INVESTIGATION OF DIETHYLENETRIAMINE/TANNIC ACID (DETA/TA) COATED LAYER ONTO THE MEMBRANE SURFACE FOR SEPARATION OF OIL-IN-WATER EMULSIONS

MOHAMAD FARHAN BIN MOHAMAD TAUPIK

UNIVERSITI SAINS MALAYSIA

2017

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by

MOHAMAD FARHAN BIN MOHAMAD TAUPIK

Thesis submitted in partial fulfilment of the requirement for the degree of

Bachelor of Chemical Engineering

May 2017

ACKNOWLEDGEMENT

First, I express my profound thanks and praise to ALLAH, the Almighty, the most Gracious, the most Merciful and peace be upon His Prophet Mohammad (Sallahu alihi wa sallam). I am grateful to the God for the good health and well-being that were necessary to complete this report.

I am highly grateful to my supervisor Dr. Suzylawati Ismail for her guidance, encouragement, expert suggestions and generous support throughout this work. I would also like to extend my heartfelt thanks to UiTM lecturer, Madam Faraziehan Senusi for her support throughout the work. She is my second of the most important person after my supervisor during this study. I really was honoured to have the opportunity to work under the supervision of both of them.

I would also like to express my appreciation to all of the School of Chemical Engineering Universiti Sains Malaysia's academic and administrative staffs, laboratory technicians, postgraduate students and fellow course mates, for their continuous support and help rendered throughout my studies. I would also to special thanks to final year project coordinator, Associate Professor Dr. Mohd Azmier Ahmad for his assistance and dedicated involvement in every step throughout the process. Without him, this report would have never been accomplished. Thank you very much for your support and understanding throughout the year.

Most importantly, I am thankful to my beloved parents, Mohamad Taupik bin Majid and Sarina binti Ismail for supporting me during the period of my study. Special thanks goes to Nurul Afiqah binti Mohd Ariffin for her continual support, constant prayers and encouragement. Thank you very much to all of you.

Mohamad Farhan bin Mohamad Taupik

May 2017

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SYMBOL	DESCRIPTION	UNIT
A	Membrane effective area	m^2
J	Pure water flux	$L\ m^{-2}\ h^{-1}$
P_F	Feed pressure	bar
P_R	Retentate pressure	bar
P_P	Permeate pressure	bar
R_q	Root-mean-squared roughness	nm
R_a	Roughness average	nm
ρ_w	Density of water	$g\ cm^{-3}$
Δt	Changes in time period of permeate collected	h
ΔM	Changes in mass of permeate collected	g

LIST OF ABBREVIATIONS

AFM	Atomic force microscopy
DETA	Diethylenetriamine
FRR	Flux recovery ratio
O/W	Oil-in-water
rpm	Rotation per minute
RFR	Relative flux reduction
SEM	Scanning Electron Microscope
TA	Tannic acid
TMP	Transmembrane Pressure
W/O	Water-in-oil
WCA	Water contact angle

PENYIASATAN LAPISAN SALUTAN DIETILENATRIAMINA/ASID TANIK (DETA/TA) DI ATAS PERMUKAAN MEMBRAN UNTUK PENYINKIRAN EMULSI MINYAK-DALAM-AIR

ABSTRAK

Dalam beberapa tahun ini pencemaran air telah menjadi masalah global disebabkan kenaikan penghasilan sisa minyak. Fenomena ini menjadi semakin teruk akibat aktiviti-aktiviti industri disebabkan kenaikan jumlah minyak yang digunakan dalam industri ini. Pelbagai usaha telah dijalankan bagi mengurangkan tahap kepekatan minyak daripada efluen industri. Sistem penurasan membran telah dicadangkan sebagai satu teknik alternatif untuk mengatasi kelemahan rawatan air sisa minyak secara konvensional. Walaubagaimanapun, masih terdapat pelbagai cabaran dalam usaha untuk mengkomersilkan penurasan membran seperti kestabilan permukaan membran, kecekapan penyinkiran minyak dan keserasian antara larutan salutan dan bahan membran. Untuk mengatasi masalah ini, satu salutan lapisan hidrofilik Dietilenatriamina/Asid Tanik (DETA/TA) telah disalut pada permukaan luar Polivinilidena Fluorida (PVDF) membrane melalui kaedah penyalutan poliphenolik. Parameter untuk menyediakan permukaan hidrofilik (nisbah jisim DETA/TA, kepekatan Asid Tanik (TA), pH larutan salutan and masa penyalutan) telah dikaji dan dioptimumkan. Daripada pemerhatian didapati bahawa nisbah DETA/TA 2:1 menghasilkan permukaan polimer dengan sudut sentuhan air (WCA) yang lebih rendah. Peningkatan kandungan TA dalam larutan salutan sebanyak 5 g/L telah membawa kepada penurunan WCA daripada 39.5° kepada 19.4°. Sifat hidrofilik lapisan salutan dianalisa dari segi kekasaran permukaan, struktur fizikal dan sudut sentuhan air. Didapati bahawa WCA bagi permukaan PVDF membran bersalut yang disediakan secara salutan poliphenolik adalah kurang berbanding permukaan asal. Suatu sistem penurasan aliran silang telah direka untuk menilai prestasi antitempel daripada membran modifikasi dalam terma penyingkiran minyak. Parameter operasi iaitu Tekanan Transmembran (TMP) terhadap penyingkiran minyak telah dikaji. Prestasi antitempel telah disiasat bagi membran asal dan membran modifikasi. Bagaimanapun kedua-dua membran tidak menunjukkan ciri antitempel yang bagus. Sebagai tambahan, kelihatan bahawa PVDF membran modifikasi mempunyai penyinkiran minyak yang lebih banyak daripada membran asal pada kepekatan dan keadaan operasi yang sama.

INVESTIGATION OF DIETHYLENETRIAMINE/TANNIC ACID (DETA/TA) COATED LAYER ONTO THE MEMBRANE SURFACE FOR SEPARATION OF OIL-IN-WATER EMULSIONS.

ABSTRACT

In recent years the water pollution became a global concern due to the increasing of the waste oil generation. This phenomenon was exacerbated by the expansion of industrial activities due to the increasing in the amount of oil used in this industries. Many efforts were conducted to reduce the level concentration of oil from the industrial effluents. Membrane filtration system was proposed as an alternative technique to overcome disadvantages of the conventional oily wastewater treatment. However, there are still many challenges in order to commercialize the membrane filtration such as membrane surface stability, oil rejection efficiency and compatibility between coating solution and membrane material. In order to solve this problem, a hydrophilic coated layer of Diethylenetriamine/Tannic Acid (DETA/TA) had been coated on the outer surface of the Polyvinylidene Fluoride (PVDF) membrane via polyphenolic coating method. Parameters to prepare hydrophilic surface (mass ratio of DETA/TA, concentration of Tannic Acid (TA), pH of coating solution and coating time) had been studied and optimized. It was observed that the DETA/TA ratio of 2:1 did produce polymeric surface with lower water contact angle (WCA). The increasing of TA content in the coating solution up to 5 g/L led to the decreased of WCA from 39.5° to 19.4°. The hydrophilicity of the coated layers were analysed in terms of surface roughness, physical structure and water contact angle. It was found that the WCA of the coated PVDF membranes surfaces prepared via polyphenolic coating were less than the native surface.

A cross flow filtration system was designed to evaluate the antifouling performance of modified membranes in term of oil removal. The operating parameter which is Transmembrane Pressure (TMP) on the oil removal were studied. The antifouling performance was investigated for native and modified membrane. However both membranes not showed with good antifouling property. In addition, it was observed that the modified PVDF membrane had higher oil rejection than unmodified ones at the same feed concentrations and operating conditions.

CHAPTER ONE

INTRODUCTION

1.1 Research background

Malaysia pursued rapid industrialization such as oil and gas industry, petrochemical and transportation, which leads in increasing in the amount of oil used in this industries. It is reported that the estimated volume of wastewater generated by municipal and industrial sectors is about 2.97 billion cubic meters per year (Azman et al.,2013). This issue is supported by International Environmental Technology Centre (IETC, 2013) which is reported the global consumption of lubricating oil is estimated about 45 million tons per year by 2015 and Asia accounts for almost 30% of global waste oil generation. Due to the improper dumping and collection practices, about 50% of lubricating oil ended up as waste lubricating oil, thus resulted about 20 million tons of waste oil. The estimated amount of waste oil available for recycling and destruction is only about 16 million tons per year. With the increasing of the oil consumption in the industries, it will generate a high level concentration of oil in the effluents. Therefore, oily wastewater treatment is urgently needed in today’s field of environmental engineering problems.

The three broad categories in which industrial oily wastewater exist are free-floating oil, unstable oil/water emulsion and stable oil/water emulsion. Free-floating oil or unstable oil/water emulsions can be readily removed by using conventional separation processes. However, for removing stable oil/water emulsion, those conventional processes are not found to be so effective. It is because the emulsion droplets, which are of micron and submicron size, require a very long residence time to rise onto the top for enabling gravity separation and even addition of chemicals cannot break the emulsions effectively. To solve this problems new sophisticated methods such as thermal demulsification, biological method have been developed. The normal separation of oily wastewater treatment which is flotation are not recommended for treatment, especially where the oil droplets are finely dispersed and the concentration is very low (Otitoju et al., 2016).

Fabrics and metal meshes usually have large pore size (about tens of micrometers) which could be only used for the separation of oil water mixtures but not effective for oil/water emulsions (the droplets is about 0.1-10 µm), ultrathin films have extremely high flux but usually suffer from low mechanical strength (Shi et al., 2016). Under such circumstances, the use of membranes offers a potential solution to the problem of micron sized oily wastewater. The porous membrane matrix can promote coalescence of micron and submicron oil droplets into larger ones that can be easily separated by gravity (Hlavacek, 1995).

Membrane separation is widely used to remove various undesired substances from waters, especially for oily wastewater. To date, there is only a few studies reported on the surface modification of membranes using polyphenolic coating as an alternative to polydopamine coating (Wang et al., 2014). Therefore, in this study, an attempt is made to use Diethylenediamine/Tannic Acid (DETA/TA) coated layer onto the PVDF membrane surface for separation of oil-in-water emulsions.

1.2 Problem statement

The emulsion oil is difficult to separate in wastewater treatment. The efficiency of the separation of oil-in-water emulsion need to be increased. Thus, the modification of commercial PVDF membrane incorporated with DETA/TA coated layer is needed in order to improve the performance of the separation. However, the parameters of the surface modification by coating DETA/TA on commercial PVDF membrane are still unclear such as the mass ratio, concentration, pH and the coating time.

Although mussel-inspired coating with dopamine onto membrane surface is a preferred for oil-in-water emulsion separation, its widespread use is restricted due to its relatively high cost which led to the researches on alternative non-conventional and low-cost of coating. Therefore, there is a need for the development of low cost coated membrane from cheap available materials.

1.3 Research objective

Based on the above problem statement, therefore the objectives of this research are:

1 To investigate the effect of DETA/TA coating parameters onto modified membrane surface.

2 To evaluate the performance of DETA/TA modified membrane for the separation of emulsion oil.

3 To characterize the properties of DETA/TA coated layer onto membrane surface.

1.4 Research scope

For this research, it was found that there were lot of researches has been done on the oily wastewater treatment especially on membrane filtration system. But till there is gray area towards the selection of suitable membrane depends upon the chemicals used, processes involved and type of oily wastewater generated by industries. Hence there is a scope for selection of parameters for surface modification of PVDF membrane for the better performance of to separate the oil-in-water emulsion by using cross flow filtration.

1.5 Organization of Thesis

This thesis consists of five main chapters and each chapter contributes to the sequence of this study. The following are the contents for each chapter in this study.

Chapter 1 (Introduction) introduces the research background, problem statement, research objectives and organization of thesis.

Chapter 2 (Literature Review) discusses the chronological developments of membrane filtration towards emulsion oil were described. Past researches focused on the developments of surface modification were reviewed.

Chapter 3 cover the testing methodology and the experimental work is discussed. Following that is the determination of testing method, specifications of the methods used, experimental preparations and procedure, instrumentations. Characterization techniques on the membrane surfaces were covered in this chapter.

Chapter 4 (Results and Discussions) represents the major section in this thesis in which all experimental results achieved from experimental work based on the objectives stated in Chapter 1 were discussed. The findings included the optimum coating conditions of DETA/TA coated layer onto PVDF membrane, membrane characterization, oil rejection efficiency, water and emulsion flux and surface morphology were presented and discussed.

Outcomes of the study presented in Chapter 4 were summarized in Chapter 5 (Conclusions and Recommendations). Concluding remarks were recorded for each of the findings on the aspect of membranes modification, membrane characterization and flux performance. Recommendations for the future work were proposed based on the limitations encountered in the present study.

CHAPTER TWO

LITERATURE REVIEW

2.1 Polyvinylidene fluoride

Polyvinylidene fluoride (PVDF) is a pure thermoplastic fluoropolymer produced by the polymerization of vinylidene difluoride with a chemical formula of $C_2H_2F_2$. PVDF membranes consist of a semi-crystalline polymer structure that has good thermal stability, chemical resistance, excellent processability, ultraviolet and radiation resistance, climate resistance, and easily controlled morphology and porosity. Numerous physical and chemical methods have been used to improve the hydrophilicity of PVDF membrane, including surface coating or modification, melt-intercalation, or polymer blend melt techniques, to prepare functionalized membranes (Otitoju et al., 2016). These modification procedures can be enhanced by the interfacial energy of hydrophilic structures, which results in an increase in the water flux, fouling resistance, and thermal stability.

In contrast with other organic polymers such as PSF, PES, PVDF is relatively more hydrophobic, which may not be as high as polypropylene (PP) and polytetrafluoroethylene (PTFE). Generally, the hydrophobicity of any polymeric material is generally associated with its critical surface tensions. Moreover, since the fabrication of PP and PTFE membranes are common (Otitoju et al., 2016), PVDF has remain one of the best options of membrane material for the applications for oily wastewater separation.

PVDF easily dissolves in common organic solvents such as N,N-dimethylacetamide (DMAc), N,N-dimethylformamide (DMF), N-methylpyrrolydone

(NMP) and Acetone, and as a result, porous PVDF membranes is easily formed via a simple non-solvent induced phase separation (NIPS). Furthermore, its excellent thermal stability, semi-crystalline nature has made PVDF an interesting membrane material for oily wastewater separation (Otitoju et al., 2016).

2.2 Membrane wettability

Membranes can be manufactures in a wide variety of materials. These materials differ in their performance characteristics including mechanical strength, fouling resistance, hydrophobicity, hydrophilicity, and chemical tolerance. For the perspective of hydrophobicity and hydrophilicity of the membrane, hydrophilic membranes tends to exhibit greater fouling resistance than hydrophobic membranes. Hydrophobic particles such as latex particles tend to cluster or group together to form colloidal particles because this lowers the interfacial free energy due to surface area exposure. To prevent fouling, a membrane requires a surface chemistry which prefers binding to water over other materials. This implies that the material must be very hydrophilic (Michael Pilutti, 2003). From the Table 2.1 below, the calculated of some polymeric materials are shown.

Table 2.1: Calculated surface tension of some polymeric materials (Michael Pilutti, 2003)

Chemical name	Surface tension
Polytetrafluoroethelyne	18
Polyvinylidene Fluoride	25
Polypropylene	29
Poly Vinyl Chloride	39
Polysulfone	41
Polycarbonate	42
Polyacrylonitrile	44
Cellulose	44

Despite the pore size and membrane morphology, the degree of hydrophilicity or hydrophobicity influences the wettability and applied pressure requirements for water flow through the membrane. There is wide variety of materials that available in the markets that have vary chemical and mechanical properties including mechanical strength, burst pressure, oxidant tolerance, VOC tolerance, pH operating range, and so forth (Michael Pilutti, 2003). The membrane selection is crucial. Thus, compatible material with raw water quality, pretreatment requirements, and other operating conditions is important. There are several example of the material construction for membrane such as polypropylene, polyethersulfone, polysulfone, cellulose derivative and many others.

2.3 Oil-in-water emulsion

An emulsion is defined as two immiscible liquids wherein droplets of one phase (the dispersed or internal phase) are encapsulated within sheets of another phase (the continuous or external phase). There are two basic forms of emulsion. The first is the oil-in-water (O/W) emulsion in which oil droplets are dispersed and encapsulated within the water column. The second is the water-in-oil (W/O) emulsion in which droplets of water are dispersed and encapsulated within the oil. For either type of stable emulsion to form, three basic conditions must be met; (a) the two liquids must be immiscible or mutually insoluble in each other, (b) sufficient agitation must be applied to disperse one liquid into the other, (c) and an emulsifying agent or a combination of emulsifiers must be present (Chen & Tao, 2005).

Other than a considerable change in the dispersion state of the oil droplets, the emulsification of the two immiscible liquids (water and oil) also results in a considerable rearrangement of the oil-water interface (Floury et al., 2010) where mainly two classes of molecules can be adsorbed: amphiphilic macromolecules (mainly proteins) and low molecular weight emulsifiers (lecithins, monoglycerides, tweens, spans, etc.) (Burgaud et al., 1990).

Proteins and low molecular weight emulsifiers help the production and the stabilization of emulsions. Proteins play two major roles: on the one hand, they lower surface tension between the interfaces that are formed during the emulsification process, and on the other hand, they form a macromolecular layer surrounding the dispersed particles which structurally stabilizes the emulsions by reducing the rate of coalescence. In food emulsions, stability is usually achieved by the application of proteins as the main stabilizer (Floury et al., 2000).

2.4 Surface modification of PVDF membranes

Polymers are attractive materials for various applications, such as membrane filtration, coatings, composites, microelectronic devices, thin-film technology, and biomaterials. The performance of polymeric materials in many applications relies largely upon the combination of bulk (e.g. mechanical) properties in combination with the properties of their surfaces. However, polymers very often do not possess the surface properties needed for these applications. Vice versa, those polymers that have good surface properties frequently do not possess the mechanical properties that are critical for their successful application. Due to this dilemma, surface modification of polymers without changing the bulk properties has been a topical aim in research for many years, mostly, because surface modification provides a potentially easier route than e.g. polymer blending to obtain new polymer properties (Gopal et al., 2003; Kato et al., 2003).

The surface modification of PVDF membranes is effective and frequently used method to enhance the performance of PVDF membrane for oily wastewater separation. In surface on, the aims of the modification are largely two-fold: 1) minimization of undesired interactions (adsorption or adhesion, or in more general terms membrane fouling) that reduce the performance as described previously and 2) improvement of the selectivity or even the of entirely novel separation functions (Ulbricht, 2006). Many surface modification have been adopted to reduce membrane fouling.

The surface modification can be mainly classified into two categories such as the physical modification and chemical modification. The physical modification signifies that the hydrophilic modifiers exist on PVDF membrane surface via physical interaction but not covalently bonded. In other words, the chemical composition of

PVDF membrane remains unchanged although the chemical reaction may be required during the modification. The physical modification of PVDF membranes can be achieved by two ways: (a) the hydrophilic organic material is directly coated or deposited on membrane surface (further treatment is conducted sometimes) providing a strong binding force between hydrophilic coatings and substrates, (b) the PVDF membrane is firstly immersed in or coated by a solution of chemically active monomers. Then, the monomers are immobilized onto membrane surface by crosslinking or polymerization reaction without the chemical participation of PVDF membrane. Surface coating is also an effective method for membrane surface modification (Kang & Cao, 2014). The hydrophilic organic/inorganic material for surface modification of PVDF membranes that has been used with PVDF for oily wastewater separation include polydopamine, polyaniline, chitosan and citric acid monohydrate (CAM) (Otitoju et al., 2016) .

Numerous approaches have been demonstrated in surface modification to address these issues over the past years. Recently, mussel-inspired coating approach with dopamine (DA) has been widely utilized to modify various materials for its stability, simplicity, and versatility, although the exact polymerization and interaction mechanism of the adhesive pDA layer was kept unknown so far. Different from traditional coating strategies, the mussel-inspired coating protocol involves an oxidative polymerization process, yielding polydopamine (pDA) coatings that adhere to virtually all types of substrates with high binding strength (Cheng et al., 2015). Although polydopamine (pDA) is simple to apply to substrates, deposits on a wide range of materials and offers many potential applied uses, however the high costs of dopamine and the characteristically dark colour of pDA coatings may be impediments for some practical applications (Sileika et al., 2013).

Most recently, polyphenol/Fe^{3+} complex was used to prepare multifunctional filtration membranes which can be applied in practical water treatment (Kim et al., 2015). In these cases, Tannic acid (TA) was a water-soluble high molecular weight polyphenolic compound containing sufficient galloyl groups, which could provide binding sites for metal ions to chelate. Metal chelation was a salient feature of TA molecule (like many other polyphenols), upon which it acted as a polydentate ligand for metalion coordination and then the resulted cross-linking network is simultaneously adsorbed on substrates surfaces. However, the coordination bonds are instable in the cross-linking coating under acidic condition. Therefore, covalent bonds are preferred to make a more robust deposited coating on substrates than coordination ones. Lee et al. (2007) pointed out that phenolic groups and amino groups are the two crucial points for the formation of covalent bonds in PDA network. Inspired by this thought, Wu et al. (2014) fabricated coatings with catechol and amino groups containing chemicals on polypropylene membrane surface.

In this work, Tannic acid (TA) was used to provide phenol groups and diethlyenetriamine (DETA) was adapted to provide amino groups for the formation of covalent bonds. We analysed the influences of DETA/TA ratio and deposition time on the coating formation. The performance of modified membrane was also evaluated and compared with the native membranes. The surface morphology, chemical structure and hydrophilicity of the modified membranes were also detailed investigated.

2.5 Contact angle measurement

Studies concerning the interaction between a solid and liquid require reliable experimental values of contact angle. The quantitative evaluation of the wetting of a solid by a liquid is made in terms of the contact angle θ. Figure 2.1 shows the schematic diagram for the contact angle and the interfacial tensions at the three phase boundary.

The most important relation regarding the contact angle is the Young's equation that relates the contact angle θ, liquid surface tension γLV, solid surface energy γSV, solid-liquid surface tension γSL, as expressed in Equation 2.1 (Jun, 2008);

$$\gamma SV = \gamma SL + \gamma \mathrm{LV} \cos \theta \qquad (2.1)$$

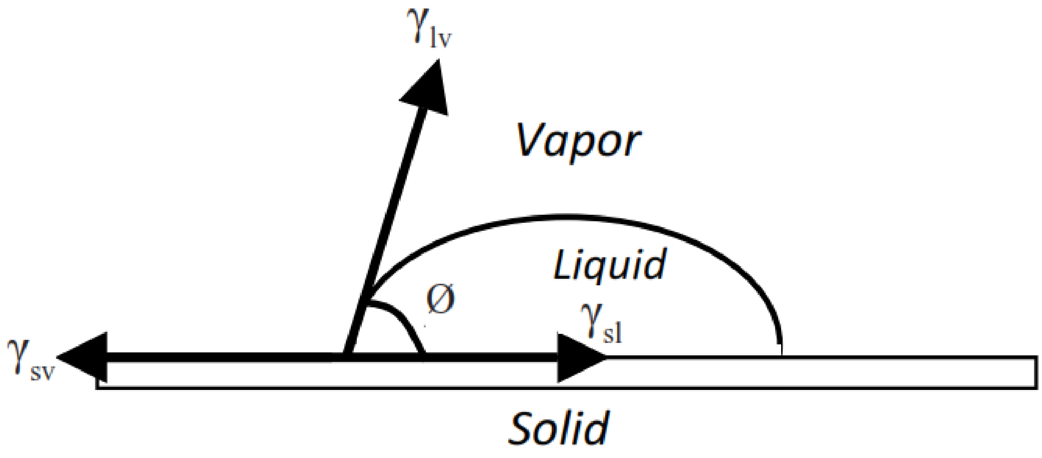

Figure 2.1: Illustration of a liquid droplet resting on a solid surface with contact angle (Lawrence, 2004)

Contact angle is a widely used analysis for characterization of membrane hydrophilic/hydrophobic behaviour, the effect of chemical modification like cross-linking on the latter or by introducing hydrophilic or hydrophobic solvent stable polymeric materials as support membranes in the search of optimal flux without sacrificing selectivity. Contact angle is related to the roughness parameter of the outer membrane surfaces. It is considered as key feature for deeper understanding of other techniques like permporometry, related to the sorption layer thickness.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Materials

Polyvinylidene Fluoride (PVDF) membrane (Durapore® Membrane Filters) was supplied by Merck Milipore Ltd. (Ireland). Tannic acid (TA), Diethlyenetriamine (DETA) and Isopropanol (IPA) were purchased from Merck (Darmstadt, Germany). Tris-base (purity 99.8 %) and Tween-80 were purchased from Friendemann Schmidt Chemical (Germany). Sodium Hydroxide (NaOH) was purchased from R&M Chemicals (Selangor, Malaysia). Hydrochloric acid, HCl (purity 36.5-38.0 %) was purchased from J.T. Baker Chemical (US).

3.2 Experimental Procedures

The overall experimental activities carried out in this study are presented in the following schematic flow diagram (Figure 3.1)

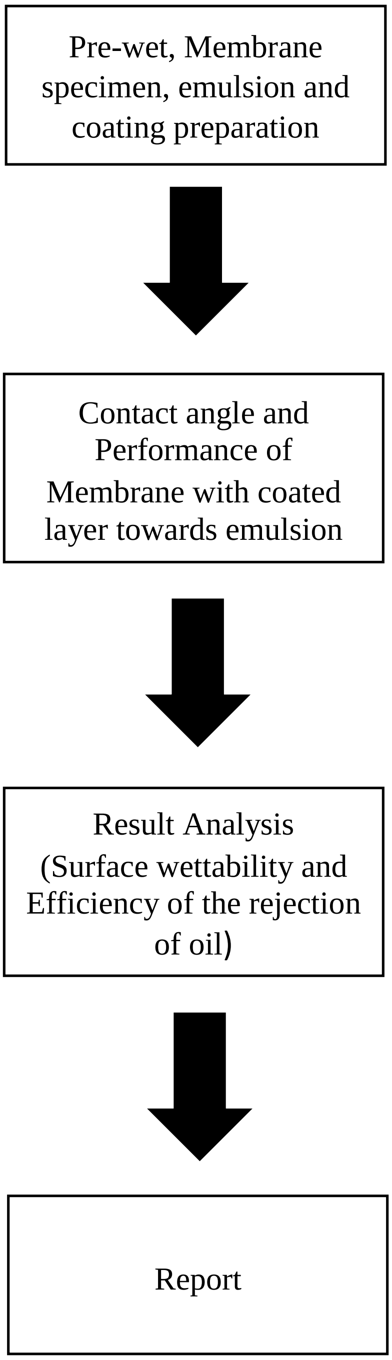

Figure 3.1 : Flowchart of experimental work

3.3 Preparation of DETA/TA polyphenolic coated layer

The polyphenolic coating of TA and DETA on the membrane surfaces is affected by several parameters, such as DETA/TA ratio, TA concentration, pH coating solution and coating time. In the following sections, these methodology were shown as below.

3.3.1 Effect of DETA/TA ratio

The membranes were prepared according to Zhang et al. (2016) with some modifications. Membrane samples were pre-wetted in 25% v/v Isopropanol (IPA) for 24 hours. After that the membrane samples were washed with deionized water three times. Then, immersed in deionized water (DI) and placed in water bath at 55 °C for 24 h.

DETA and TA were dissolved in a Tris-HCI buffer solution (at pH 8.5) with different mass ratios (0:1, 1:0, 1:1, 2:1, 4:1, 6:1, 8:1 and 10:1). For each ratio, the concentration of TA was kept as 2 g/L. The mixture solution was shaken using incubator shaker for 6 hour under room temperature. Then, the samples were soaked in 25% v/v Isopropanol (IPA) for 15 minutes. After that the samples were washed with deionized water three times. Then, immersed in deionized water (DI) overnight at room temperature.

Next, the samples were dried in a vacuum oven at 50 °C to constant weight. As a control experiment, a sample was immersed in a TA solution without DETA. This procedure was repeated two times to collect the optimum mass ratio for other parameters.

3.3.2 Effect of TA concentrations

The preparation of the TA/DETA film was similar to the above preparation process. DETA and TA were dissolved in a Tris-HCl buffer solution (at pH 8.5) with different concentration of TA (0 g/L to 0.6 g/L). For each solution, the mass of DETA was kept as the optimum mass from previous experiment. This procedure was repeated two times to collect the optimum concentration of TA for the next parameter.

3.3.3 Effect of pH coating solution

The preparation of the DETA/TA film was similar to the above preparation process. DETA and TA were dissolved in a Tris-base buffer solution with different pH (pH 5, pH 6, pH 7, pH 8, pH 9 and pH 10) by adding HCl or NaOH. For each solution, the mass of DETA was kept as the optimum mass and the concentration TA was kept as the optimum concentration from previous method. This procedure was repeated two times to collect the optimum pH of coating solution for other parameters.

3.3.4 Effect of coating time

The preparation of the TA/DETA film was similar to the above preparation process. DETA and TA were dissolved in a Tris-base buffer solution with different reaction time (2 h, 4 h, 5 h, 7 h, 8 h, and 9h). For each solution, the pH, mass ratio and concentration of TA was kept as the optimum mass from previous optimum parameters.

3.4 Preparation of emulsion oil

In order to prepare 1500 ppm of emulsion oil, 4.8 g of diesel was added into 3 L of deionized water with 0.42 g of Tween-80 as emulsifier with different mass ratio of 9:1. Next, the solution was then stirred under 6000 rpm for 40 minutes. The droplet sizes are in the range of 2 to 10 µm under optical microscopy observation.

3.5 Antifouling experiment on the emulsion separation

The compaction of the membrane was carried out by passing pure water through it at 2.0 bar for 30 min before the experiment started in order to avoid the effects of compaction (Susanto et al., 2009). Next, diesel and pure water were emulsified and used as the oil-in-water emulsion in concentration of 1500 ppm.

This method was carried out in one cycle of flux performance which included three stages. The first stage was referred to 150 min pure water permeation. The second stage was 180 min of emulsion solution microfiltration. Then followed by pure water flux for 150 min for the third stage, after cleaning process by flushing the pure water at 30 min at the same TMP. Next, the pure water flux and antifouling experiments of membrane were then determined at different TMP (1 bar and 1.5 bar) and constant room temperature, by a cross flow filtration system. The flux of the membrane was obtained by Equation 3.1;

$$J = \frac{\Delta M}{\rho_w A \Delta t} \tag{3.1}$$

Where the flux (J) is pure water or filtrate flux (L m^{-2} h^{-1}), ΔM (g) is the mass of permeate collected during a time period of Δt (h), ρ_w is the density of water, and A is the membrane active area.

3.6 Characterization of emulsion

The prepared oil-in-water emulsion with concentration of 1500 ppm was characterized in terms of average emulsion droplet size. The size distribution of the emulsion droplets in the feed was determined using a laser particle size analyzer (Malvern Mastersizer 2000, Model APA 5005) from which the average droplet size was calculated.

3.7 Characterization of the DETA/TA/PDVF membranes

The prepared membranes were characterized by morphological analysis. The surface morphology of the membranes was investigated with a field emission scanning electron microscopy (SEM, Quanta FEG 650). SEM analysis provided the images of membrane cross-section and top surface. Water contact angle (WCA) was measured on the membrane surface by using a goniometer (Ramé - Hart Instruments Co.). A drop of 2 μL water was dripped on the membrane surface, digital photos were pictured using a camera, and then WCA was calculated by the system software.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Polyphenolic coating of DETA and TA on the membrane surfaces

The polyphenolic coating of TA and DETA on the membrane surfaces is affected by several parameters, such as DETA/TA ratio, TA concentration, pH coating solution and coating time. In the following sections, these parameters will be discussed.

4.1.1 Effect of DETA/TA ratio

The mass ratio of DETA/TA was varied in the coating procedure while keeping the deposition time as 6 h with pH 8.5. Figure 4.1 shows the effect of DETA/TA ratio was varied 0:1 to 10:1.

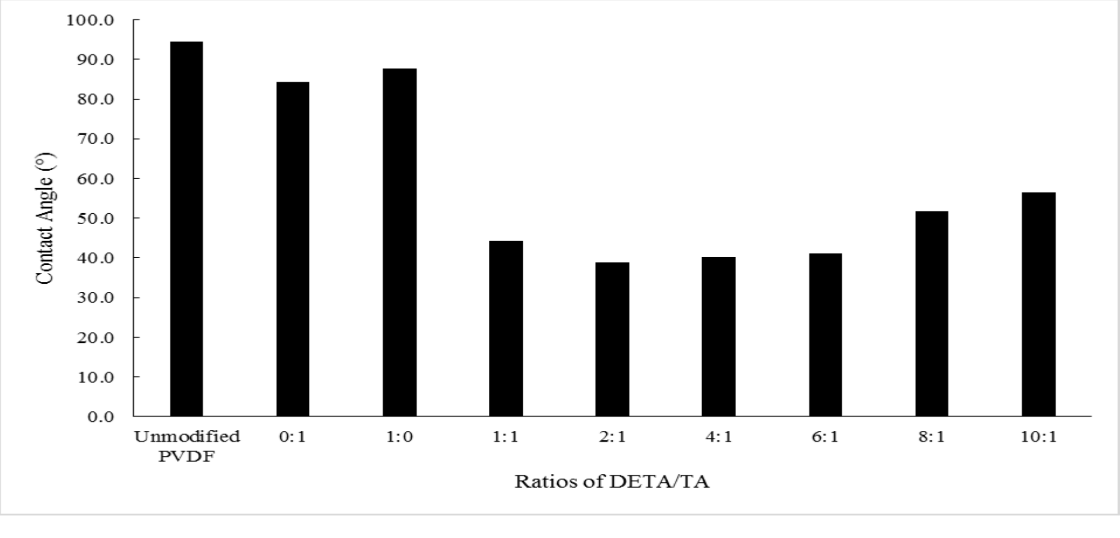

Figure 4.1: Water contact angle on the effect DETA/TA ratios

Unmodified PVDF membrane is on low wettability which the water contact angle (WCA) is 94.6°. This shows the membrane is a hydrophobic membrane. Thus the effect of DETA/TA ratio was carried out to make the membrane become hydrophilic by modifying the surface. From Figure 4. WCA for the mass ratio of 0:1 which contains only TA without DETA is 84.3°. The WCA is slightly decreases from the native PVDF. The same trends is shown by the ratio of 1:0 which contains only DETA without TA and the WCA is 87.8°. This is because the coating is not occur yet for both ratios. The WCA start decrease dramatically from ratio of 1:1 until reaches the minimum value of 38.8° for DETA/TA ratio of 2:1. It should be emphasized that the WCA is only 84.3° without DETA, indicating DETA participates and accelerates the coating process. The DETA/TA solution with a mass ratio of 1:1 to 10:1 turns dark yellow and opaque after coating, whereas the solution with a ratio of 0:1 and 1:0 remains transparent. The WCA increases back from mass ratio 4:1 to 10:1.

The trends obtained from the effect of DETA/TA ratio on this study was agreed by Zhang et al. (2016), that increase of DETA/TA ratio declined hydrophobic interaction with the membrane surfaces because the aromatic rings decrease. The report also showed the addition of excess DETA could destructed the non-covalent interaction among TA molecules. The ratio of 2:1 will be used to study the other parameters.

4.1.2 Effect of TA concentrations

The concentration of TA was varied in the coating procedure with DETA/TA ratio of 2:1 and fixed the coating time for the coating as 6 h. As shown in Figure 4.2, the WCA reaches the optimum value of 19.4° around a TA concentration of 5 g/L. Furthermore, the WCA was changed slightly with an increase of TA/DETA ratio from 1:1 to 10:1.

Therefore, it implied that the concentration of TA rather than DETA played a dominant factor in affecting the surface hydrophilicity of membranes.

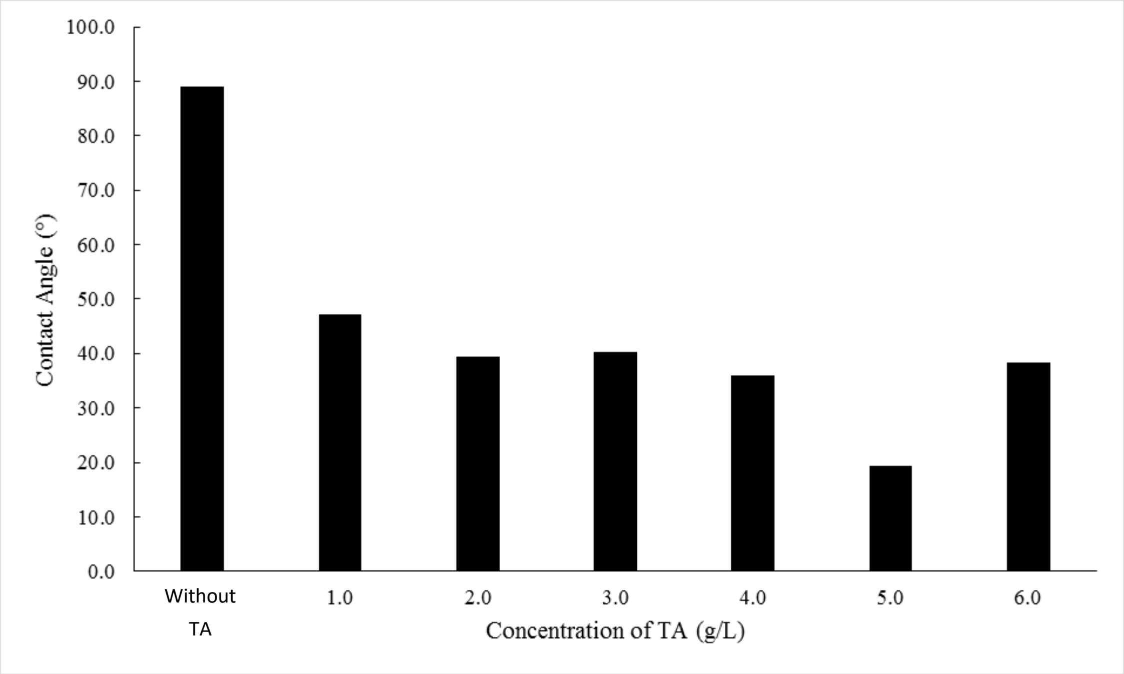

Figure 4.2: Water contact angle on the effect TA concentration

The hydroxyl groups from galloyl and catechol of TA, providing hydrogen bonding sites to adsorb water molecule, took the main contribution in enhancing the surface hydrophilicity of TA-DETA/PVDF membranes. This parameter was support by Fan et al. (2015) and other researchers that the concentration of monomer which is TA had significant effect on the growth of coating during the coating reaction. Hence, TA concentration of 5 g/L will be used to study the next parameters.

4.1.3 Effect of pH coating solution

The pH of the coating solution was adjusted in the coating procedure while keeping the reaction time for the coating as 6 h and DETA/TA ratio of 2:1 with the TA concentration of 5 g/L. Figure 4.3 illustrated that the WCA reaches the minimum value of 22.3° around a coating solution of pH 9. The favourable pH for the coating process in the range of pH 8.5 to pH 9. Therefore, pH 8.5 was chose as the optimum pH in this experiment.

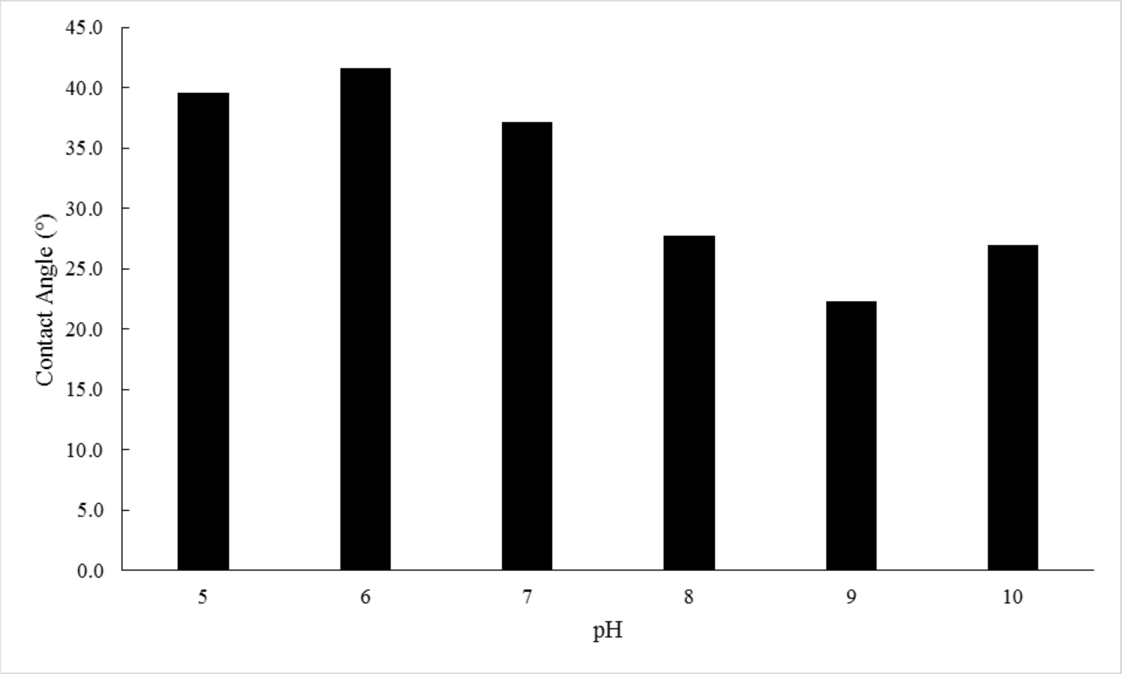

Figure 4.3: Water contact angle on the pH of coating solution

The optimum pH of this coating solution also supported by studies on the polymerization of dopamine in TRIS buffer which reported at pH 8.8 (Li et al., 2014). Prodpan et al., (2012) and Zhand et al., (2010) also reported that the possibility of TA