VOLUME REDUCTION AND WATER RECOVERY OF PALM OIL MILL EFFLUENT (POME) USING MEMBRANE DISTILLATION

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VOLUME REDUCTION AND WATER RECOVERY OF PALM OIL MILL EFFLUENT (POME) USING MEMBRANE DISTILLATION

by

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LIST OF SYMBOLS

Symbol	Description	Unit
β	Selectivity	-
M	Molar concentration	mol/L
J	Permeate flux	kg/(m^2.h)
ΔW	Amount of distillate	kg
A	Effective area of membrane	m^2
Δt	Sampling time	h
R	Rejection of nutrient	%
C_f	Concentration of feed	mg/L
C_p	Concentration of permeate	mg/L
Ka	Mass transfer coefficient	m/s

LIST OF ABBREVIATIONS

MD	Membrane Distillation
POME	Palm Oil Mill Effluent
BOD	Biochemical Oxygen Demand
DCMD	Direct Contact Membrane Distillation
TiO_2	Titanium Dioxide
PVDF	Polyvinylidene fluoride
LEP	Liquid Entry Pressure
AGMD	Air Gap Membrane Distillation
SGMD	Sweeping Gas Membrane Distillation
VMD	Vacuum Membrane Distillation
GOR	Gained Output Ratio value
LEPw	Liquid Entry Pressure for Water
SEM	Scanning Electrode Microscopy
RO	Reverse Osmosis
HRT	Hydraulic Retention Time
TSS	Total Suspended Solid
TOC	Total Organic Carbon
TDS	Total Dissolved Solid
OMW	Olive Mill Wastewater

PENGURANGAN VOLUME DAN AIR MENDAPATKAN PALM OIL MILL EFLUEN (POME) MENGGUNAKAN MEMBRAN PENYULINGAN

ABSTRAK

Kilang-kilang minyak sawit yang terkenal dalam menghasilkan efluen tercemar dengan jumlah yang besar. POME mentah adalah berasid, bersuhu tinggi, bahan apungan dan yang paling penting BOD yang tinggi. Jika bahan buangan ini tidak dirawat dengan betul, ia boleh menimbulkan sebagai pencemar organik yang tinggi. Untuk mengatasi masalah ini, membran penyulingan merupakan alternatif untuk kaedah rawatan konvensional kerana ia boleh mengendalikan penyelesaian dengan muatan pepejal yang tinggi. Dalam kajian ini, kepekatan POME yang berbeza (mentah, termendap dan ditapis) dengan jumlah bahan apungan yang berbeza ditapis untuk mendapat pemulihan air pada pada suhu pelepasan asalnya (80°C). Kesan pemendapan POME kepada prestasi membran MD dan pencириannya dikaji menggunakan ‘contact angle’, SEM, FTIR, porometry dan pengukuran LEP. Daripada kajian ini, pemendapan POME menyebabkan menurun daripada sudut kenalan membran kerana sifat hydrophilic POME pepejal terampai. Membran mempunyai fluks sederhana (4.33 kg / m^2h) dan keupayaan penyingkiran nutrien yang cemerlang iaitu lebih dari 99.99%. Oleh itu, pra-ditapis POME adalah cara yang praktikal untuk digunakan dalam proses DCMD untuk mendapat pemulihan air yang tinggi dan mengurangkan kecenderungan kekotoran membran.

VOLUME REDUCTION AND WATER RECOVERY OF PALM OIL MILL EFFLUENT (POME) USING MEMBRANE DISTILLATION

ABSTRACT

The palm oil mills are well-known for producing huge amounts of polluting effluent. Raw POME is acidic, has high temperature, suspended solid and most important, high organic biochemical oxygen demand (BOD). If it is not properly treated, it could pose environmental burden. To overcome this problem, membrane distillation is an alternative for the conventional treatment method as it could handle solution with high solid loading. In this study, a different concentration of POME (raw, sedimented and filtered) with different Total Suspended Solid (TSS) is filtered by using direct contact membrane distillation (DCMD) to recover the water at its original discharge temperature (80°C). The impact of POME deposition on the performance of MD membrane and their characterization such as contact angle, SEM, FTiR, porometry and LEP measurement were reported. It was found that POME deposition caused the decreased of the membrane contact angle due to the hydrophilic nature of POME suspended solid. The membrane has moderate flux (4.33 kg/m^2h) and an excellence nutrient removal capability of more than 99%. Thus, pre-filtered POME is a practical way to be used in direct contact membrane distillation (DCMD) process in order to obtained high water recovery and mitigated the fouling tendency.

CHAPTER ONE

INTRODUCTION

1.1 Research background

Palm oil industry has become Malaysian very important agriculture-based industry since 1971 (Wu, et al., 2007). With such a huge production, the palm oil milling process consumes a large amount of process water which known as palm oil mill effluent (POME) with high organic load. According to Ahmad et al. (2003), it is estimated that more than 50% of water will end up as POME from 5-7.5 tonnes of water is required for every tonne of crude palm oil produced. POME is a colloidal suspension consists of 95-96% water, thick brownish liquid, with 0.6-0.7% oil, 4-5% total solids and contains bit amount of minerals and heavy metals (Ahmad, et al., 2006). If this highly polluting wastewater was discharged without being treated, it will cause serious environmental problem (Aziz, et al., 2015).

Several treatment technologies such as conventional biological treatments of anaerobic digestion have been established and applied to treat POME. Nonetheless, biological treatment needs tedious maintenance and monitoring. This is because biological treatment is highly depend on microorganisms to break down the pollutants. Microorganisms is very sensitive to environmental changes and need to be take care in order to maintain the favourable environment (Ahmad, et al., 2003).

According to Aziz et al. (2015), membrane technology is a promising technology for the treatment of POME and amongst the membrane technology, membrane distillation is the cutting edge technology to treat high suspended solid effluent like POME. Membrane distillation (MD) is a thermally driven process where vapour molecules transported through porous hydrophobic membranes (El-Bourawi, et al., 2006). Membrane distillation operates at low temperatures compared to conventional distillation process and compared to pressure-driven membrane process such as reverse osmosis (RO), hydrostatic pressure in MD is lower (Alkhudhiri, et al., 2012). It is cost effective as it requires less expensive material, high rejection factor and less fouling tendency since the surface is non-wetting (Mohammad Rezaei, 2007). MD also reduced chemical interaction between membrane and process solution and could achieve 100% rejection theoretically (Lawson & Douglas, 1997).

According to Madaki & Lau (2013), POME is originally high in temperature which is around 80-90 °C. Thus, MD is the best choice to treat POME since MD can separate supply solutions at a temperature well below the boiling point and under atmospheric pressure. Typical supply temperatures around 30-60°C permit re-use of residual heat flows, and the use of alternative energy sources such as sun, wind and geothermic (EMIS, 2013).

MD also offers 100% retention for non-volatile dissolved substances, whereby there is no limit on the supply concentration. El-Abbassi, et al. (2009) has been investigated the possibility of olive mill wastewaters (OMW) treatment and concentration by membrane distillation. The results obtained shows the efficiency of DCMD for OMW treatment and concentration high which is more than 99%.

1.2 Problem Statement

Various technologies have been established and applied in order to treat POME, however, it suffered from serious problem like low efficiency, high cost and high fouling tendency. For example, ponding system and conventional biological treatments of anaerobic digestion have high capital investment and maintenance cost and unsatisfactory performance while for conventional biological treatments of anaerobic digestion, requires tedious maintenance and monitoring (Tabassum, et al., 2015).

In this study, membrane distillation is used to treat POME. Membrane distillation has many advantageous over the other technology, however the problem of membrane wettability and membrane fouling a major obstacle in the widespread use of the membrane technologies (Gryta, et al., 2006). Fouling can cause the membrane permeability to decrease due to suspended or dissolved substances from the POME that contains several components deposited on the membrane and/or within the membrane pores (Gryta, 2008). For this reason, POME cannot be treated directly by membrane techniques.

Therefore, to control the membrane fouling, feed pre-treatment are applied to the POME. POME was pre-treated by reducing the concentration of the POME. By introducing the pre-treatment of the POME, it can reduce the interaction between feed solution and membrane surface which can lead to the reduction in the tendency of fouling.

1.3 Research Objectives

This research aims,

i. To recover the water from POME using membrane distillation.
ii. To evaluate the fouling tendency of POME on the membrane surface based on the compositions of the POME.

CHAPTER TWO

LITERATURE REVIEW

2.1 Palm Oil Mill Effluent (POME)

Palm oil industry is one of the largest international agro-based industries. Palm oil is important in both food and non-food sector, for example, its use in emulsion-based powdered and consumer foods such as pourable margarine, mayonnaise, soup-mixes, imitation cheese and micro-encapsulated palm oil for food sector and production of soaps and detergents, pharmaceutical products, cosmetics and oleochemical products for non-food sector. Palm and palm kernel oil also offer good and competitive alternative to tallow and coconut oil because of the similarities of their fatty acid compositions (MPOB, 2017).

Malaysia is known as the second largest producer of palm oil in the world. The total production of palm oil in Malaysia was 45.6% which contributes to 14.96 million tonnes. It was forecasted that in years 2000-2020 in million tonnes, the demand will be higher with the increasing demand of world of the total palm oil (Sumathi, et al., 2008). The huge production of palm oil correspond to the large amount of wastewater generates which is known as the palm oil mill effluent (POME).

Palm oil mill effluent (POME) which contain high concentration of organic matter will pollute our stream if the treatment process is not efficient. It is a thick brownish liquid discharged at pH ranging of 4.0 to 5.0, at high temperature of 80 to 90°C with the biological oxygen demand (BOD) in the range of 10,250 to 43,750 mg/L and chemical oxygen demand in the range of 15,000 to 100,000 mg/L and high suspended solids and salt content (5000 to 54,000 mg/L) (Tabassum, et al., 2015). Based on Agensi Inovasi Malaysia (2011) ; MPOB (2014), about 60 million tonnes of palm oil mill effluent

(POME) is generated from 421 palm oil mills in Malaysia in 2010 which would cause major source of pollution if it was discharged directly into water sources.

The treatment and disposal method of POME have been performed in a lot of studies, like, decanting and drying (Edewor, 1986), using a pond system (Chin, et al., 1996), various aerobic and anaerobic treatment (Chan, et al., 2012; Poh & Chong, 2009) and membrane technology (Ahmad, et al., 2006; Ahmad, et al., 2003). However, these application technologies still facing the operational and effluent quality problem.

The most conventional method for treating POME is the ponding system with more than 85% of palm oil mills in Malaysia using Ponding system for POME treatment. However, Ponding system in full scale operation required have high capital investment and maintenance cost with unsatisfactory performance. The open lagoon POME also have long hydraulic retention time (HRT), foul smell, large occupied area and greenhouse gas emissions.

While the anaerobic digestion able to meet the current regulatory effluent discharge standard of three-day biological oxygen demand (BOD) 100 mg/L, the current limit set by the Department of Environment (DOE), Malaysia. However, such biological practices are only applicable in the palm oil mills which acquire large area of lands. Besides, the existing technologies are unable to consistently meet the proposed stringent BOD regulatory discharge standard of 20 mg/L to be imposed by the DOE, Malaysia (Tabassum, et al., 2015).

Thus, another method of treating the POME carried out so that it can reduced the problem related to environment and in order to meet the standard imposed by the DOE, Malaysia. Membrane technology is a highly potential solution for the treatment of POME since the current conventional treatment system shows its lack of efficiency and this unfortunately leads to the environmental pollution issues.

2.2 Membrane Technology

Membrane technology has become an impressive separation technology over the past decade. Microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO) and membrane distillation (MD) are the example of membrane technologies. Membrane technology is more and more often used for treatment of wastewater such POME, desalination and food industry and now even more attractive compared to conventional separation (Alkhudhiri, et al. 2012; Wu, et al. 2007). Md Tamez, et al. (2007) also compared the performance of membrane technology and conventional for removal of arsenic. Conventional technology required high cost as it required conventional filter and huge amount of chemical reagent while membrane technology almost no chemical reagent necessary and the maintenance cost also low.

Among these membrane technologies, only MD is a thermal-driven separation process while the rest are the pressure-driven separation technologies (Mohammad Rezaei, 2007). According to Alkhudhiri, et al. (2012), MD has less fouling tendency compared to RO as the size of the pore membrane for MD relatively larger than other separation process. MD system also feasible as it can be combined with other separation processes such as UF to create an integrated separation system.

2.3 Membrane Distillation

Membrane distillation (MD) is a comparatively new process that being investigated worldwide. It has a lot of attractive features, for example, it operates at low temperatures compared to conventional process as the solution is not necessarily heated up to boiling point. Moreover, MD also has lower hydrostatic pressure than that used in pressure-driven membrane like reverse osmosis (RO). Thus, MD is expected to be a cost effective process, which requires less demanding of membrane characteristics too (Lawson & Douglas, 1997; Alkhudhiri, et al. 2012).

Membrane distillation (MD) is a thermally driven process, which the feed cannot penetrate the membrane and only vapour molecules can pass through porous hydrophobic membranes (El-Bourawi, et al., 2006). According to the Alkhudhiri et al. (2012), MD configuration can be divided into 4 types, which are Direct Contact Membrane Distillation (DCMD), Air Gap Membrane Distillation (AGMD), Sweeping Gas Membrane Distillation (SGMD) and Vacuum Membrane Distillation (VMD).

DCMD is a form of MD where the hot solution which is the feed is in direct contact with the hot membrane side surface as shown in Figure 2.1. Thus, the evaporation process will takes place on the feed-membrane surface. The vapour will moved across the membrane to the permeate side by the pressure difference and it will condense inside the membrane module. Since the membrane characteristic is hydrophobic, only gas phase exists inside the membranes pores and the feed cannot penetrate the membrane. Among all the MD configuration, DCMD is the simplest and widely used in desalination process and food industries.

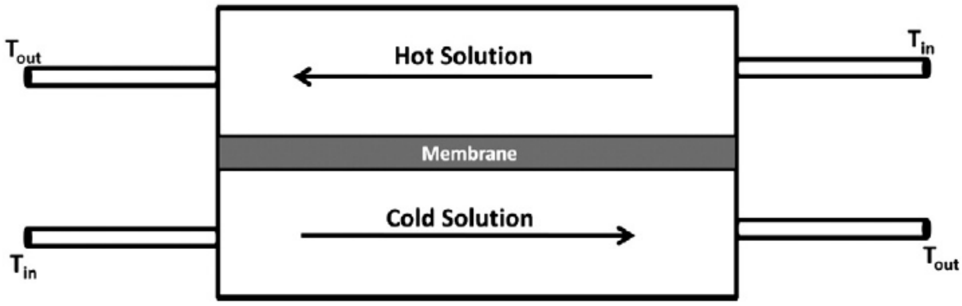

Figure 2.1 Direct Contact Membrane Distillation (DCMD) configuration
(Alkhudhiri, et al., 2012)

According to the Drioli et al. (2015), the easiest and simplest configuration of membrane distillation is DCMD, thus has been studied widely. It also state that DCMD has flux that is more stable as compared to that VMD when using feed that have fouling tendency. Summers et al. (2012) stated that DCMD have high gained output ratio (GOR) as compared to that VMD and AGMD. GOR is the ratio of the latent heat of evaporation of unit mass of product water to the amount of energy used by a desalination system to yield that unit mass of product or to measure how much thermal energy being used up in a desalination system. The MD configuration will give a better performance as the GOR value high because it consumed small amount of energy. Therefore, DCMD is the best choice to be used as it has high GOR compared to AGMD and VMD. Ding et al. (2006) compared the performance of three membrane distillation which is DCMD, SGMD and VMD for the removal of ammonia from water. The result for the experiment conducted and the summary of the operating condition is shown in Table 2.1.

Table 2.1 The summary of operating condition and the result of the experiment *(Ding, et al., 2006)*

Items	VMD	SGMD	DCMD
Pore size (μm)	0.1 and 0.2	0.2	0.1
u_f (m/s)	0.15–1.12	0.35–0.70	0.29–0.74
u_p (m/s)		0.35–2.94	0.29–0.70
t_f (°C)	42.4–55.7	50–65	50–61.2
Vacuum degree (kPa)	90–97		
$c_{f,0}^{0}$ (mol/L)	0–1.2 mol/L	0–0.2 mol/L	0–0.2 mol/L
pH in the feed	9–13	9–13	10
K_a ($\times 10^5$ m/s)	1–4.7	1–2.2	1.2–2.3
β	4–11	8–14	16–23

The symbol K_a represent the mass transfer coefficient while β represents selectivity, the separation performances in this case represent the favourable transport of ammonia. From the Table 2.1, it was found that under the same operating condition, VMD shows the highest K_a but the lowest β, SGMD gives moderate K_a but lowest β and lastly DCMD has highest β while K_a was moderate. Since DCMD gives highest β, therefore, it is the most suitable configuration for ammonia removal.

2.4 Membrane Distillation (MD) to treat POME

Among the waste that generated from palm oil production process in mills, POME is considered the most harmful waste if discharged untreated. POME made up of about 0.6-0.7% oil, 4-5% total solid including 2-4% suspended solids, 95-96% water and also rich in mineral content (Hassan, et al., 2006). Several treatment technologies have developed and employed to treat POME over the last two decades, for example treatment based on anaerobic and aerobic processes and ponding system. However, these biological treatment of anaerobic and aerobic system required tedious maintenance and monitoring since the processes rely solely on microorganisms to degrade the pollutants and the microorganisms itself are very sensitive to changes in their environment (Ahmad, et al., 2003).

Membrane distillation separation processes such as DCMD receiving a lot of attention and widely applied in chemical, food, or pharmaceutical industry and in environmental protection (Tomaszewska, 2012). In the present study, membrane distillation was used to treat POME.

Pre-treatment of POME is carried out in order to reduce the high content of suspended solids and oil in the sample before proceed to membrane distillation process. According to Ahmad et al. (2003), there are two distinct pre-treatment processes which is physical and chemical treatment. It also stated that both physical and chemical processes important in membrane separation process because of the highly suspended solids and oil in POME can cause membrane fouling, thus reduce membrane life.

Direct Contact Membrane Distillation (DCMD) separation technology has been widely applied in various industrial effluent treatment plants. Mokhtar et al. (2015) studied the performance of DCMD technology for treatment of wastewater from rubber industry in Malaysia. Figure 2.2 shows the removal efficiency of the PVDF-C15A membrane using DCMD.

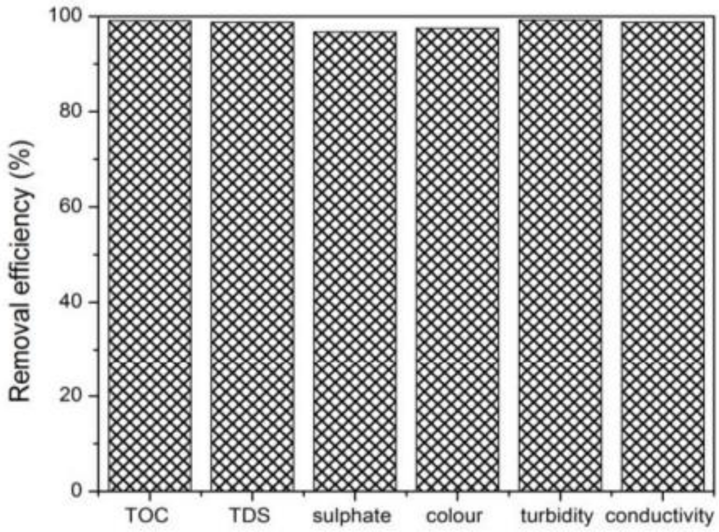

Figure 2.2 The removal efficiency of the PVDF-C15A membrane using DCMD
(Mokhtar, et al., 2015)

From the result above, it was found that TOC removal efficiency is more than 99% rejection which means that almost all the large macromolecular organic carbon been retained from passing through membrane while for the TDS and conductivity removal efficiency of the DCMD system, showing approximately 98.7%. This shows DCMD is possible to be used for the treatment of rubber wastewater which reduce significantly important parameters such TOC, TDS, colour and turbidity to a very low level of concentration, thus allows production of high purity water.

Meanwhile, El-Abbassi et al. (2009) studied the possibility of olive mill wastewaters (OMW) treatment and concentration by DCMD. From experimental result shown in Figure 2.3, it is found that DCMD process was applied successfully to treat and concentrate OMW. The highest concentration factor exhibited by TF200 membrane due to high permeate flux ($J_0 = 7.68 \pm 0.22$ L/h m^2) compared to GVHP membrane ($J_0 = 4.954 \pm 0.14$ L/h m^2). It can be observed that OMW concentration depends on the membrane characteristics.

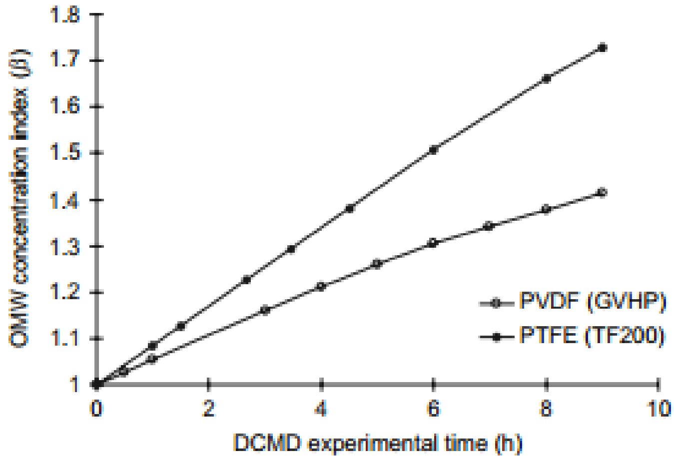

Figure 2.3 Evolution of the concentration factor (β), of OMW polyphenols in feed by DCMD using TF200 and GVHP membranes. (T_f = 40°C and T_p = 20°C). (El-Abbassi, et al., 2009)

Based on the studies that have been described above, it can be concluded that POME have high probability to be treated successfully by using direct contact membrane distillation (DCMD).

CHAPTER THREE

MATERIALS AND METHODS

3.1 Materials

Porous flat sheet membranes were fabricated from polyvinylidene fluoride, PVDF (Solef® TA6010, Solvay Solexis). The casting solutions were prepared by dissolving PVDF in N-methyl-2-pyrrolidone, NMP (Merck, Germany) (purity (GC) ⩾99.5%). A commercial titanium dioxide (TiO2) nanoparticle (Aeroxide P25) was obtained from Degussa.

3.2 Preparation of TiO2 Suspension

TiO_2 nanoparticles were first chemically modified by adding 1M solution of Silane solution for 1 day. Then TiO_2 nanoparticles were collected by centrifugation and dried at 70°C for a day in oven. After that, the modified particles were dried in an oven at 70^{o}C for 24h and then cooled to room temperature in a vacuum chamber for 1h. The modified titanium oxide was then ground by using a mortar and pestle to reduce the number of large agglomerate. For this purpose, 5g of modified titanium oxide was ground to fine powder. Afterward, the 0.1 g powder was dispersed in NMP by sonication in sonication bath (Transconic 460 35 kHz, Germany) for 15 min. Samples treated by silane.

3.3 Membrane formation

The membrane casting solutions were prepared by dissolving pre-dried PVDF (24 hour oven drying at 70°C) and using NMP as a solvent in a 200 mL beaker. It followed by adding 0.1g of pre-dispersed modified/unmodified TiO_2 nanoparticles in NMP and sonicated for 15 min. Composition of the PVDF/NMP solutions was kept constant at 20:80 by weight percentage. The solution was prepared at 40°C and stirred for 24 h to form a homogenous solution. Before casting, all the PVDF solution was cooled to room temperature in the incubator for 24 h. The polymer solution was then cast (at a nominal thickness of 200 μm) using a thin film applicator (Elcometer 4340) on a flat glass plate that was wrapped with tightly woven polyester fabric (Holleytex 3329, Ahlstrom). The nascent membrane was immediately immersed into the first isopropanol coagulation bath for 2 sec, and then immerse into the second water coagulation bath (called dual coagulation method) for 24 h to allow of the total solidification of the formed morphology as well as to remove the residual solvent. The formed membranes were further dried under ambient condition for 2 days (Ahmad & Ramli, 2013).

3.4 Preparation POME

For this study, Palm Oil Mill Effluent (POME) which obtained from United Palm-Oil Mill, Sungai Kechil, Nibong Tebal is used to recover clean water. The properties are summarized in Table 3.1.

Table 3.1 The properties of POME (Wu, et al., 2007)

Parameter	Mean
pH	4.52 ± 0.05
Total Suspended Solid (TSS) (mg/l)	25,800 ± 1510
Turbidity (NTU)	22,667 ± 1242
Total Dissolved Solid (TDS) (mg/l)	17,033 ± 252
Chemical Oxygen Demand (COD) (mg/l)	70,900 ± 4431
Protein (g/l)	12.9 ± 2.97
Carbohydrate (g/l)	28.9 ± 1.60

3.5 Research Flow Chart

Figure 3.1 shows the flow chart of research study.

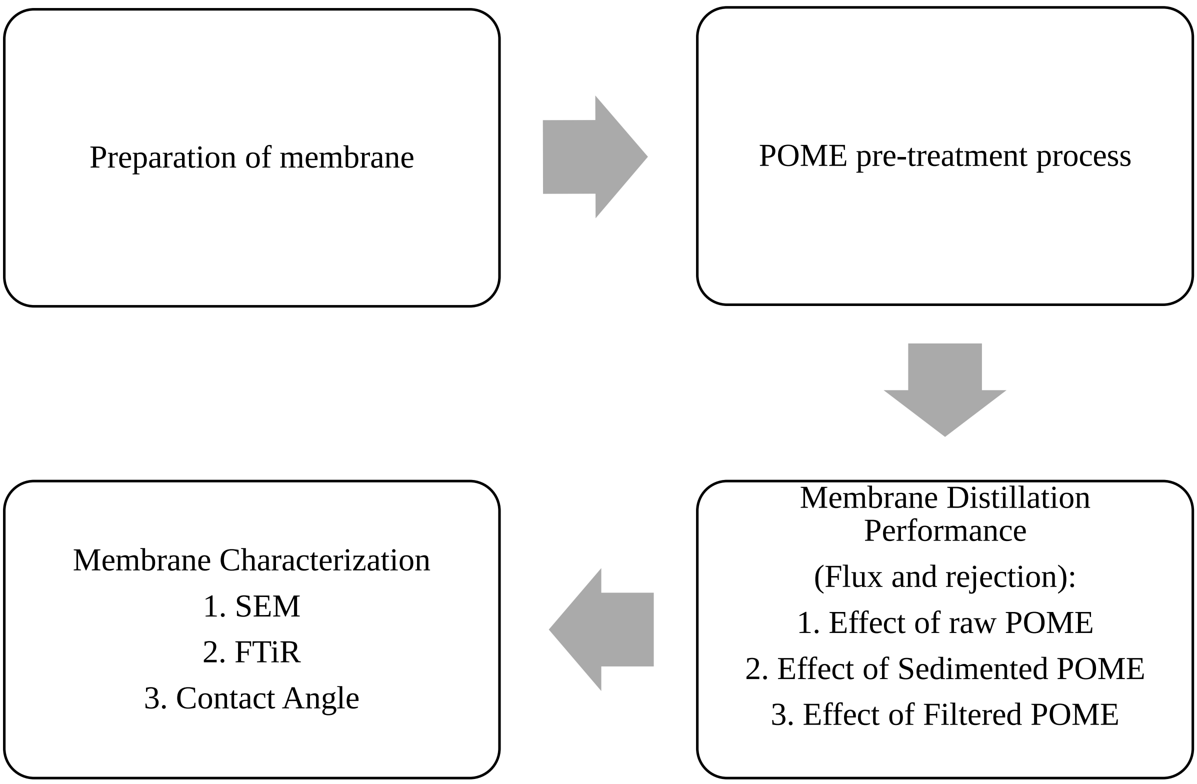

Figure 3.1 Flow Chart of Water Recovery of POME using Membrane Distillation

3.6 Palm Oil Mill Effluent (POME) and its pre-treatment

Raw POME was prepared by taking 500 ml POME and air bubbled to make sure it is well-mixed. Next, the sedimented POME was prepared by allowing 500 ml POME to sediment for 24 hours. After that, the supernatant was harvest and used as feed to the MD system. Lastly, POME is prepared by filtering 500 ml of POME using funnel with filter paper of standard code H with 12.5 cm diameter. The filtrate was then fed to the MD system.

3.7 Membrane performance in a direct contact membrane distillation (DCMD) process

Performance of the membrane distillation (MD) is examined using the direct contact membrane distillation (DCMD) set-up as shown in Figure 3.2. The cell is placed in a horizontal configuration. The hot feed solution (POME) was placed in a water bath with the temperature maintained to 80°C. Both the hot feed and cooling stream (6.2°C) were circulated under the same flow rate (0.5LPM) across the upper and lower part of flat membrane. The amount of permeate was measured using an electrical balance (FX-3000i from A&D Company) and the values was recorded using data acquisition system. Distilled water was used in the cold distillate reservoir.

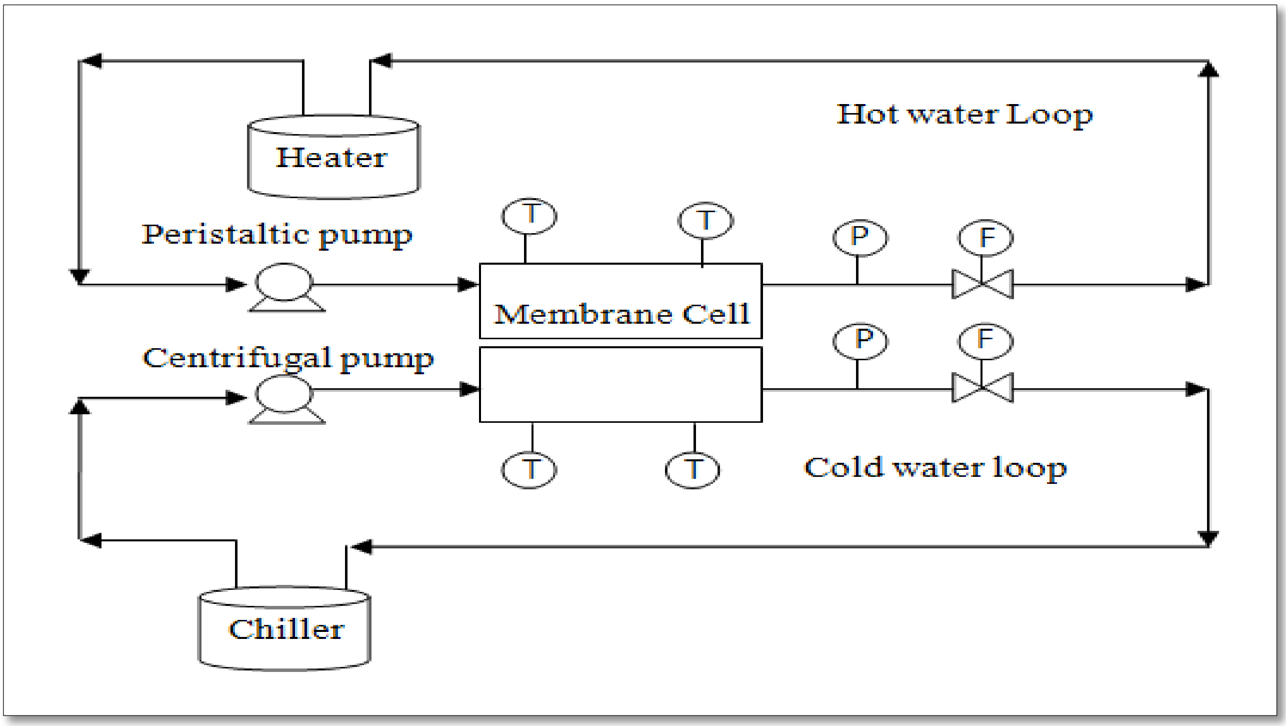

Figure 3.2 The schematic representation of direct contact membrane distillation setup

3.5 Membrane Characterization

3.5.1 Surface morphology of membranes

The morphology of the top surface (the surface in contact with the precipitation bath or the non-solvent) was characterized by using scanning electron microscope (SEM, Crest System (M) Sdn.Bhd, and Quanta Feg. 450).

3.5.2 Pore size distribution and LEPw of membranes

Pore size of the membranes was determined using gas flow/liquid displacement method via Capillary Flow Porometer Porolux 1000 (CNG Instruments). Membrane samples with a diameter of 10mm were characterized using the "dry up–wet up" method. In this method, gas flow was measured as a function of transmembrane pressure, through wetted membrane with porefil (pore size) and water (LEPw).

3.5.3 Membrane wettability

The membrane wettability is characterized by static contact angle of the membrane samples, which was measured, based on sessile drop technique using a DropMeter A-100 contact angle system (Rame-Hart Instrument Co., U.S.A.). The membrane sample was stuck onto a glass slide using double-sided tape to ensure its top surface was upward and flat. A droplet (~13 μL) of deionized water was dropped onto the dry membrane surface using a microsyringe. Immediately, a microscope with long working distance 6.5×objectives was used to capture micrographs at high frequency (100 Pcs/s). The reported contact angles were average values from the measurements taken at 10 different locations on the membrane surface, as a measure to minimize random error.

3.5.4 Fourier transform infrared spectroscopy (FTIR)

The acquired Fourier transform infrared spectroscopy (FTIR) spectra were obtained from the neat PVDF and PVDF/TiO_2 membrane surfaces using an FTIR spectroscopy (Thermo Scientific, Nicolet iS10, USA) to determine the crystallinity based on the peak from the graph. The value of the peak is summarized on Table 3.2. The FTIR spectroscopy was equipped with an OMNI-Sample Attenuated Total Reflection (ATR) smart accessory with diamond crystal operated at 45^{o}. The membranes were undergone 32 scans at a resolution of 4 cm^{-1} within wave number of 4000–400 cm^{-1} (Ngang, et al., 2012)

Table 3.2 Absorption FTIR bands characteristics of α, β and γ-PVDF *(Martins, et al., 2014)*

	α	**β**	**γ**
Wavenumber (cm^{-1})	408	510	431
	532	840	512
	614	1279	776
	766		812
	795		833
	855		840
	976		1234

3.5.5 Permeation flux and COD value measurements

A laboratory scale membrane distillation unit was used to study the permeation flux and solute retention of the hydrophobic membrane by using 500ml of POME as model solution. The porous membrane with different morphology is tightly clamped between two acrylic plates, which were divided into hot and cold flow streams. The cold stream is below the porous membrane while the hot stream is on top of it. The POME solution was circulated in the hot stream under operating temperature of 80^{o}C. While in the cool site, the chiller temperature is kept constant at 19^{o}C. Both liquids were circulated in each cell by two independent pumps at atmospheric pressure. The DCMD flux was calculated, in every case, by measuring the weight of condensate collected in the permeate chamber within a predetermined time. The experimental performances of the membrane were evaluated based on COD value and permeation flux (J) as show in equation (1).

$$J = \frac{\Delta W}{A\Delta t} \tag{1}$$

Where J is the permeation flux ($kgm^{-2}h^{-1}$), ΔW is the quantity of distillate (kg), A is the effective inner surface area of the porous membranes (m^2) and Δt is the sampling time (h).

While for the rejection of nutrient of the membrane, R, the following equation were used to calculate the R value:

$$R = (1 - \frac{VpCp/JwAmt}{Cf}) \times 100\% \tag{2}$$

where V_p is the permeate volume, C_f and C_p are the concentration of feed and permeate, respectively, A_m is the membrane area and t is time (Khayet et al., 2010; Souhaimi, 2011).

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Membrane Characterization before and after POME filtration

4.1.1 Contact angle

Figure 4.1 shows the reduction of contact angle upon POME filtration (raw, sedimented and filtered). TiO_2-PVDF membrane (virgin membrane) has an initial contact angle of 124.7±9°. However, upon of raw POME deposition on the membrane surface the contact angle was reduced to 40.0±6° which is the lowest compared to MD membrane used for sedimented POME (48.1±0.5°) and filtered POME (51.9±2°) treatments. The water contact measurement showed that the deposited POME increased the membrane wettability significantly due the combined adhesion of hydrophilic organic and inorganic $CaCO_3$ on the membrane (Naidu, et al., 2017). While for the filtered POME, it showed that the hydrophilicity of the MD membrane increase slightly to 51.9±2° which prove that suspended particles are relatively hydrophilic.

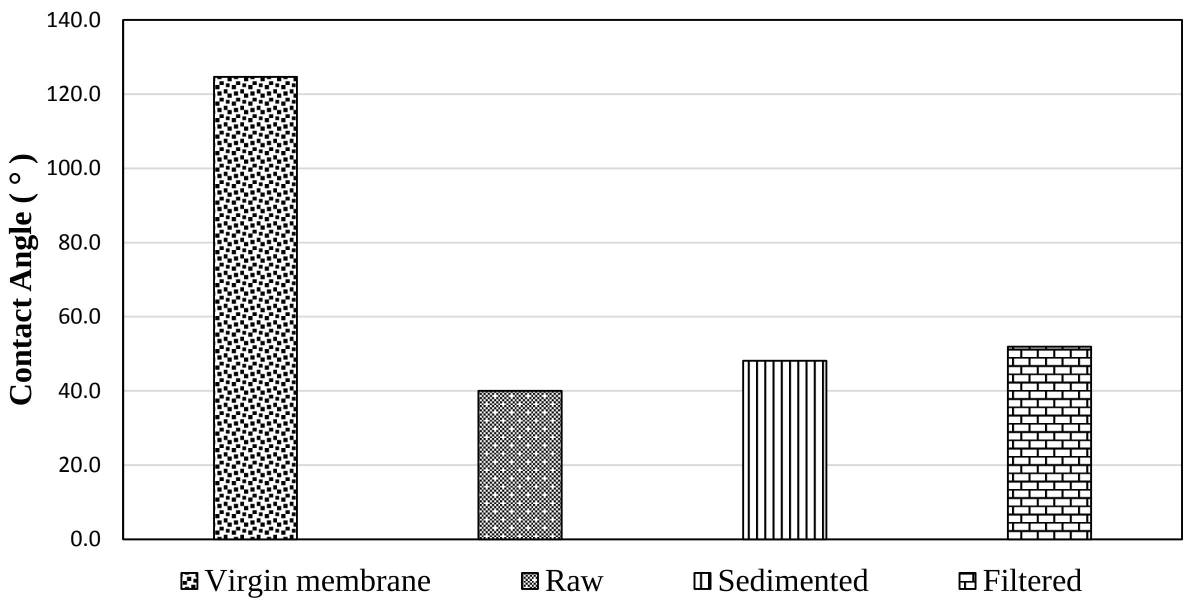

Figure 4.1 Contact angle for membrane

4.1.2 Scanning Electron Microscope (SEM)

The effect of different POME (raw, sedimented and filtered) and their deposition on TiO2-PVDF membrane structure is presented in Figure 4.2. After the membrane being used to treat the raw POME, the structure of the membrane was dramatically changed where a deposit layer (Figure 4.2 (b)) covered almost all the membrane surface.

Figure 4.2 (b) shows the membrane structure after been used to treat sedimented POME. It can be seen that the membrane structure used to treat sedimented POME results almost the same with membrane used to treat raw POME where the membrane surface mainly covered by the deposit layer. There is a slight change on the membrane surface when it used to treat filtered POME as can be seen in Figure 4.2 (d) where the flake size was bigger. Figure 4.2 (d) also shows that the nodular structure of the PVDF is still observable after filtration.

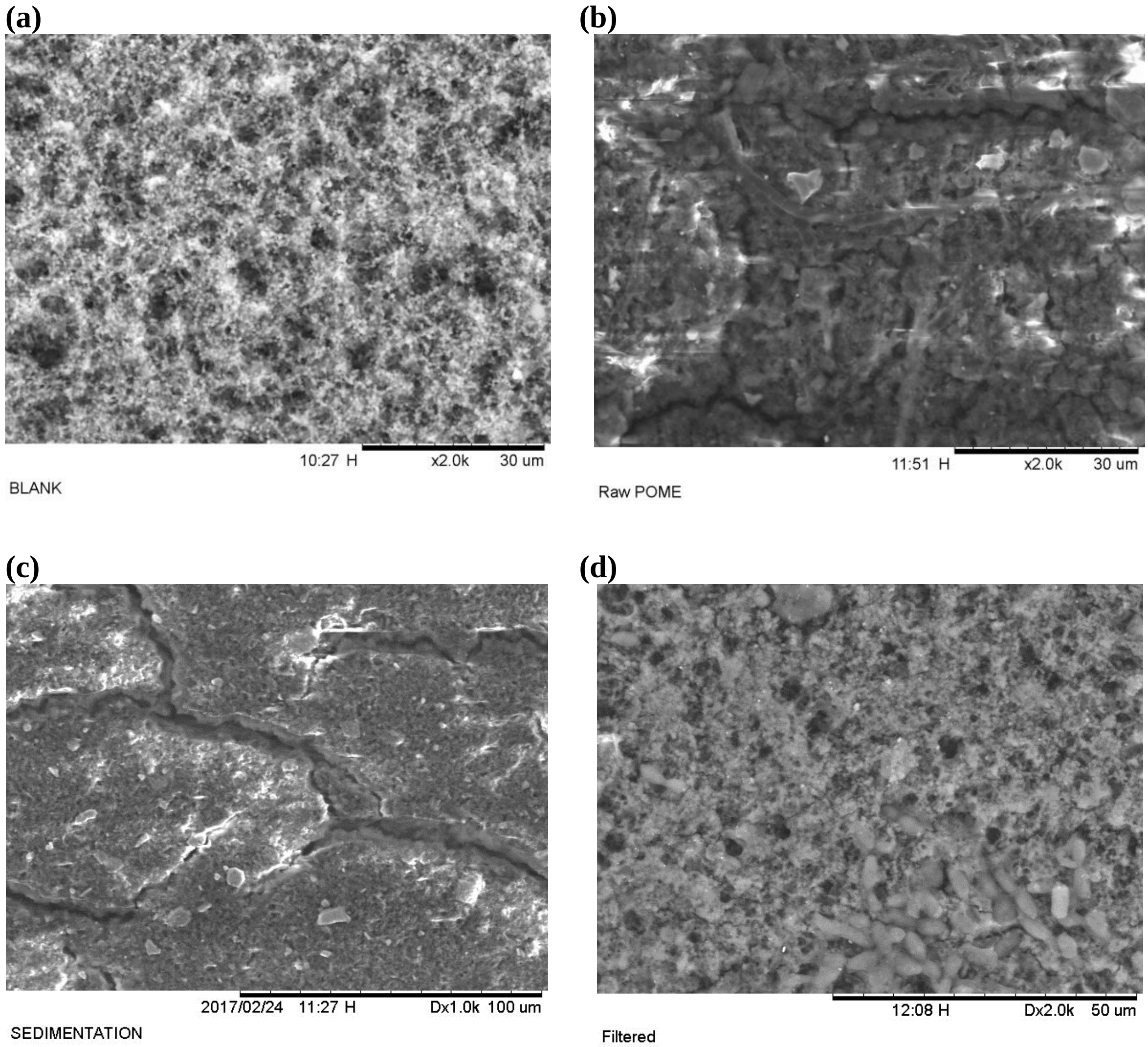

Figure 4.2 SEM top surface for (a) TiO2-PVDF membrane (virgin membrane), (b) Membrane with raw POME, (c) Membrane with sedimented POME, (d). Membrane with filtered POME at 2K magnification