical removal of a certain way of the trapped particle size of contaminants. The difference in pressure driven membrane separation process is generally divided into microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) of four kinds. Besides, membrane separation process is also characterized by particle size membrane molecular weight cut-off (MWCO) reasonable certainty, and the process generally has no phase change, a direct realization of oil–water separator; without pharmaceutical dosing, so less pollution; reprocessing costs low, the separation process has less energy consumption; separation of water has low oil content, so optimal quality of treated water (Li et al., 2013); (Ngang et al., 2012).

Separation is accomplished via mechanical sieving in MF and UF operations while in NF and RO, separation is achieved through capillary flow or solution diffusion. MF and UF, low-pressure driven operations have been widely used for treatment of oily wastewater. The key difference for both processes is in the

membranes' surface pore size used which defines their application. Although MF offers high flux, it possesses a high risk of oil breakthrough during oily wastewater separation. Conversely, UF which has a tighter pore size, is able to guarantee production of higher quality permeates. UF has proven to be efficient due to its suitable pore sizes, sieving mechanism and the capability of removing emulsified oil droplets without any de-emulsification processes. However, the tendency of fouling limits the potential of both MF and UF processes (Otitoju et al., 2016). Fouling usually causes serious flux reduction that affects effluent quality and membrane life span. Frequent membrane cleaning or replacement was needed to overcome fouling issue resulting in greater operating cost (Ngang et al., 2017).

2.4   Nature of flux decline

The two important factors result in reduction of membrane flux below that of the corresponding pure solvent flow over time under constant transmembrane pressure (TMP) are concentration polarization and membrane fouling (Shi et al., 2014). Large-scale membrane systems operate in a cyclic mode which clean-in-place operation alternates with the normal run. Flux decline within a cycle is due to concentration polarization while fouling results in flux reduction from cycle to cycle (Koltuniewicz and Noworyta, 1995). In general, concentration polarization is a reversible phenomenon and can be controlled in a membrane module by velocity adjustment, pulsation, ultrasound, or an electric field. On the other hand, membrane fouling is more complicated as it is a group of physical, chemical, and biological effects leading to irreversible loss of membrane permeability (Sablani et al., 2001).

2.4.1 Concentration polarization

Concentration polarization is a natural consequence of the semi-permeability and selectivity of a membrane. It results in an accumulation of rejected solutes or particles in a mass transfer boundary layer adjacent to the membrane surface. In UF, this is a particular issue during filtration of low molecular-weight solutes or macromolecules. When these solutes are carried by the permeation flow, solvent molecules pass the membrane but the larger solutes are rejected and retained at the membrane surface. These rejected solutes are comparatively slow to diffuse back to the bulk solution resulting in a concentration gradient just above the membrane surface. Sometimes, the concentration of those molecules near the membrane wall can reach 20–50 times that in the bulk solution. Such a high concentration of material accumulating at the membrane impedes the solvent flow through the membrane, and creates an osmotic back pressure that reduces the effective TMP of the system (Shi et al., 2014).

2.4.2 Membrane fouling

Membrane fouling, taking place when the solute in the feed solution leaves the liquid phase to form a deposit on either the membrane surface, known as external fouling or inside its porous structure, known as internal fouling (Shi et al., 2014). To be more specific, there are five different ways where the solute can accumulate on or inside membrane surface. (Figure 2.1) In complete pore blocking, the pore is blocked by a large particle so no water can pass through. In standard blocking, small particles coat inside of the pores, narrowing the channels and hence lowering the flux. In intermediate blocking, a layer of particles or droplets is accumulating on the surface, narrowing the pore entrances since particles partially blocked the entrances (Dickhout et al., 2017).

On the other hand, cake filtration is the formation of a layer of particles on the surface of the membrane. Although this layer is permeable, it narrows the pore size, and only allowing small particles to pass. In oil layer blocking, oil droplets are coalescing on the membrane surface to form a continuous oil layer on the surface. This differs from cake layer formation since fouling layer no longer consists of separate particles. Besides, oil can form a liquid lining inside the pores, thus reducing the effective pore radius. This difference will affect permeation and cleanability of the membrane (Dickhout et al., 2017).
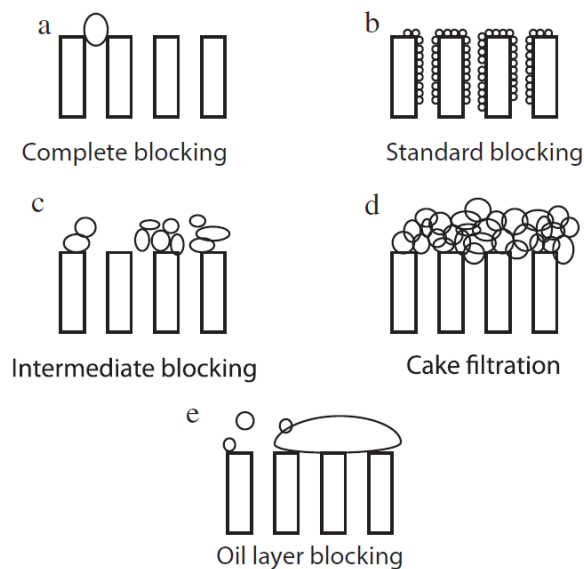
Figure 2.1: Different fouling mechanism taking place on or inside membrane surface (Dickhout et al., 2017).

As comparison to the reversible nature of concentration polarisation, fouling may cause irreversible loss of membrane permeability. Based on membranes' relative resistance to cleaning, there are reversible and irreversible fouling. Reversible fouling is the type that can be removed easily by cleaning while irreversible fouling still remains after the cleaning (Shi et al., 2014). Membrane cleaning methods such as air scouring, backwashing, and chemical cleaning by oxidants and acids (Li et al., 2017).

2.5   Membrane material

Membranes can be made of polymeric or ceramic. Ceramic, which also known as inorganic membranes, made from materials such as silica, metal oxides or carbon that have superior thermal and chemical stability. They are widely used for MF, UF and NF applications. Most ceramic membranes are relatively inert to treatment with steam, solvents, strong acids as compared with polymeric material and thus have a very long expected lifespan. These membranes do suffer from fouling, but the flux can be restored by harsh cleaning methods. Besides, ceramic membranes do not suffer from swelling in the presence of solvents unlike polymeric membranes. However, their high production costs and their weight become the major drawbacks. In addition, modifying ceramic membranes for molecular affinity separation is much more difficult than for polymeric membranes (Dickhout et al., 2017).

Polymeric membranes, which also known as organic membranes dominate the existing membrane market. They are the backbone of UF and MF. Various polymeric membranes such as such as cellulose derivatives, polyvinylidenedifluoride (PVDF), polysulfone (PS), polyether sulfone (PES), polyacrylonitrile (PAN), polytetrafluoroethylene (PTFE) and polyvinylchloride (PVC) have been widely adopted in treatment of oily wastewater (Otitoju et al., 2016). These membranes can be either made from pure polymers or from polymers blended with compounds to improve the membrane performance and thus tailored to the specific needs of the process they are used in for selective separation. The polymers blending with compounds is kind of a modification to the membrane surface to improve the functionality of the membrane (Dickhout et al., 2017).

2.5.1 Considerations of membrane material

In the recent year, polyvinylidene fluoride (PVDF) is one of the most extensively applied membrane materials and has been paid much attention by researchers and manufacturers. So far, there have been numerous articles reporting on the application fields of PVDF membranes, including microfiltration (MF), ultrafiltration (UF), membrane bioreactor (MBR), membrane distillation, gas separation and stripping, pollutants removal from water (e.g., boron, volatile organic compounds and ammonia), recovery of biofuels, separator for lithium ion battery, ion exchange process and others. In addition, many commercial membranes in the market are also fabricated with PVDF materials (Kang and Cao, 2014).

PVDF is a semi-crystalline polymer contains of 59.4 wt% fluorine and 3 wt% hydrogen. It is produced by polymerization in emulsion or suspension using free radical initiators, forming a repeating unit of $-CH_2-CF_2-$ (Liu et al., 2011). PVDF have been widely adopted because of high mechanical strength, good chemical resistance and thermal stability as well as excellent aging resistance. Moreover, PVDF shows good processability to prepare flat sheet, hollow fiber or tubular membranes and ease of dissolving in some common solvents such as N,N-dimethylacetamide (DMAc), dimethylformamide (DMF) and N-methyl-2-pyrrolidone (NMP) and acetone. Hence, porous PVDF membranes can be produced via phase inversion method by a simple immersion precipitation process (Kang and Cao, 2014).

However, PVDF is relatively more hydrophobic which may not be as high as polypropylene (PP) and polytetrafluoroethylene (PTFE). The hydrophobicity of materials is often associated with their surface tensions. By referring to Table 2.1, low critical surface tension indicates high hydrophobicity (Nohmi and Yamada, 1983). The

hydrophobicity is the common disadvantage of polymeric membranes, which results in low water permeation rates.

Table 2.1: Critical surface tensions of major polymeric membrane materials (Nohmi and Yamada, 1983)

Polymer	Critical surface tension (dynes/cm)
Polyacrylonitrite (PAN)	44
Polysulfone (PS)	41
Polyphenylene oxide (PPO)	41
Polyethylene (PE)	31
Polypropylene (PP)	29
Polyvinylidene fluoride (PVDF)	25-28.5
Polyfluoroethylene (PFE)	22
Polytetrafluoroethylene (PTFE)	18.5
Fluorinated ethylene propylene (FEP)	16
Ethylentetrafluoroethylene (ETFE)	17

Various studies have concluded that intrinsic hydrophobicity of membrane materials is one of the primary reasons for fouling. Industrial effluent to be treated contains organic foulants that are usually attracted to hydrophobic membrane surfaces and pores, and adsorbed onto them (Jhaveri and Murthy, 2016). While there have been many studies on using PVDF membrane and its modification for different industrial application, substituting with other membrane materials that are less hydrophobic is one of the consideration among researchers to increase hydrophilicity of membrane surface. Membrane surface plays a determining role in permeation and separation properties since interactions between membrane and foulants take place mainly at the surface (Garcia-Ivars et al., 2014). To best of our knowledge, there has been less study of using polyacrylonitrile (PAN) membrane. Thus, PAN has great prospect as its

hydrophobicity is less than PVDF (Nohmi and Yamada, 1983) and it is still under developed.

2.6 Membrane modification

Polymeric membranes have a highly hydrophobic surface, on which the organic pollutants are more easily to be adsorbed during the filtration process, resulting in serious membrane fouling. Intensive efforts have been made to deal with this fouling issue. Recently, membrane modification has been given increased attention since it can effectively slow down the membrane fouling. Numerous studies reported that membrane modification could change the hydrophobic nature of membranes into hydrophilic ones by two categories, surface modification and blending modification (Li et al., 2016).

2.6.1 Surface modification

Surface modification can be further classified into division: surface coating and surface grafting. Surface coating is carried out by depositing a thin functional hydrophilic layer onto the membrane surface. However, poor stability was presented on the modified membranes by surface coating method. The coating layer could be detached from the membrane surface after filtration process because of weak physical interactions between the membrane surface and the coating layer. Alternatively, by using chemical grafting method, the hydrophilic substances could be strongly combined with the membrane surface by covalent bonds. In this method, membranes are irradiated in the presence of monomer or any other additive in vapour or solution state. The irradiation source could either be UV irradiation, X-ray irradiation, low temperature plasma or electron beam (Garcia-Ivars et al., 2014). In contrast to surface coating, covalent attachment of graft chains on the membrane surface avoids their

delamination and offers a long-term chemical stability of grafted chains. Nonetheless, the modification process through chemical grafting was not controllable. The hydrophilic substances were readily accumulating in the membrane pores, resulting in blockage of membrane pores (Li et al., 2016); (Liu et al., 2011).

2.6.2   Blending modification

As for blending modification, hydrophilic polymers, amphiphilic polymers and nanoparticle materials can be blended together. Blending modification is the simplest and most economic approach. The hydrophilic membrane with other desirable properties can be obtained synchronously during the membrane preparation process without any pre-treatment or post-treatment procedures, which is usually adopted in surface coating or surface grafting techniques. More importantly, most of the surface grafting techniques focused on the flat sheet membranes, which limited its application in the modification of hollow fibre membranes; while blending some additives with polymeric materials and subsequent spinning hollow fibre would integrate both phase inversion preparation and hydrophilic modification together in a single-step process (Liu et al., 2011).

Further, during surface modification, a functional layer was either coated or grafted on the top and/or bottom surface of the membrane, excluding the pores inside membrane; on the other hand, through blending, both the surfaces and inside-pores of the membrane were able to modified simultaneously through the synergy effect between polymeric materials and compatible additives (Liu et al., 2011). However, the blending modification process exhibited the issue of heterogeneous mixture of hydrophilic substance and membrane material (Li et al., 2016).

2.7   Nanoparticles' achievement

Membrane modification which has been successful to fabricate membranes with better antifouling properties is by incorporating nanoparticles (NPs), which also known as hydrophilic additives together. Some of the nanoparticles reported include metal-based NPs: TiO_2, SiO_2, Al_2O_3, Si, Ag, ZnO, ZrO_2, $Mg(OH)_2$, $CaCO_3$, and $TiSiO_4$; carbon-based NPs: graphene oxide (GO) and carbon nanotubes (CNTs); and NP composites: $GO–SiO_2$, $GO–TiO_2$, $SiO_2–TiO_2$, and $Ag–SiO_2$. Metal-based NPs are relatively preferable because of their easy and well-developed synthesis method, cost effectiveness and improvement in hydrophilicity of membrane (Jhaveri and Murthy).

2.7.1   Zinc Oxide (ZnO)

In comparison with TiO_2, SiO_2 and Al_2O_3, less attention has been paid to utilize ZnO for membrane modification. Its nanoscale with a large surface area can adsorb hydroxyl groups, thus exhibiting strong hydrophilic properties. Moreover, the price of ZnO is lower, accounting for only ¼ of the price of TiO_2 or Al_2O_3 (Li et al., 2016). In the future, ZnO may be an excellent hydrophilic additive over TiO_2 for improved antifouling performance and moderate price.

According to previous studies, ZnO-modified PES membranes along with PEG 400 as the pore former additive showed that addition of ZnO in PES structure led to improved hydrophilicity, porosity and enhancement in water flux, flux recovery and antifouling ability of the membranes. The optimum concentration of ZnO is 0.4 wt% as the water flux showed improvement of 254% relative to that of the PES membrane (Shen et al., 2012). Further, the pure water fluxes of PES/ZnO membranes were reported to increase by about 110–220% when compared with PES membrane. Addition of ZnO was favourable to the enhancement of compaction resistance and

antifouling property by reducing their reversible fouling resistance of membranes (Zhao et al., 2015).

Besides, modification of PVDF/ZnO with different dosages ranging from 6.7% to 26.7% of PVDF weight showed all the modified membranes achieved almost 100% water flux recovery after physical cleaning, while the raw membrane only reached 78% recovery. This promotion related to the increase of membrane hydrophilicity due to implantation of nano-ZnO into membrane inner surface. In addition, optimum dosage was 6.7% ZnO as water permeability of the modified membrane almost doubled (Liang et al., 2012). For PSf/ZnO membranes, reduction of hydrophobicity of Psf membranes at an optimized quantity of 2 wt% was shown along with enhancement of water permeability (2.14×10^{-11} to $25.45 \times 10^{-11} \, m^3 \, s^{-1} \, Pa^{-1}$) (Leo et al., 2012).

Modification of PVC ultrafiltration membrane with ZnO together with PEG 6kDa as a pore former additive showed water flux increased up to 3 wt %, which was the optimized amount of ZnO. Flux recovery ratio also reached from 69% to above 90% at 3 wt% ZnO addition as indication of improvement in membrane' antifouling properties (Rabiee et al., 2015).

2.7.2 Titanium oxide (TiO$_2$)

Recently, titanium dioxide (TiO$_2$) has been the major focus of numerous researches, because of its photocatalytic effects which decompose organic chemicals and kill bacteria, relatively cheap, chemical stability, optical property and non-toxicity. Dispersion of TiO$_2$ nanoparticle in PVDF matrix improved the hydrophilicity of PVDF membranes as well as can mitigates the biofouling problem of PVDF membrane (Otitoju et al., 2016). As for PVC ultrafiltration membrane modified with TiO$_2$, its addition up to 2 wt% has resulted in higher water flux, more recovery ratio and better

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antifouling properties. It was due to increment of membrane hydrophilicity and more fingerlike pores across the membranes (Behboudia et al., 2016).

2.7.3   Calcium Carbonate (CaCO$_3$)

Calcium carbonate nanoparticles (CCNP) are the largest commercially produced nanoparticles because of their extensive use in rubber, plastics, paints, paper, medicine and food products. In addition, they are easier for synthesis and comparatively cheaper than other nanoparticles. To the best of our knowledge, there are very few reports on CCNPs in the membrane technology. The membrane preparation steps are easier since these naturally hydrophilic particles can be directly brought to use in membrane technology to improve hydrophilicity. Surface atoms of CCNPs tend to get hydroxylated to form Ca–OH groups in water resulting in enhancement of hydrophilicity. Moreover, the calcium carbonate addition in some polymer composites has shown enhancement in mechanical properties especially tensile strength and possess antibacterial properties (Nair et al., 2013).

According to Nair et al. (2013), incorporation of CCNPs showed increase in hydrophilicity and reduction of fouling phenomenon. In addition, 10 wt% of CCNP addition resulted in largest increase in water flux and a maximum FRR of 71%.

Besides, Melbiah et al. (2017) reported that incorporation of amphibilic copolymer, PF127 and inorganic CCNPs into PAN membrane matrix resulted in significant enhancement of membrane surface hydrophilicity which led to the significant increase of pure water flux as well as antifouling property. Best results were obtained for membrane consists of the highest quantity of nanoparticles (0.75 wt%). The membrane showed as high as 90% flux recovery after a simple water wash which evidenced for its excellent antifouling property.

CHAPTER 3

MATERIALS AND METHODS

3.1   Materials

Polyacrylonitrile (PAN) as ultrafiltration membrane forming material was purchased from Sigma Aldrich. N-methyl pyrrolidinone (NMP), used as the solvent was supplied by Merck, Germany.

In addition, nanoparticles such as calcium carbonate and titanium oxide were procured from R & M Chemicals, United Kingdom while zinc oxide were purchased from Fisher Scientific, United Kingdom. These nanoparticles have blended together during membrane preparation for development of membranes' antifouling properties.

3.2   Experimental activities

The overall experimental activities carried out in this study are presented in Figure 3.1.
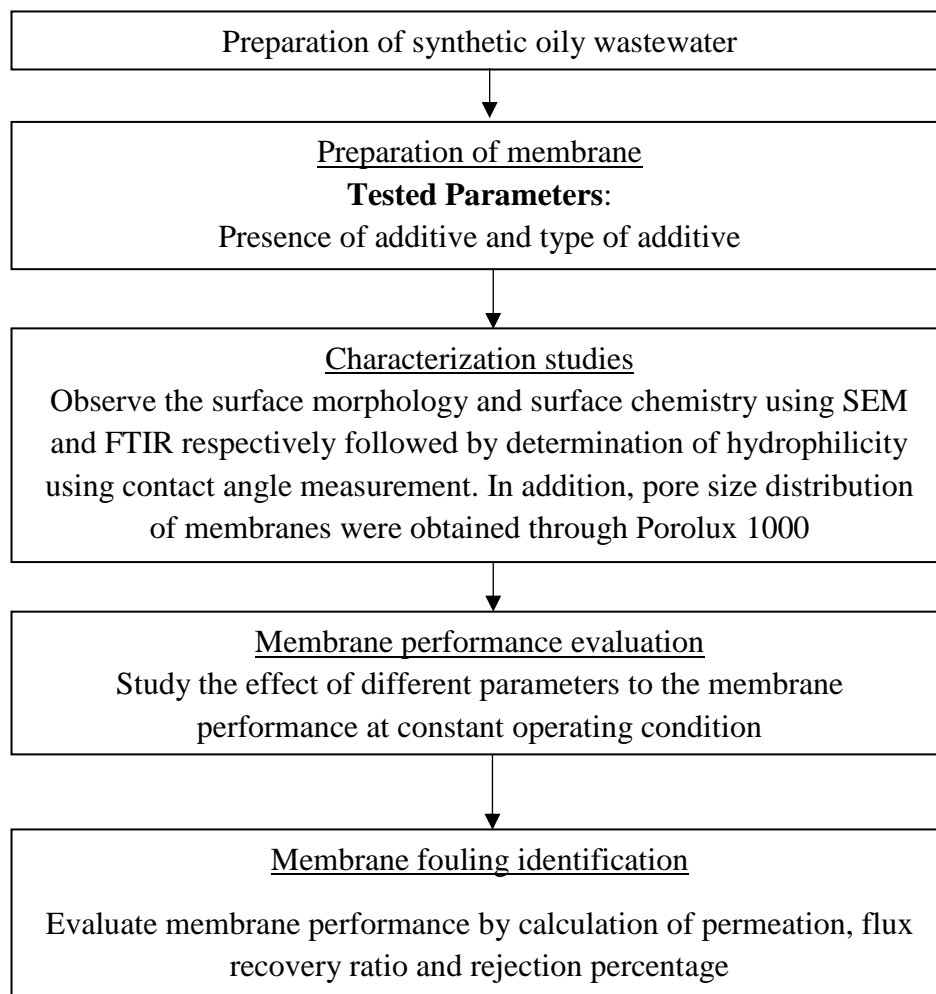
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┌─────────────────────────────────────────────────────┐
│        Preparation of synthetic oily wastewater       │
└─────────────────────────────────────────────────────┘
                          │
                          ▼
┌─────────────────────────────────────────────────────┐
│                Preparation of membrane                │
│                  **Tested Parameters**:               │
│         Presence of additive and type of additive     │
└─────────────────────────────────────────────────────┘
                          │
                          ▼
┌─────────────────────────────────────────────────────┐
│                Characterization studies               │
│   Observe the surface morphology and surface chemistry│
│   using SEM and FTIR respectively followed by         │
│   determination of hydrophilicity using contact angle │
│   measurement. In addition, pore size distribution    │
│   of membranes were obtained through Porolux 1000     │
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┌─────────────────────────────────────────────────────┐
│            Membrane performance evaluation            │
│       Study the effect of different parameters to the │
│       membrane performance at constant operating      │
│                     condition                         │
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┌─────────────────────────────────────────────────────┐
│              Membrane fouling identification          │
│   Evaluate membrane performance by calculation of     │
│   permeation, flux recovery ratio and rejection       │
│                    percentage                         │
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Figure 3.1: Process flow diagrams of experimental activities

3.3   Equipment and instrumentations

3.3.1   Preparation of oil emulsion

Oil emulsion was prepared freshly prior to the filtration experiment. Firstly, 1500 ppm of oil emulsion was prepared by dispersing 4.0 g of diesel into 3 L distilled water. 0.5 g of surfactant (Tween 80) was then added into the solutions to stabilize the oil emulsion. The prepared oil emulsion was then dispersed using a homogenizer (Ultra Turrax T50) as shown in Figure 3.2 at speed of 6000 rpm for 40 min at room temperature. (Ngang et al., 2017).

Figure 3.2: Homogenizer to blend distilled water with diesel and Tween 80

3.3.2 Membrane Preparation

The UF flat sheet asymmetric membranes were prepared via the immersion precipitation phase inversion method. At first, the predetermined amount of TiO_2 was dispersed in NMP solvent under sonication for 30 min to obtain homogenous suspensions. After that, PAN powders was added to the mixtures, and stirred at 330 rpm and 50 °C to dissolve. The solution was continuously stirred overnight at same speed and same temperature to ensure a complete dissolution of the polymers. The final solution was subjected to further degas for at least 2 hours to remove any possible air bubbles.

The solution was then cast on the glass plate that wrapped with membrane support (polyester cloth) using a finely polished glass rod to a membrane thickness of 0.20 mm at a speed of 9 cm/s. Subsequently, it was immediately immersed into the water bath of deionized water at room temperature to allow the phase inversion to

occur for 24 h to remove the residual solvent. The membrane was dried completely and kept in the sealed plastic prior to use.

A similar procedure was followed for the preparation of other membranes with compositions as summarized in Table 3.1. The additive either was TiO_2, $CaCO_3$ or ZnO.

Table 3.1: Membranes composition

Type of membrane	Composition (wt %)		
	PAN	Additive	NMP
Pure PAN	12	0	88
Modified	12	2	86

3.4 Membrane Characterizations

3.4.1 Contact angle

The membrane hydrophilicity was measured by surface contact angle. Generally, the smaller the contact angle is, the more hydrophilic the membrane is as schematically displayed in Figure 3.3. The contact angles of membranes were measured at room temperature by the sessile drop method using contact angle instrument (Rame-Hart Model 300 Advanced Goniometer, USA). A deionized water droplet was dropped on the top surface of the membrane, and then the contact angle between the water and the membrane was measured until no change was observed. At least, five different locations on membrane surface were chosen randomly to yield average contact angle value.

Figure 3.3: Concept of contact angle measurement of hydrophobic surface (left) and hydrophilic surface (right) (Jhaveri and Murthy, 2016)

3.4.2 Morphology of membranes

The surface morphology of pure and modified membranes were observed using scanning electron microscopy (SEM, HITACHI S-3000, Japan). Samples were cut into small pieces and coated with a thin film of gold to make them conductive.

3.4.3 Surface chemistry of membranes

The surface chemistry of membranes were recorded using Fourier-transform infrared spectrometer (FTIR) in the range of $600 - 4000$ cm^{-1}. The Thermo Scientific Nicolet iS-10 FTIR spectrometer is able to identify and verify materials present in membrane through generation of peak numbers.

3.4.4 Pore size distribution of membranes

The pore size of membranes can be determined by using Porolux 1000, Germany. Before measurement of pore size, the membrane need to be cut into diameter of 10 mm and then immersed in porefil liquid for 30 minutes to ensure the pores are filled with porefil. Measurement is then taken after turning on nitrogen gas and compressed air supplies. A report is generated for each membrane. Data required for determination of pore size is diameter (x) and corrected differential filter flow (f).