GREYWATER TREATMENT

USING MODIFIED PVDF MEMBRANE

GOH JIAN LOON

UNIVERSITI SAINS MALAYSIA

2022

GREYWATER TREATMENT USING MODIFIED PVDF MEMBRANE

By

GOH JIAN LOON

Report 2 submitted in fulfilment of the requirements

for degree of

Bachelor of Chemical Engineering

July 2022

ACKNOWLEDGEMENT

Firstly, I would like to express my deepest gratitude towards my supervisor, Associate Prof. Ir. Dr. Leo Cheo Peng and his postgraduate student as the co-supervisor, Miss Hong Chia Huey that has guided me through completing this report with their knowledge and experience.

Apart from that, I also would like to thank my family members and friends that have given me the moral support throughout my writing of this report which allows me to keep going on in completing the final year project.

A special thank you to the School of Chemical Engineering, USM for allowing me to use the analytical chemistry laboratory and membrane laboratory for me to conduct my lab works from morning to evening every week. Besides that, a big thank you for preparing the facilities which have facilitated me to complete my work in accordance with my planning.

Once again, I would like to thank all the people that have been involved with me, either directly or indirectly which I may have missed to mention them in the accomplishment of this final year project.

Goh Jian Loon

July 2022

TABLE OF CONTENTS

CHAPTER 4: RESULTS AND DISCUSSION

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

Symbol	Description	Unit
Polyvinylidene fluoride	PVDF	-
Polyvinyl Chloride	PVC	-
Biological oxygen demand	BOD	Mg/L
Chemical oxygen demand	COD	Mg/L
Total suspended solids	TSS	Mg/L
Ethylenediaminetetraacetic acid	EDTA	-

GREYWATER TREAMENT USING MODIFIED PVDF MEMBRANE

ABSTRACT

Lignin is a sustainable substance which can be extracted from a wide range of lignocellulosic biowastes in Malaysia. It can be blended into PVDF membranes to enhance the membrane morphology for oil-water filtration. PVDF polymeric matrix membrane is superb in terms of chemical and thermal stabilities, which make it very promising to be utilised as a membrane matrix for water separation. However, poor hydrophilic property of the PVDF has led to the severe fouling during operation.

Thus, current work is performed to increase the surface hydrophilicity and change surface roughness of the membrane which could reduce membrane fouling and reduce the extent of permeate flux decline. Lignin dissolved in sodium hydroxide solution can be coated with calcium carbonate to improve the surface hydrophilicity which correlate the membrane fouling and change the surface roughness of the membrane which correlate the flux decline.

In this work, the polyvinylidene fluoride (PVDF) membrane was coated with lignin and calcium carbonate to improve the filtration of oil water emulsion. 0.75wt. % lignin dissolved in 0.5wt. % sodium hydroxide solution with varied calcium carbonate concentration (1wt. %, 3wt. % and 5wt. %). Surface modification permits the enhancement of membrane properties without affecting the existing membrane formulation.

Membrane characterizations were performed using contact angle goniometer, RS Weight and UV-vis spectrophotometer to determine the water contact angle, permeate flux and percent of oil rejection respectively.

In conclusion, the lignin-CaCO3 modified membrane rejected up to 99.50% of oil, the lignin modified membrane rejected up to 94.5% of oil and the neat PVDF membrane only rejected 83.30% of oil. The water contact angle as measure by the water angle goniometer of the lignin-CaCO3 modified membrane is much lesser than that of lignin modified membrane. The water contact angle is less than 90 degree. This implies that the membrane is hydrophilic.

Modified PVDF membrane is capable of rejecting up to 99.5% of oil which implies that it could be an ideal solution to remove the oil particulates from the greywater which comes mainly from baths, showers, hand basins, washing machines, dishwashers and kitchen sinks. Oil removal from greywater is a must before discharging as it can interfere with biological life in surface water and create unsightly films. Oil enter the drainage system and mix with other sanitary waste, congeal and harden in the pipe. Also, oil can cause unpleasant odors when mix with other substances in the water and can result in sewer overflows due to reduced capacity or burst drain,

CHAPTER 1

INTRODUCTION

1.1 PVDF membrane

According to the world population clock, the number of people on earth exceeded 7.5 billion in year 2017 and is projected to reach 10 billion by year 2050. There are vast amount of water around the globe but pure drinking water is a major problem all around the world especially for the developing and undeveloped countries. Improving the efficiency and reducing the cost of water treatment are main obstacles that need to be combat in order to overcome the scarcity of portable water.

Oily wastewater resulting from the oil extraction process comprises of different types of hydrocarbon such as benzene, phenols, humus and polycyclic aromatics [39, 40, and 41]. Treatment of this wastewater is a must prior to release into the environment to avoid the pollution on the water bodies such as seashore, estuaries, rivers, soil, and even the air via organic content [43]. Membrane technology has been utilized extensively to filter organic substances, such as dissolved oil in untreated oil field wastewater [44].

In the United States of America, the volume of oily wastewater generated annually is estimated to be 33 billion barrels for oil and gas onshore, which cannot be re-injected to oil wells or discharged to the environment. This is because they contain high amounts of different type organic materials [45, 46]. According to the Clean Water Act (CWA) of the United States of America, the grease and oil concentration in discharge water should not be more than 15 ppm. Hence, the particles and oil droplets treatment from oil-field wastewater is required prior to discharging or reusing the water [47, 48, 49].

Conventional techniques in wastewater treatment such as coalescer plates and gravity separators are incapable of producing highly purified water for environment discharging or re-injection purposes. Recently, there are many researchers have attempted to enhance the process in this approach. Membrane ultrafiltration (UF) has been used in wide number of cases efficient treatment for oil-field wastewater. However, in the long-term process ultrafiltration membranes may not be ideal enough to productively treat oil-field wastewater. [50]

This is due to the fact that membrane can be easily fouled which lead to membrane flux drop directly, as a result of oil adsorption and accumulation of rejected oil, suspended solids, and other components of oil-field wastewater on the membrane surface (external fouling) or in the membrane pores (internal fouling) [51, 52, 53, 54]. Hence, several techniques were used to produce anti-fouling in replacement of UF membrane for the long-term process. [55] One of the recent techniques is modified PVDF membrane.

The usage of polyvinylidene fluoride (PVDF) as membrane materials is becoming more prevalent owing to its outstanding properties including thermal stability, chemical resistance and excellent mechanical strength. In addition to that, PVDF is stable when attacked by corrosive chemicals and organic compounds such as acids and oxidants. [9] Nevertheless, membranes made from PVDF might be susceptible to fouling owing to the material's strong hydrophobicity. The significance and promising applications of PVDF membranes include water treatment such as production of drinking water, wastewater treatment, and pre-treatment for reverse osmosis systems. [9]

Conventional PVDF membrane can achieve up to 83.3% percent rejection of oil whereas lignin modified membrane can reject up to 99.3 % of oil. Surface modification permits the enhancement of membrane properties without affecting the existing membrane formulation. [14]

In order to improve the surface hydrophilicity on the hydrophobic PVDF membrane, nanoparticles or lignin dissolved in alkaline solution can be used. The fouling constituents often present in water source are organics which readily attach to a hydrophobic surface. In another words, hydrophobic surface can be easily fouled. Lignin dissolved in sodium hydroxide solution can be coated with calcium carbonate to improve the surface hydrophilicity which correlate the membrane fouling and change the surface roughness of the membrane which correlate the flux decline.

Figure 1 depicts the effect of membrane modified with hydrophilic material.

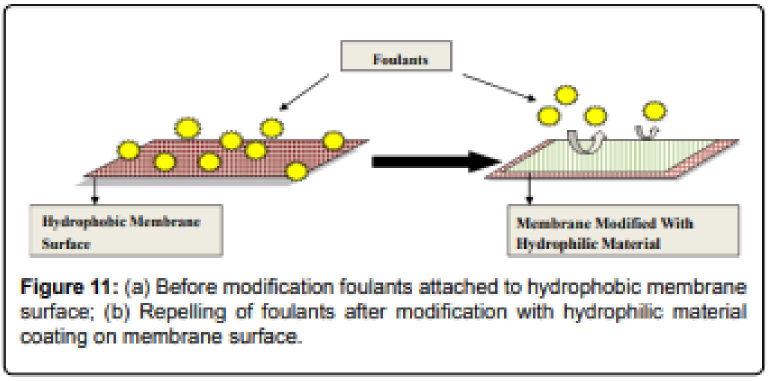


Figure 11: (a) Before modification foulants attached to hydrophobic membrane surface; (b) Repelling of foulants after modification with hydrophilic material coating on membrane surface.

***Figure 1**: Schematic diagram of fouling on hydrophobic membrane (on the left) and repelling of foulants on modified membrane [13]*

1.2 Problem Statement

PVDF membrane has been used extensively in many applications especially in wastewater treatment applications. Up to this date, modified PVDF membrane are becoming more prevalent. There are various materials that can be used to modify PVDF membrane for wastewater treatment.

Lignin dissolved in NaOH solution and calcium carbonate as modified PVDF membrane could be a potential candidate for greywater treatment. This is because lignin dissolution in sodium hydroxide and calcium carbonate can change the surface roughness and surface hydrophilicity which indirectly affect the flux decline and membrane fouling. Also, lignin is a sustainable chemical that can be extracted from wide array of lignocellulosic bio-waste.

1.3 Research Objectives

There are several detailed objectives to answer the identified problem statement.

1. To modify the PVDF membrane using lignin/calcium carbonate.
2. To study the effect of calcium carbonate on the separation performance of PVDF membrane coated in lignin/calcium carbonate.

CHAPTER 2

LITERATURE REVIEW

2.1 Grey water

Grey water can be defined as the urban wastewater that comprises of water from baths, showers, hand basins, washing machines, dishwashers and kitchen sinks but excludes streams from toilets Grey water contains coarse particles, oil, food residues, shampoo, hair, tooth paste, detergent, soap and etc. [8] Due to low levels of contaminating pathogens and nitrogen, grey water can be reused and recycle.[18] Grey water characteristics are highly variable because of living habits of the people involved and the products they used. [6] Some of the characteristics of greywater reported in different studies is tabulated in Table 1 as shown below.

Table 1: *Characteristics of greywater reported in different studies*

Parameter	Reference					
	[16]	[15]	[4]	[3]	[1]	[17]
pH	6.3-7.1	-	-	-	6.3-7.0	-
Turbidity (NTU)	85	-	-	-	32	29
Oil and Grease (mg/L)	7	-	-	-	-	-
BOD (mg/L)	37-69	59-149	50-100	95	280-690	167

COD (mg/L)	101-143	92-322	100-200	270	700-890	-
TSS (mg/L)	-	-	1389	-	85-286	-

Table 2 presents some of the biological parameters in the greywater together with their concentrations reported in different studies.

***Table 2**: Biological characteristics of greywater in different studies*

Name of microbe	Concentration (counts/100ml)	References
Total coliforms	1.2 X 10^3- 8.2 X 10^8	[32]
E.coli	Up to 6.5 X 10^6	[33]
Faecal coliforms	Up to 1 X 10^6	[34]
Pseudomonas aeruginosa	1.4 X 10^4	[35]
Staphylococcus aureus	1.2 X 10^2 – 1.8 X 10^3	[36]
Salmonella typhi	5.4 X 10^3	[37]
Salmonella spp.	3.1 X 10^3	[38]

2.2 Recent PVDF membrane progress in greywater treatment

Recent progress of PVDF membrane in greywater treatment is tabulated in Table 3 as shown below.

***Table 3**: Recent progress of PVDF membrane in greywater treatment*

Process	Removal efficiency	Membrane characteristics, operation condition	Membrane Performance	Reference
Aerobic membrane bioreactor	77-78% of COD removal	Flat sheet PVDF membrane, 0.1 μm of pore size	Transmembrane pressure increased to 0.5–0.6 bar within 12 h	[12]
Aerobic membrane bioreactor	90.6–99.7% of COD removal, 93.7–99.6% BOD5 removal, N98.2% of TSS removal.	Hollow fiber PVDF membrane, 0.04 μm of pore size.	Not reported	[10]
Aerobic membrane bioreactor	75–100% of COD removal, 98–100% of TSS removal	Hollow fiber PVDF membrane, 0.04 μm of pore size.	No fouling was observed during 24 days	[11]

2.3 PVDF membrane

PVDF is a semi-crystalline polymer comprises of 59.4 wt. % fluorine and 3 wt. % hydrogen, with a glass transition temperature of approximately 234 K, melting temperature of about 433 K and a thermal decomposition temperature of above 589 K. The macromolecular linear chain structure of PVDF is $–CH_2CF_2-$ (the bond energy of C-F, C-H and C-C is 453 kJ/mol, 414.5 kJ/mol and 347.5 kJ/mol respectively). The polymer structure is considered to be one of the promising membrane material owing to its thermal stability, high chemical resistance against corrosive chemicals, mechanical strength and membrane forming ability. PVDF is capable of dissolving in various polar solvents such as N, N-dimethylacetamide, and dimethyl sulfoxide, N, N-dimethylformamide and N-methyl-2-pryyolidone because of the polar property. [19-22]

However, PVDF membrane is a naturally hydrophobic membrane because of its low surface-energy and critical surface tension. The contact angle formed between liquid-gas tangent and membrane-liquid boundary determine the hydrophilic-hydrophobic properties of the membrane. A contact angle less than 90° indicates hydrophilic behaviors whereas contact angle more than 90° implies that the surface is hydrophobic. [22]

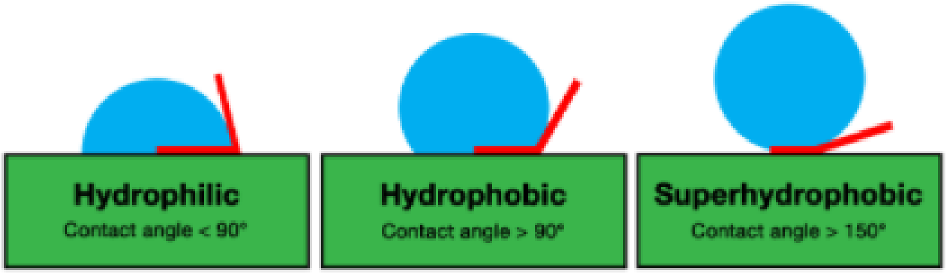


***Figure 2**: Schematic illustration of water contact angle on hydrophilic-hydrophobic properties*

Hydrophobic membrane could be easily fouled. The fouling constituents often present in water source are organics which readily attach to a hydrophobic surface. [7] There are various drawbacks of membrane fouling which includes decline in permeation flux and reduction in membrane life during filtration operation. [23] The major reason for hydrophobic membrane fouling with organic compounds and microorganisms is that there are almost zero hydrogen bonding interaction between the membrane interface and water in the boundary layer. [24]

Foulants molecules have a high tendency to adsorb onto the membrane surface and dominate the boundary layer is because of the repulsion of water molecules from the hydrophobic membrane surfaces. When the fouling advances, membrane flux declines. Hence higher operating pressure is required and more energy must be expended to achieve the desired throughput. [24, 25]

In contrast, hydrophilic membrane has a high surface tension and is capable of forming hydrogen bonding with the surrounding water molecules. This reconstruct a thin water boundary between the membrane and bulk solution. This later can prevent or reduce the amount of pollutants such as microbes and organic molecules from adhering to the membrane surface. [26]

2.4 Modification of PVDF membrane

Fouling can be reduced by surface modification of PVDF membrane by coating hydrophilic layer of various nanoparticle on its surface via crosslinking or physical adsorption.[13] Different nanoparticle such as Fe, Alumina, Graphene oxide, mesoporous silica, GO-Ag Silver, Zinc Oxide, Cooper, Titania, Zeolite, Iron Oxide, Zirconium are used in surface modification with improved antifouling properties, higher flux and salt rejection. [2]

Besides that, lignin dissolved in sodium hydroxide solution can also be used to modify the PVDF membrane for improving surface hydrophilicity which can reduce fouling. The PVDF membrane are modified with lignin content, NaOH solution and varied concentration of calcium carbonate. [14]. In order to increase the surface hydrophilicity and change surface roughness of the membrane which could reduce membrane fouling and reduce the extent of permeate flux decline, lignin is dissolved in sodium hydroxide solution can be coated with calcium carbonate. Surface hydrophilicity correlates the membrane fouling and surface roughness of the membrane correlates the flux decline.

2.5 Lignin modified membrane

***Table 4**: Recent lignin modified membrane*

Method	Effects	Reference
Blending of lignin into polyvinyl chloride (PVC) dope solution	Chemical oxygen demand (COD), oil rejection and suspended solid removal of PVC membrane increases	[29]
Lignin as addictive in fabrication of polyethersulfone (PES) membrane	Rejection of organic pollutants decreases and water permeability increase.	[30]
Blending of peanut shell powder comprises of lignin into polysulfone (PSf) membrane	Higher water permeability	[31]

2.6 Surface modification methods

The advantages and disadvantages of each modification methods are tabulated as shown in Table 5.

***Table 5**: Advantages and disadvantages of each modification methods [28]*

Modification method	Flux after modification	Simplicity	Reproducibility	Environmental aspects	Cost effectiveness
Coating	Medium	High	High	High	High
Composites	High	High	Low	High	High
Grafting by chemical	High	High	High	Low	High
Grafting by radiation	High	Low	Low	Low	High
Grafting by plasma	High	Low	Low	High	High
Combined methods	Low	Low	High	Low	High

There are various methods that can be used to enhance the hydrophilicity of the PVDF membranes including blending, co-polymerization, surface grafting and surface coating. Compared with these methods, surface coating has attracted mounting interest owing to its high efficiency, simple and high-usage. [27]

Coating is a method wherein the coating material forms a thin layer that non-covalently adheres to the substrate. In other words, the membrane is dipped into polymer-containing solution in order to improve the hydrophilicity and antifouling property of existing membrane.

Poly (vinyl alcohol) (PVA), chitosan and poly (ether block amide) (PEBAX), lignin are hydrophilic polymers that are commonly used for hydrophilic modification of PVDF membranes. [27]

CHAPTER 3

METHODOLOGY

3.1 Research Flow

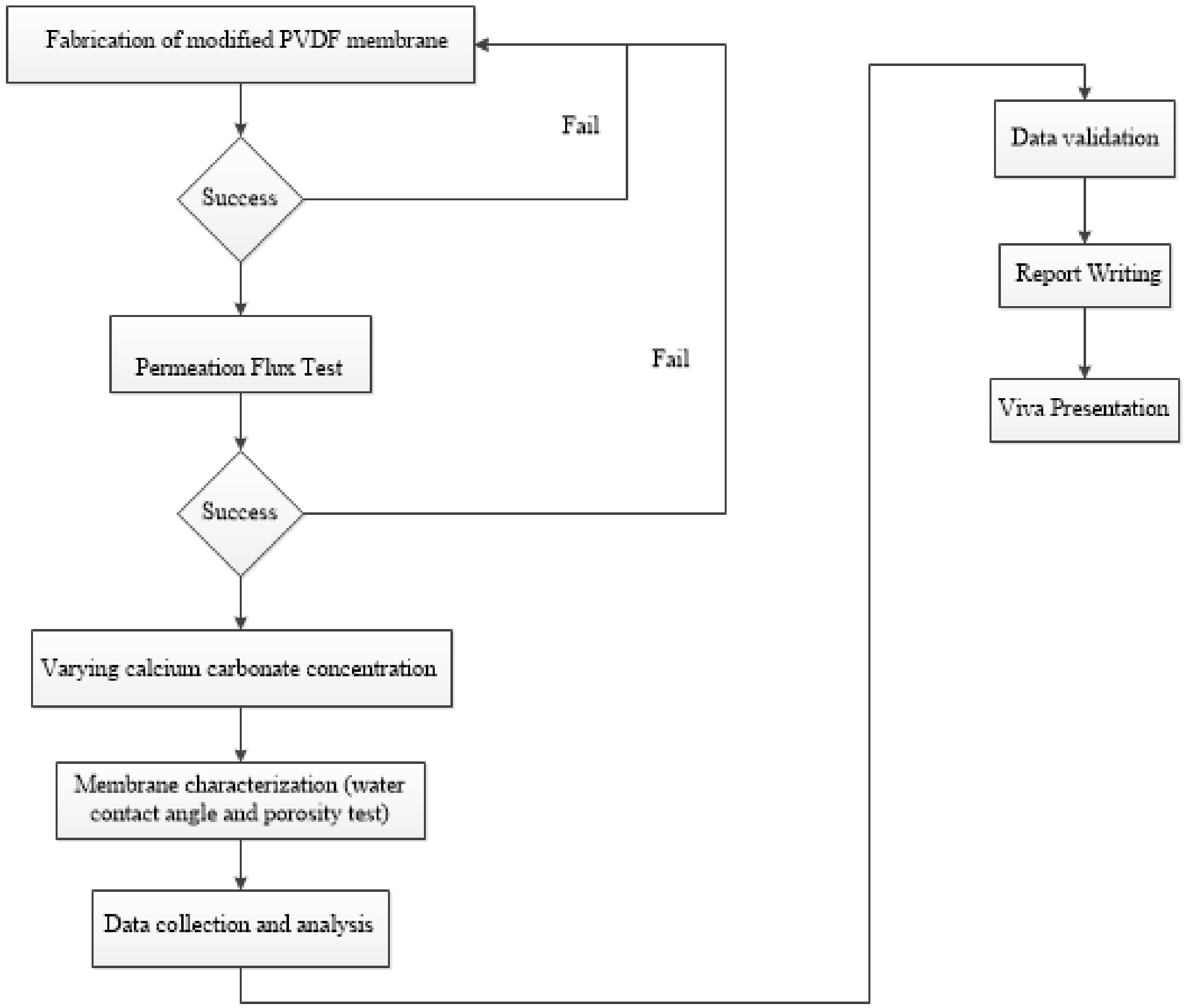


***Figure 3**: Schematic diagram of research flow*

3.2 Membrane Modification Procedures

First and foremost, 23 pieces with length of 70 cm of PVDF membrane was cut from bundles of PVDF membrane. Next, 1000 ml of ethanol solution was prepared to wash the PVDF membrane. The PVDF membrane was then immersed in 1000 ml of ethanol solution to ensure there are no contaminants inside the PVDF membrane. PVDF membrane was left aside for 30 minutes. Lignin solution was prepared by dissolving the 0.75wt% of lignin into 0.5 wt% sodium hydroxide solution as depicted in Figure 3. 0.75wt% of lignin with 0.5 wt% sodium hydroxide solution acts as the control of the experiment. Lignin used is from BOSF and country of origin is Brazil. The PVDF membrane is bought from China.

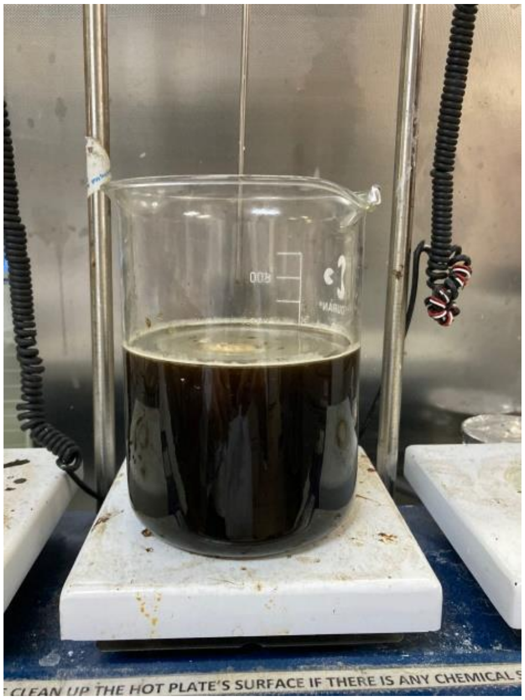


***Figure 4**: Lignin solution*

Lignin-CaCO3 solutions were prepared by dissolving the 0.75 wt. % of lignin and different concentration of CaCO3 (1 wt. %, 3wt. % and 5wt. %) into 0.5 wt. % sodium hydroxide solution as shown in Figure 4. 23 pieces of PVDF membrane is then immersed into lignin solution and lignin-CaCO3 solution respectively for 24 hours.

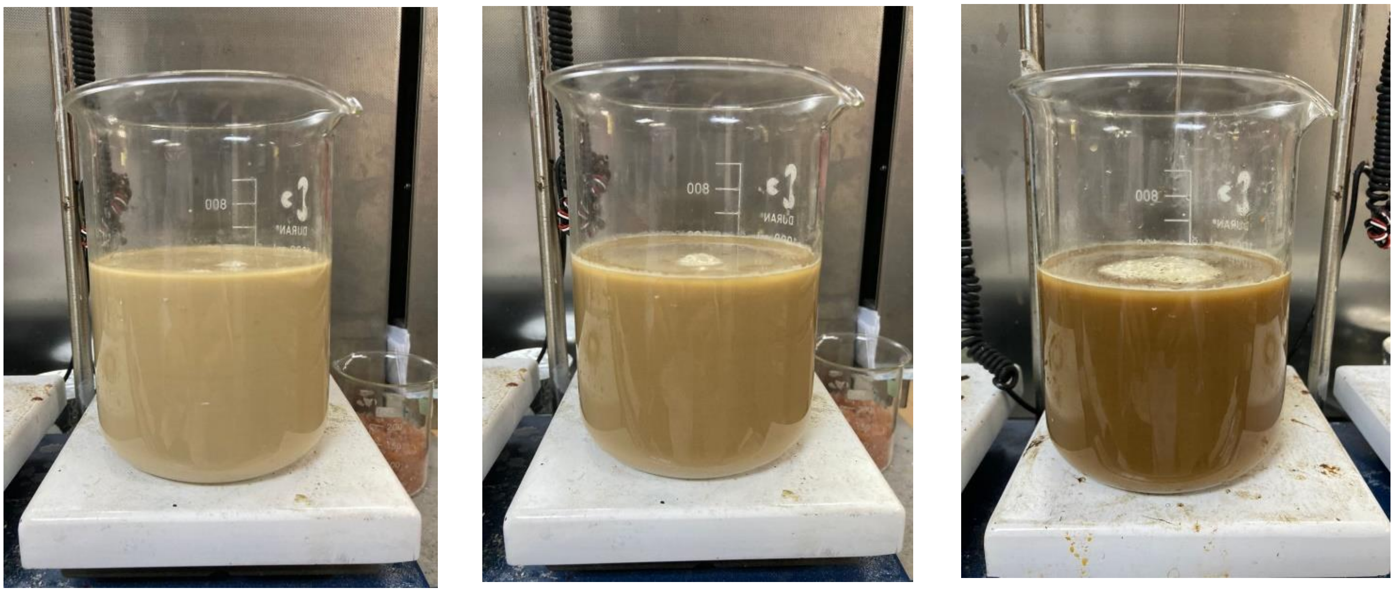


***Figure 5**: Lignin-1wt. % CaCO3 solution (left), lignin-3wt. % CaCO3 solution (middle) and lignin-5wt. % CaCO3 solution (right)*

Last but not least, the modified membrane was then rinsed with deionized water and dried for 24 hours by clamping the modified PVDF membrane on retort stand. The setup is shown as in Figure 6.

***Figure 6**: Drying of modified PVDF membrane*

3.3 Oil Water Emulsion Preparation

Firstly, oil and water were mixed together in the ratio of 1:100 ml. Three drops of tween-80 was added into the oil-water solution. Next, the solution was then sonicated for 15 minutes and stirred using magnetic stirrer for 15 minutes. The oil used can be retrieved from 99 Speedmart, the brand name is Mazola and it comprises of 100 % corn oil. The oil-water emulsion was used to simulate real life greywater .

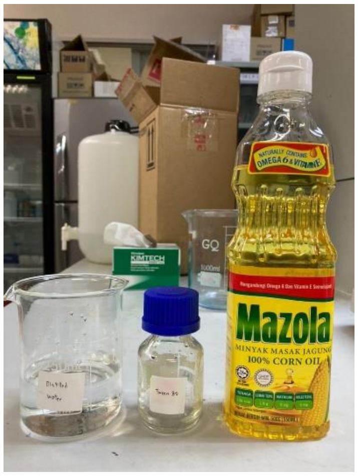


***Figure 7**: Distilled water, Tween-80 and oil*

3.4 Membrane Fabrication

Firstly, epoxy glue was prepared by mixing epoxy resin and epoxy hardener in 1:1 ratio. The epoxy glue used was bought from Shopee, the brand name is Araldite epoxy glue.

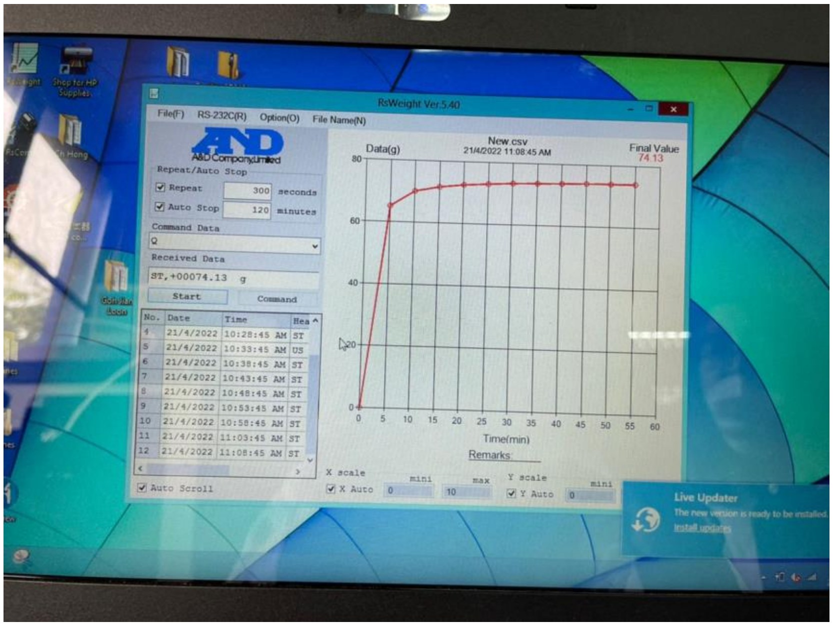
***Figure 8**: Araldite epoxy resin and epoxy hardener*

Next, 20 pieces of dried modified PVDF membrane was then glued at the PVC pipe using epoxy glue while 3 pieces of dried modified PVDF membrane was kept for membrane characterization. The epoxy glue was applied on every pieces of PVDF membrane and on the PVC pipe. Then, the PVDF membrane was dried for approximately 2 hours as shown in Figure 8.

***Figure 9**: Drying of modified PVDF membrane on PVC pipe after applying epoxy glue*

3.5 Permeate flux test

Firstly, 25 ml of emulsion solution was collected as before filtration sample and another 75 ml of emulsion solution was passed through the modified PVDF membrane in the pipe. The permeate flux of the solution was determined by using RSWeight computer software. A graph of flow versus time was shown as in Figure 9. As an alternative, the permeate flux can also be determined at home. For every 5 minutes, the weight of the beaker was determined till 120 minutes.



Repeat/Auto Stop
☑ Repeat 300 seconds
☑ Auto Stop 120 minutes
Command Data: Q
Received Data: ST,+00074.13 g
Final Value 74.13

No.	Date	Time	Hea
4	21/4/2022	10:28:45 AM	ST
5	21/4/2022	10:33:45 AM	US
6	21/4/2022	10:38:45 AM	ST
7	21/4/2022	10:43:45 AM	ST
8	21/4/2022	10:48:45 AM	ST
9	21/4/2022	10:53:45 AM	ST
10	21/4/2022	10:58:45 AM	ST
11	21/4/2022	11:03:45 AM	ST
12	21/4/2022	11:08:45 AM	ST

☑ Auto Scroll
X scale: ☑ X Auto, mini 0, max 10
Y scale: ☑ Y Auto, mini 0

***Figure 10**: Graph of flow versus time measured using RSWeight*

3.6 Diffusivity test

Before filtration sample, after filtration sample and distilled water were collected and transferred to cuvette as shown in Figure 10. Diffusivity test was conducted by using UV spectrophotometer to observe the absorbance of each solution as shown in Figure 11. If the diffusivity test and flow rate is not ideal, the membrane needs to be refabricated.

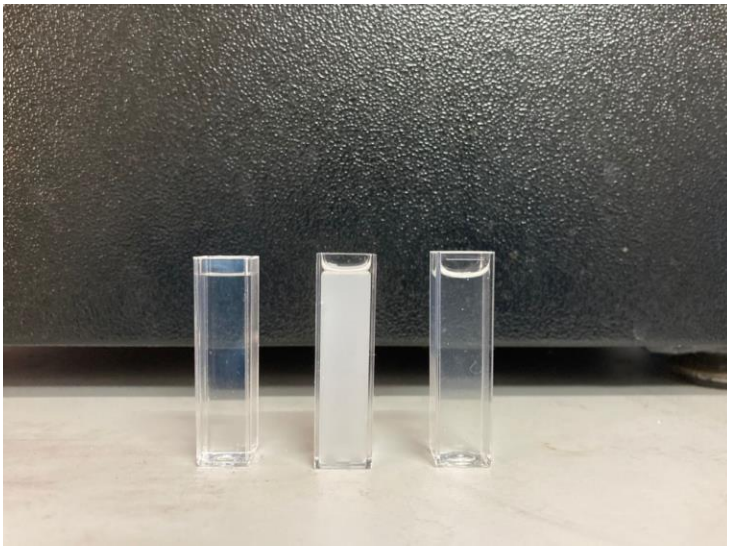


***Figure 11**: After filtration sample (left), before filtration sample (middle) and distilled water (right)*

***Figure 12**: UV-Vis spectrophotometer in analytical chemistry laboratory*

3.7 Water contact angle test

The water contact angle is determined using the water angle goniometer with sessile drop method. An automated syringe is used to drop a droplet of constant volume deionized (DI) water onto the surface of the membrane at room temperature. The step is repeated for 3 times at different spots of the membrane surface and the average value is calculated.

The instrument comprises of a few key components which includes a tilting stage, a monochromatic light source, and high resolution camera and contact angle analysis software. The high resolution 1920 X 1080 camera is capable of capturing up to 30 frames per second which permits for in-depth analysis in the software. The manual focusing lens implies that on have complete control over the sharpness of the image. The camera lens can be twisted to focus on the sample. The powerful monochromatic backlight helps the software to detect the edges of the water droplet accurately. The adjustable sample stage makes it easier to retrieve a level surface and prevent the water droplet from moving during deposition. The stage can be lowered and raised without affecting the level. [56] The captured image by the water angle goniometer was shown in Figure 12.

Water angle goniometer	
Brand	**CYEEYO**
Model	**CY-JCJ01**
Country of origin	**China**