SUPERHYDROPHOBIC PVDF/NMP-$CaCO_3$ NANOPARTICLES MEMBRANE FOR MEMBRANE FILTRATION OF OIL-WATER SEPARATION

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by

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LIST OF ABBREVIATIONS

PVDF	Polyvinylidene difluoride
NMP	N-methyl-2-pyrrolidne
$CaCO_3$	Calcium Carbonate
UV-Vis	Ultraviolet-Visible
PET	Polyethylene Terephthalate

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ABSTRAK

Kalsium karbonat, $CaCO_3$, telah digunakan secara luas di pelbagai membran aplikasi seperti dalam proses penyulingan membran dan penapisan membrane. Bahan ini selalu digunakan dalam pelbagai asas membrane seperti membrane PVDF yang mana penambahan bahan ini akan menaiktarafkan morfologi sesebuah membrane dalam proses tertentu. Membran PVDF dikenali sebagai salah satu nenbran yang mempunyai ciri-ciri hidrofobik, jadi untuk meningkatkan prestasi siri-siri ini, penambahan bahan kimia yang lain boleh membantu. Membran PVDF menunjukkan kebolehan pencantuman yang tinggi yang mana mampu untuk menghalang protin untuk melalui membran tersebut. Tambahan lagi, dalam projek kajian ini, eksperimen telah dijalankan untuk mengubah ciri-ciri hidrofobik membrane PVDF kepada *superhydrophobic* membrane dengan penambahan $CaCO_3$ nanopartikal. Dengan penambahan ini, sudut darjah air, tahap keliangan dan akan menambahbaikkan tujuan untuk menapis minyak. Dalam projek ini, kepekatan nanopartikel yang berbeza akan digunakan yang mana jurang nilainya bermula dari (1-6 wt%) dengan menggunakan peratusan berat untuk pelarut NMP yang sama.

Pengkarakteran membrane ini dijalankan dengan menggunakan sudut darjah air, tahap keliangan dan peratusan penolakan minyak. Campuran $CaCO_3$ yang berbeza kepakatan menyebabkan sudut darjah air untuk mempunyai nilai darjah yang bermula dari 148.5º hingga 154.6º yang mana nilai ini menunjukkan bahawa membran ini mempunyai ciri-ciri *superhydrophobic*. Tahap keliangan membrane untuk semua membrane telah menunjukkan nilai lebih daripada 80% yang mana menunjukkan penambahan nanopartikal ini telah menyebabkan morfologi membran itu berubah. Peratusan penolakn minyak yang paling tinggi adalah 101.1%.

Dalam kajian projek ini, semakin tinggi kepekatan jumlah $CaCO_3$, tidak akan menghasilkan membran yang mempunyai kadar penolakan munyak yang bagus disebabkan oleh peningkatan jumlah partikal minyak yang masuk ke dalam liang-liang membrane. Oleh sebab itu, kami menyatakn bahawa penambahan $CaCO_3$ nanopartikal ke dalam membrane PVDF menunjukkan hasil yang mempunyai potensi dalam proses penapisan minyak daripada pembuangan dengan penambahbaikkan dari segi ciri-ciri *antifouling* dan kekuatan mekanikal membrane.

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ABSTRACT

Calcium carbonate, $CaCO_3$, have been used widely for the application of membrane such as membrane distillation and membrane filtration. It is often used in various kind of membrane based like PVDF membrane which the priority of this introduction is to improve the morphology of the membrane to be used in particular process. PVDF membrane is known one of the membranes that have the hydrophobic properties but in order to enhance these properties, addition of other chemical substances can be helpful. PVDF membrane also possess high binding capacity which can prevents protein to pass through the membrane. Furthermore, in this research project, experiment have been conducted to change the hydrophobicity of PVDF membrane to have the ability of superhydrophobic membrane properties by addition of $CaCO_3$ nanoparticles. This addition will cause changes in water contact angle, porosity and also improve our target to do filtration for oily wastewater. In this project, different concentration of $CaCO_3$ was used which ranged from (1-6 wt%) with constant weight percent of NMP solvent.

Membrane characterization were performed using the water contact angle, membrane porosity and oil rejection percentage were calculated. The mixture of different concentration of $CaCO_3$ causes the water contact angle to be range from 148.5º to 154.6º which gives the membrane a superhydrophobic properties. Membrane porosity for all membrane showed value more than 80% which indicates the addition of nanoparticles does change the morphology of the membrane. The highest oil rejection from membrane was 101.1% which showed that the addition of nanoparticles will increase the superhydrophobic properties of the membranes. In this research project, the higher the concentration of nanoparticles, does not produce better oil rejection of the membrane due to the increasing of the oil particles in the membrane pore. Thus,

we conclude that introducing of $CaCO_3$ nanoparticles in PVDF membrane have promising results in oily wastewater filtration with inserting more antifouling properties and mechanical strength.

CHAPTER 1

INTRODUCTION

1.1 Oil-water Separation

Oil spillage news to the environment have already been in the news each year and this incident can leads to a serious damage to the living things either in the aquatic or in the forest itself. As for the recent years, it is reported on 2nd May 2019 by the Earth and Sea Observation System (EASOS) Marine Watch system from the Malaysian government, there was oil spill happens located roughly 11km off the coast of Johor which measuring around 5km^2 in area and could have been affecting the coastal town of Bandar Penawar within days (*Marine Watch: Preventing Oil Spill Disaster In Johor CASE STUDY CASE STUDY*, n.d.). Besides that, there is considerably amount of oil release from processed industry such as petroleum refining, food, textile, steel and aluminum industries (Usman et al., 2021). It is also stated in an article, the discharge of the oil towards the environment can contaminates the biotic and aquatic environment which results in destroying its ecosystem (Usman et al., 2021). Because of these incidents, there has a lot of researched and studied have and still being carried out to prevent damage towards the environments. Because of significant differences in physical properties of oil and water such as its densities and conductivities, there have been many conventional methods that are being used such as gravity sedimentation, centrifugation, electrolytic separation, adsorption separation and biodegradation have been introduced. The drawback of these conventional method is that it is high cost in terms of energy, large area required to install, can lead to secondary pollutants to be generated and rather inefficient in preventing oil diffusion (Usman et al., 2021) (Liu et al., 2018).

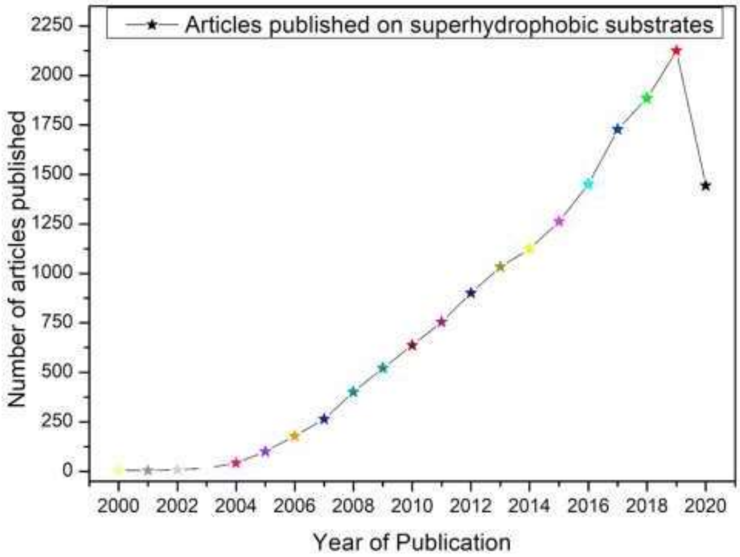

Figure 1 1: Articles publication on superhydrophobic membrane

As early in 2004, filter membrane with superhydrophobic membrane properties have been used in the oil-water separation process. Figure 1 shows the statistical publications of superhydrophobic properties from 2000 to 2020. For a substance or component to be called as superhydrophobic is the substances must show contact angle of 150º with water and have low sliding angle or low contact angle hysteresis and also an oil contact angle of below than 5º (Eom et al., 2013; Usman et al., 2021). Hysteresis is the dependence of the state of a system on its history.

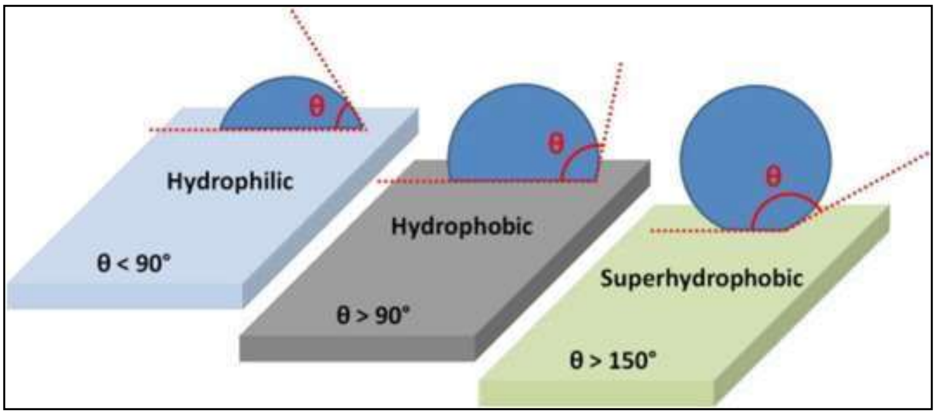

Figure 1 2: Water contact angle of superhydrophobic membrane

Since the superhydrophobic membrane is highly permissible to other substance than water, it must have a high anti-fouling property, and can have advantages in withstand a high temperature, pH, and chemical so that the oil-water separation process can be carry out efficiently.

1.2 Research Objectives

I. To synthesize and characterize the PVDF membrane.

II. To fabricate the PVDF membrane with $CaCO_3$ nanoparticles

III. To analyze oil-water filtration efficiency.

CHAPTER 2

LITERATURE REVIEW

2.1 Treatment of oily wastewater

Various techniques and process has been proposed for treatment of oily wastewater for the past years in physical, biological, and chemical aspects such as centrifugal separation, floatation, skimming and dissolved air flotation, coagulation-floatation, filtration, membranes process, evaporation, adsorption and advanced oxidation. In the past studies, as researched by (Zhong et al (2003), they have developed a study on the oil that are collected from a petrochemical plant in China with a combination of process of treatment for oil removal from wastewater which are microfiltration and flocculation. This shows that, the process of removing oil from wastewater can comes in sequence of steps and not only comes from a single step process. Furthermore, the observation of this literature review is further discussed in this report which presented the physical treatment, chemical treatment and also mechanical treatment.

2.1.1 Physical methods

Physical methods of treatment for oil wastewater is defined as a process of separation or isolation of the oil without degradation of the compounds. The most common examples for physical method for oil wastewater treatment are gravity separation (GS) and dissolved air flotation (DAF). GS is a process where the oil particles was separated using the differences of density between the oil and water. Currently, it is stated that GS is a process where it is usually used for the first stage of separation for dispersed and floating oil but it is not applicable for emulsified oil (Abuhasel et al., 2021). This is because GS is only a simple method of separation and it is reported that there have been not many recent researches about GS process for oil wastewater treatment.

Next, the dissolved air flotation where in this process there is an introduced of air under pressure at the bottom of basin and the operation of this air under pressure was when the air under pressure produces air bubbles which reaches the top side of the basin, this air bubbles will bring together with the pollutant which oil included in the oil wastewater. DAF methods is much more reliable in treating the oil wastewater compared to GS method which instead of depending on the density differences of oil and water, the pollutant will be removed by the air bubbles that are produced and it is capable to be used for emulsified oil wastewater (Abuhasel et al., 2021). Table 2.1.1 shows the summary of advantages and disadvantages of GS and DAF methods to treat oil wastewater.

Table 2.1. 1 Advantages and disadvantages of mentioned physical methods

Physical Methods	Advantages	Disadvantages
Gravity Separation	1. Simple system.	1. Applicable only for dispersed and floating oil. 2. Not applicable for emulsified oil. 3. Limited separation capacity. 4. Need large place for process. 5. Complex management and operation process. 6. Not much improvement and research from 2018 to recent.
Dissolved Air Flotation	1. Applicable to used in emulsified oil. 2. Improved surfaces loading. 3. Requires small space of operational process.	1. High operating cost to generate microbubbles. 2. Ultrafine bubbles are preferred due to large surface area of bubbles. 3. High capital cost.

2.1.2 Chemical Methods

In chemical methods, the most common method that have been used in the industries to remove oil and grease from wastewater are flocculation and electrochemical (ET) technologies (Abuhasel et al., 2021). Flocculation is a method where the large solids in the wastewater will form larger clusters or called as flocs and it is removed from the water while ET is a separation of the flocculated solid sludge from the treated wastewater (Chen, 2004)(Cleanawater, 2019). These both methods are stated popular in the treatment process for oily wastewater that came from the palm oil mill effluent (POME). Furthermore, to indicate whether the flocculation achieves the best result, it depends on its flocculants used in the process. Flocculants is a substance that will promote the process of agglomeration of the particles in the wastewater and it is stated the common flocculant used in oily wastewater is inorganic flocculants and organic polymeric flocculants (Abuhasel et al., 2021). Although this method is commonly used, there is still drawbacks or disadvantages in the process which will be explained in table 2.1.2.

Table 2.1. 2 Advantages and disadvantages flocculation process.

Chemical Method	Advantages	Disadvantages
Flocculation	1. Efficiency of the process depends on flocculants used. 2. Easier to operates compared to membrane filtration, DAF and biological technologies.	1. Inorganic flocculants are cheap and easy to use but will exhibits low efficiency of flocculation. 2. pH indication is needed to identify the suitable flocculant to use in wastewater. 3. Organic flocculants can give impact towards environment and society if exposed due to its unbiodegradable properties. 4. Inorganic and organic pollutant can possess large volume of sludge which secondary treatment is necessary.

2.1.3 Mechanical methods

Mechanical coalescers (MC) is one of method used in treatment of oily wastewater where there is filtration process involve in this method. This method is suitable to be used for emulsified oil and it is usually used for offshore platforms. In addition, MC includes several parts which are plate coalescers, packing coalescers, coalescing filter separators and fibrous coalescers and the selection of the substances for coalescers is depend on the characteristics of the emulsified oil. For the filter separators it is important to take consideration of several factors such as high surface wetting and used lower drag force to ensure the filtration efficiency

(Abuhasel et al., 2021). Wettability state of the membrane used in the filtration process can indicates whether the membrane is hydrophilic, hydrophobic or superhydrophobic. Besides it can explain the surface energy of the membrane []. In table 2.1.3 shows the advantages and disadvantages of using MC for treatment of oily wastewater.

Table 2.1. 3 Advantages and disadvantages of mechanical coalesce.

Mechanical Method	Advantages	Disadvantages
Mechanical Coalescers (MC)	1. High efficiency in separation of liquid-liquid phase. 2. Less additional chemicals are used.	1. Exhibit long service period. 2. Usually operates for offshore platforms due to its limitation of space.

2.2 Recent superhydrophobic membrane used for oily wastewater.

Studies about superhydrophobic membrane usage for oil filtration have been increase in interest. Thus, Table 2.2.1 shows the recent studies that have been conducted for superhydrophobic membrane for oily wastewater filtration.

Table 2.2. 1 Recent studies upon superhydrophobic membrane for oil-water wastewater

Process	Membrane characteristics/ membrane component	Membrane performance	Removal efficiency	References
Lignin modified PVDF membrane with antifouling properties for oil filtration.	Lignin dissolved in NaOH with varied alkaline concentration (0.25 – 1.50 wt%) and lignin concentration (0.25-1.00 wt%)	Lignin modified showed slight low but stable flux due to reduce in membrane fouling.	Oil rejection up to 99.30% of oil.	(Zakaria et al., 2021)
Superhydrophobic and superoleophilic hybrid kaolin-based hollow fiber membrane	Sol-gel grafted method using tetraethoxysilane and methyltriethoxysilane.	Mechanical strength of KHFM was improved from 16.21 MPa to 72.33 MPa.	99.9% absorption of oil to membrane.	(Hubadillah et al., 2018)
Hydrophobic PET Track-Etched membranes for separation of oil-water emulsion.	PET TeMs with trichloro(octyl)silane.	Membranes showed stable flux and separation degree and maximum flux achieved at 700mbar.	Not reported	(Korolkov et al., 2021)

2.3 Modification of PVDF membrane for oil filtration.

PVDF membrane is modified in order to increase the potential of the membrane to enhance its superhydrophobic properties such as its water contact angle. This can be shown in several articles where the water contact angle before modification was less than after modification such as addition of $CaCO_3$ nanoparticles from 141.5º to 150.7º angle (Zaliman et al., 2022). Besides that, by adding other TiO_2 nanoparticles to PVDF membrane, the membrane reached a superhydrophilicity and later reached the superhydrophobicity characteristics after filtration (Macedonio, 2015). Furthermore, in an experiment due to introduced of $CaCO_3$ nanoparticles to PVDF membrane, this will cause the antifouling ability and underwater low oil adhesion of membrane to be decreasing which will improve the efficiency of the membrane to filter oi from oily wastewater (Wu et al., 2020).

CHAPTER 3

MATERIALS AND METHODS

3.1 Research Flow

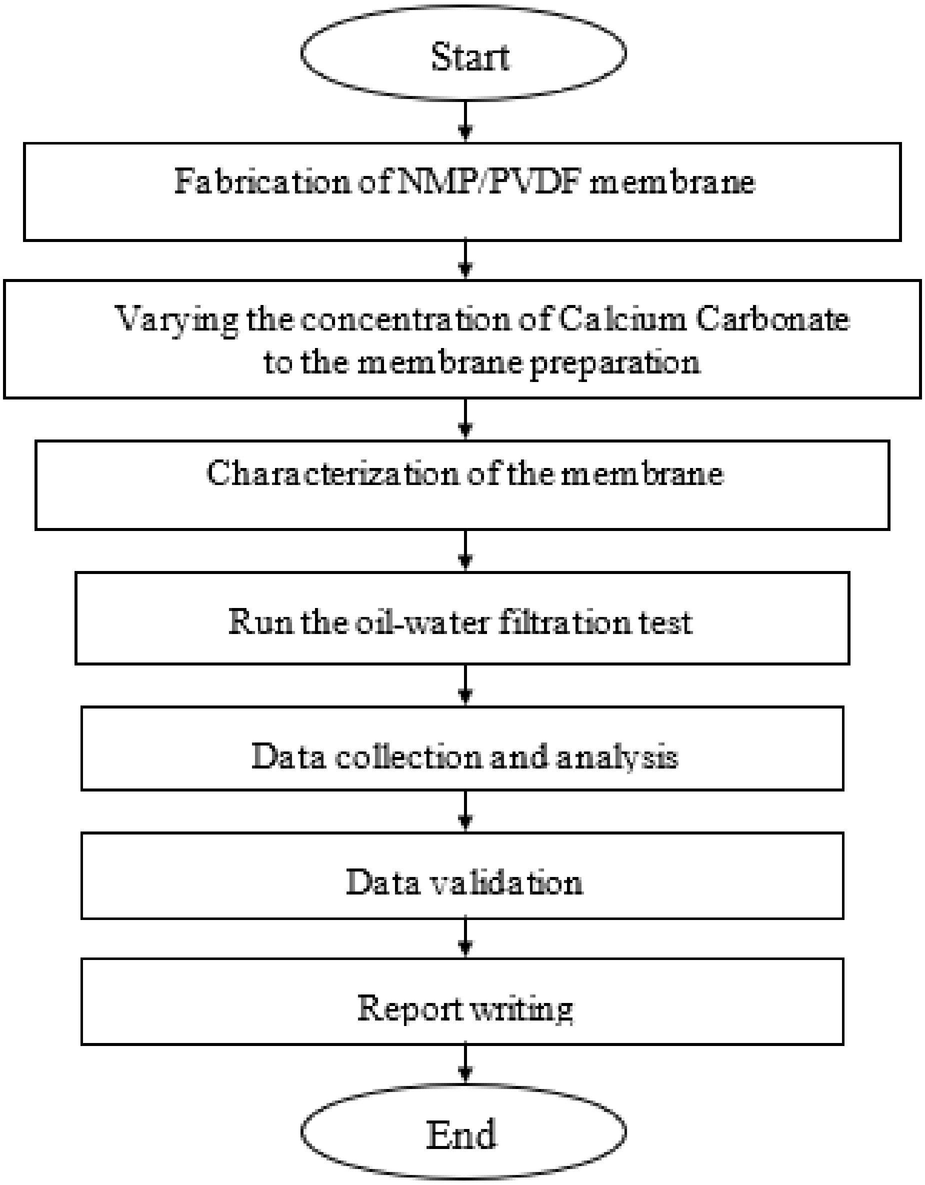

Figure 3. 1: Research project flow chart

Figure 3.1 shows the flow diagram of the research project for fabrication of NMP/PVDF-$CaCO_3$ membrane. This research project will be carried out in the separation and purification laboratory in USM. After the oil-water filtration test and characterization is done, data will be collected, analysis on the data collected will be carried out using proper equipment and instrument. Report writing will be done after all of the data required have been collected.

3.1 Method of Membrane Fabrication

The chosen fabrication method to produce desired membrane was by using the phase inversion method. Phase inversion method was chosen as it is the most common method in lab works and it is easier to produce flat sheet membrane for membrane characterization process. The steps to produce the flat sheet membrane was elaborated as it is following previously reported article with some modification (Zakaria et al., 2021). PVDF powder and NMP solvent was measured using analytical scale in the lab using the ratio of 15:85 weight percent (%) respectively for 30g amount of mixture in a beaker. PVDF powder were placed on a weighing boat while NMP solvent were placed in a beaker. NMP solvent were placed on top of a magnetic stirrer hot plate with magnet stirrer inside it. PVDF powder were added slowly to the solvent to prevent bubble forming in the mixture. The temperature and magnetic stirrer rpm were set at 60℃ and 350rpm respectively. The mixture was stirred for 6 hours. After the stirring was stopped, the solution was coated on a polyester non-woven fabric supported by glass plate with a knife gap of 0.5 mm. The coated fabric was immediately immersed into distilled water bath for phase inversion of the membrane and the duration for the immersion was 24 hours. After 24 hours, the immersed membrane was dried in room temperature in open area inside the lab for another 24 hours. The membrane was ready to be peeled for membrane characterization.

To prepare the PVDF/NMP-$CaCO_3$ membrane, the weight percent ratio is varied by using 1%, 2%, 3%, 4%, 5% and 6% concentration of calcium carbonate added with constant weight percent for PVDF powder as shown in Table 3.1. After all of the materials have been measured, the calcium carbonate will be added slowly to the NMP solvent slowly because it tends to clump quickly inside the solvent. For precaution step, the solution is degassed for 45 minutes. After degassed, then PVDF powder is added slowly to the solution and step 2 until 7 is repeated.

Table 3. 1: The dope composition of PVDF membranes and $CaCO_3$ nanoparticles added.

Membrane	NMP (%)	PVDF (%)	$CaCO_3$ (%)
M1	85	15	0
M2	84	15	1
M3	83	15	2
M4	82	15	3
M5	81	15	4
M6	80	15	5
M7	79	15	6

3.2 Facilities Required and Availability Equipment

The following Table 3.2 and Table 3.2 list out the materials and equipment needed for fabrication and characterization of membrane.

Table 3. 2: Materials used in fabrication of membrane

Materials	Purpose
N-methyl-2-pyrrolidone (NMP) (>99.5%)	To be used as solvent for membrane fabrication
PVDF powder	To be used as powder for membrane fabrication.
Calcium Carbonate nanoparticles powder	To be used as modification of the fabrication membrane.
Distilled water bath	Act as non-solvent for phase inversion of membrane fabrication.
Polyester non-woven fabric	Act as a supported fabric for membrane casting process.

Table 3. 3: Equipment used in research project

Equipment	Purpose
Gardner's knife	To cast the solution membrane with a known thickness.
Water contact angle digital microscope (WCA)	To study the superhydrophobic properties from water contact angle of membrane.
Sterlitech dead-end stirred cell HP4750 (Sterlitech Corporation, WA)	To study the hydrophobicity of the membrane.
UV-visible spectrophotometer (Cary 60, Agilent) at 225nm	To study the oil concentration of the filtrate after oil-water filtration test.
Filtration test	To conduct the oil-water filtration test on the membrane.

3.3 Membrane Characterization

3.4.1 Contact Angle Measurement

The water contact angle measurement will be done using the HiView digital microscope that is available in the laboratory. This microscope will show the water contact angle of water droplets on the membrane. The steps for measurement are list out below.

1. Flat sheet membrane will be peeled of and cut out in suitable size to be attached to a microscope slide.
2. The microscope slide will be placed on a block suitable for the microscope to get a clear and appropriate image of the water droplet angle.
3. The software download from the HiView website will measure the water contact angle.

Figure 3. 2: HiView digital microscope used for water contact angle measurement

3.4.2 Membrane Porosity

The membrane porosity measurement is following the previous published article (Zaliman et al., 2022), except using different types of alcohol. The flat sheet membrane prepared previously will cut out with the dimension of 3cmx1cm and it is peeled off from the non-woven fabric. The initial weight of the membrane is being measured before is being soaked inside a 2-propanol beaker. The membrane is left inside the beaker for 2 hours. After that, the soaked membrane that is absorbed with 2-propanol solution is lightly removed the excess alcohol with tissue and the final weight if the membrane is being measured using analytical balance immediately to prevent the alcohol to evaporate through the air and making the membrane dried. After completing this step, the calculation for membrane porosity is done using following equation:

$$\varepsilon = \frac{m_b/\rho_b}{m_b/\rho_b + m_m/\rho_m} \times 100\% \qquad (1)$$

Where m_b is the weight of 2-propanol absorbed by the membrane (g), m_m is the initial weight of membrane (g), ρ_b is the density of the 2-propanol (0.786 g/cm^3) and ρ_m is the density of PVDF (1.780 g/cm^3).

3.4 Oil-Water filtration test

For oil-water filtration test, oil-water emulsion must be prepared following the previous study (Zakaria et al., 2021), whereby the oily water mixture was prepared by mixing 1:100 ratio of oil to distilled water into a conical flask for an even mixture, an emulsifier such as polyethylene glycol (0.5mg/ml) is used in making the emulsion solution. This oil-water emulsion was ultrasonicated for 15 minutes for making the emulsion stable and the final results of the emulsion is shown in Figure 3.3 (Cui et al., 2019).

In this test a setup as shown in Figure 3.4 will be used where it uses nitrogen gas to helps the process of filtration. Sterlitech dead-end stirred cell (HP4750) will be used as the placed where the membrane and the oil-water emulsion was inserted. The arrangement of the parts in the dead-end stirred cell was shown in Figure 3.4. The operation condition for operating the set up was done in room temperature and 1 bar of pressure was used. After achieving the data required, permeation flux is calculated using equation below:

$$J = \frac{V}{A \times t} \qquad (2)$$

Where V is the volume of the permeate collected, A is the effective area of the membrane which is 14.6 cm^2 and t is the time taken for the filtration to complete. To observe the oil concentration of the filtrate, UV-Visible spectrometer (Cary 60, Agilent) was used using 225 nm of wavelength. Furthermore, the calculation of the total rejection of oil, r, was also calculated using following equation:

$$r = \left(1-\frac{C_p}{C_f}\right) \times 100\% \quad (3)$$

Where C_p is the oil concentration in the permeate while C_f is the concentration of oil in the feed solutions.

Figure 3. 3: Oil-water emulsion

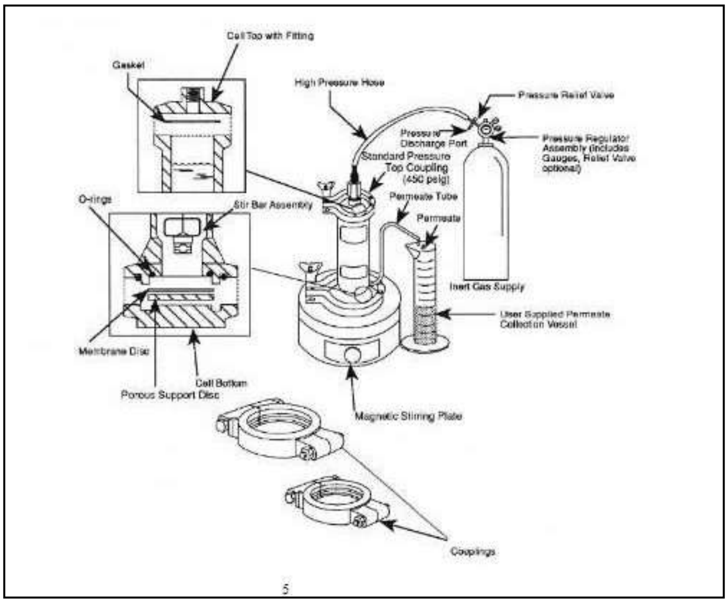

Figure 3. 4: The arrangement of filtration test and Sterlitech dead-end stirred cell (HP4750)

CHAPTER 4

RESULT AND DISCUSSION

4.1 The effects of $CaCO_3$ nanoparticles on membrane characteristics

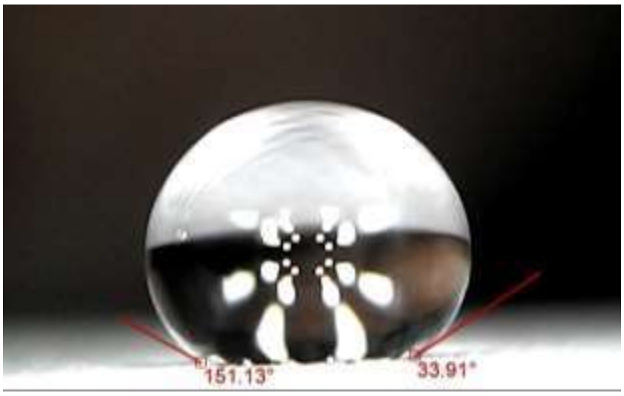

Figure 4. 1: M7 water contact angle measurement

Figure 4.1 shows the example of taking the water contact angle measurement of water droplet on PVDF/NMP membrane with 6% weight of $CaCO_3$. The water contact angle measurement of each membrane was measured to observe the hydrophobicity properties of the membrane which is tabulated and summarised in Table 4.1. As we know previously, in order for membrane to have superhydrophobic characteristics, the water contact angle of the water droplet must be ±150º. The lowest water contact angle recorded from the reasearch project is M3 and M4 with a value of 148 ± 0.5º and 148.6 ± 0.5º, respectively. The highest water contact angle measured is M6 with a value of 154.6 ± 0.5º. Although $CaCO_3$ is known for having hydrophilic properties, they still have the ability to provide hierarchical structures to the membrane which makes the membrane can have superhydrophobic water contact angle which it is being illustrate in previous report (Zaliman et al., 2022). As from Table 4.1, the higher the concentration of $CaCO_3$ in PVDF membrane, its gives not an obvious difference in terms of its water contact angle because only $CaCO_3$ is being added which gives slightly same result. Furthermore, this may also cause from the way of water contact angle is being measured because in this research, only simple technique is used which is by using only digital microscope.

Table 4. 1: Result for water contact angle and membrane porosity

Membrane	Water contact angle (°)	Membrane porosity, Ɛ
M1	149.7	91.0
M2	150.9	91.9
M3	148.5	90.2
M4	148.6	89.3
M5	149.4	89.8
M6	154.6	88.5
M7	151.1	87.6

The porosity of each membrane is taken after drying being summarized in Table 4.1, where it is being calculated using the formula that have been stated before in methodology part. From the results, the membrane porosity decreases as the increase of concentration of $CaCO_3$ nanoparticles is added to the PVDF/NMP membrane. In an article, stated that the pore distribution become much smaller when the concentration of nanoparticles is increasing (Hou et al., 2014). The lowest membrane porosity from the result obtained is M7 which contain 6% weight percent of nanoparticles while the highest membrane porosity is recorded in M2 with the value of 91.9%. This is because the nanoparticles tend to embedded in the membrane and gives a denser feeling towards the membrane as it is also proven by other researchers (Hou et al., 2014). The water contact angle measurement and membrane porosity results has demonstrated that the higher the concentration of nanoparticles inside the PVDF/NMP membrane, the rougher and denser the membrane will be where it has shown high water contact angle and less membrane porosity.

According to modified Young's equation in an article, the higher the change of the membrane surface contact angle depend on the ratio mean surface roughness of membrane to the mean surface nodule size or hollow size (Hou et al., 2014). Thus, from the result obtain for the membrane characterizations, it is proven that the water contact angle of the membrane become higher as the increase the mean ratio that has been mentioned which also meant that the hydrophobicity membrane is improved by adding $CaCO_3$ nanoparticles to the membrane.

4.2 Effect of different weight percent concentration of $CaCO_3$ nanoparticles to time taken in oil-water filtration test.

Table 4.2 shows the time taken for complete filtration of oily water mixture using the Sterlitech dead-end stirred cell HP4750. From the results obtained, it can be observed that the highest time taken for complete filtration process is taken by M2 with the value of 103 minutes and it is gradually decreasing in time taken as the weight percent concentration of $CaCO_3$ increasing. As previously mention in the membrane characterizations, the higher the number of nanoparticles in the membrane, the denser the membrane will be and the lesser the membrane porosity. If the membrane porosity is high, which means the pore distribution is high which gives the potential for the pore to be block by the emulsified oil water.

Complete blocking of the pore is described as a situation where a particle is completely covers the pore entrance whereby this phenomenon will cause the reducing of pore channel in a membrane which also reduce the membrane filtration efficiency (Tummons et al., 2020). Other factors that can be one of reason for the time taken to be high is due to formation of gel layer on top of the membrane during the oil-water filtration test. Figure 4.2 is taken in the lab during the experiments been conducted, and it is clearly be seen that there is a shiny and sticky layer on top of the membrane after undergo filtration test with oil-water emulsion. There is a similar study that showed that the gel layer formation can indicated that there is increasing in hydraulic resistance towards the membrane (Tummons et al., 2020). Gel layer formation can also be one of the reasons for the membrane fouling to happen thus causing the time taken to be high for membrane that have larger pores. The membrane that took the fastest time to complete the filtration test is M6 and M7 with the value of 28 and 25 minutes, respectively. Although both of these membranes have low percentage of membrane porosity, they can prove to be having the fastest time take to complete the oil-water filtration test. In addition. The membrane that has the highest permeate flux is M7 which may show the membrane can filtrate the oil better than M2 which shows the least permeation flux.

Table 4. 2: Results for time taken for complete filtration and permeation flux

Membrane	**Time taken for complete filtration (min)**	**Permeation flux, J (Lm^2/h)**
M1	45	92.24
M2	103	40.22
M3	86	48.38
M4	49	84.36
M5	39	106.43
M6	28	147.19
M7	25	164.71