CALCIUM CARBONATE REMOVAL VIA DIRECT CONTACT MEMBRANE DISTILLATION

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CALCIUM CARBONATE REMOVAL VIA DIRECT CONTACT MEMBRANE DISTILLATION

By

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Mohamad Fikri Bin Asrafa

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LIST OF SYMBOLS

Symbols	Description
J	Permeation flux (L/m^2.hr)
V	Permeate volume (L)
A	Membrane surface area (m^2)
t	Time (hr)
R	Solute rejection (%)
C_p	Concentration of solute in permeate (mg/L)
C_f	Concentration of solute in feed (mg/L)

LIST OF ABBREVIATIONS

Nomenclature	Description
WQA	Water Quality Association
$Ca(HCO_3)_2$	Calcium hydrogencarbonate
$Mg(HCO_3)_2$	Magnesium hydrogencarbonate
LEP	Liquid Entry Prerssure
DCMD	Direct Contact Membrane Distillation
$CaCO_3$	Calcium Carbonate
AD	Adopic Dermatis
PCC	Precipitated Calcium Carbonate
MF	Microfiltration
UF	Ultrafiltration
NF	Nanofiltration
RO	Reverse Osmosis
AOX	absorbable organic halides
COD	Chemical Oxygen Demand
PVDF	polyvinylidene fluoride
AGMD	Air Gap Membrane Distillation
TMP	Transmembrane Pressure
VLE	Vapour Liquid Equilibrium
SEM	Scanning Electron Microscopy

PEMISAHAN KALSIUM KARBONAT MENGGUNAKAN PENYULINGAN SENTUH MEMBRAN SECARA LANGSUNG

ABSTRAK

Kajian ini mengenai keupayaan membran sulingan secara langsung untuk memisahkan kalsium karbonat untuk pelembutan air. Parameter yang dikaji termasuk kepekatan larutan, suhu larutan dan kadar aliran larutan. Kepekatan larutan dimanipulasi daripada 0.1g/L $CaCO_3$ ke 9.0g/L $CaCO_3$. Hasil kajian menunjukkan fluks telap berkurang apabila kepekatan larutan bertambah. Semakin tinggi kepekatan larutan membawa kepada pemendapan zarah pada permukaan membran menyebabkan 'fouling', langsung mengurangkan fluks telap. Suhu larutan dan kadar aliran dimanipulasi daripada 60°C ke 80°C dan 18.92L/jam ke 27.85L/jam. Fluks telap meningkat secara linear dengan peningkatan suhu larutan dan kadar aliran larutan. Membran sulingan secara langsung merupakan proses dorongan haba. Oleh sebab demikian, peningkatan suhu larutan akan meningkatkan tenaga dorongan untuk wap air melepasi membran. Peningkatan kadar aliran larutan akan mengurankan sempadan suhu didalam proses membran sulingan secara langsung dan meningkatkan proses pengasingan. Fenomena 'fouling' didapati apabila 9.0g/L larutan $CaCO_3$ menjalani proses selama 8jam. Fluks telap didapati mula menurun selepas 6 jam proses dijalankan. Pemendapan zarah pada permukaan membran kelihatan membuktikan fenomena 'fouling' terjadi.

CALCIUM CARBONATE REMOVAL VIA DIRECT CONTACT MEMBRANE DISTILLATION

ABSTRACT

This research studied in the performance of direct contact membrane distillation in removing calcium carbonate solution or water softening. The important parameter investigated include feed concentration, feed temperature and feed flowrate. The feed concentration are vary from 0.1g/L $CaCO_3$ to 9.0g/L $CaCO_3$. The result indicated that permeate flux decrease as the feed concentration increase. The higher feed concentration lead to deposition of solute on the membrane surface and cause fouling, thus the permeate flux decrease. The feed temperature and feed flowrate are vary from 60°C to 80°C and 18.92L/hr to 27.85L/hr respectively. The permeate flux increase linearly with increase in feed temperature and feed flowrate. DCMD is a thermal driven process, increase in feed temperature will increase the driving force for the water vapour pass through the membrane. Increase in feed flowrate will decrease the temperature boundary layer and enhance the separation process. The fouling phenomena was observed when the 9.0g/L $CaCO_3$ run for 8 hour. Permeate flux start to decline after 6 hours of DCMD process. The observed deposition of the solute on the membrane surface prove that fouling phenomena did occur via cake deposition before wetting and pore blocking after wetting taken placed.

<center>**CHAPTER 1**</center>

<center>**INTRODUCTION**</center>

1.0.Hardness of water

Water hardness is the amount of dissolved calcium and magnesium in the water. It can be defined as the capacity of water to precipitate soap. Calcium and magnesium precipitate soap by forming a curd which causes 'bathtub ring' and dingy laundry. Hardness prevent soap from lathering by causing the development of an insoluble curdy precipitate in water. Hardness scale is usually expressed in grains per gallon or ppm of calcium carbonate equivalent. The degree of hardness is standardized by the American Society of Agricultural Engineers (S-339) and the Water Quality Association (WQA) in Table 1.1

Table 1.1 Degree of Hardness

Degree of Hardness	Grains per Gallon (gpg)	Ppm (or mg/L)
Soft	<1.0	<17.0
Slightly hard	1.0-3.5	17.1-60.0
Moderately hard	3.5-7.0	60-120
Hard	7.0-10.5	120-180
Very hard	>10.5	>180

1.1. Types of Water Hardness

There are two types of water hardness, temporary hardness and permanent hardness. Temporary hardness is caused by dissolved calcium hydrogencarbonate, $Ca(HCO_3)_2$. The rainwater which is naturally acidic react with calcium carbonate in rock to form calcium hydrogencarbonate which is soluble in water. Temporary

<center>1</center>

hardness also due to presence of magnesium hydrogencarbonate $Mg(HCO_3)_2$ (Lenntech, 2017). Temporary hardness can be removed by boiling the water. When the water are being boiled, the soluble calcium hydrogencarbonate decomposes to form calcium carbonate which is insoluble in water and carbon dioxide. The calcium carbonate forms layer of limescale. This may coat the heating element in kettles and irons. Limescale is unsightly and it clogs up hot water pipe and reboiler.

Permanent hardness is caused by dissolved calcium sulphate. Permanent hardness cannot be removed by boiling the water. Presence of calcium sulphate, calcium chloride, magnesium sulphate or magnesium chloride in the water, which do not precipitate out as the temperature of the water increase cause the hardness of the water are permanent and cannot be removed by boiling the water. Ions causing permanent hardness of water can be removed using water softener or ion exchange column (Parmam, 2017).

1.2. Impact of hard water on human and industry

According to the International Journal of Preventive Medicine proposed by Pallav Sengupta (Sengupta, 2013), the regular exposure to the density of minerals in hard water may impair the health condition. High level of calcium and magnesium can affect several organs in the body and cause health problems. One of the most severe health problem caused by the hardness of the water is an increased of risk of cardiovascular disease. Excess intake of calcium and magnesium in the hard water can cause heart disease and high blood pressure. In adults, high consumption of

hardwater can increased the risk of reproductive failure and for children can cause growth retardation.

From the industry perspective, the heavy presence of minerals in hard water can lead to pipes clogging caused by the lime scale precipitation. Clogged pipes, can make the equipment runs at lower efficient and consume more electricity. It also can leads to pipe leaking and shorten the lifespan of equipment.

1.3. Method for water softening and its associated problems

Water softening is the process where the calcium and magnesium ions are eliminated from the water to reduce the hardness of the water. Different methods and technologies are being used to soften the water. Ion exchange column are one of the methods commonly used to eliminate the calcium and magnesium ions in water. There are resins or zeolite beads that carry a negative charge. Since magnesium and calcium ions are positively charged, the ions will be attracted to the bed, therefore the amount of ions remained in the water can be reduced. However, ion exchange is often down with calcium sulphate fouling. In general, sulphuric acid is always used to regenerate the resin beds. The high content of calcium ions in the hard water react with the regenerating sulphuric acid and forms calcium sulphate as a precipitation (Tripathi, 2017). This precipitate can foul the resin beads and can block the pipes in the vessel.

Distillation is another method for water softening. Distillation is a process which the water are vaporised at elevated temperature. The water vapour will be collected in the condenser whereas impurities will leaves the

distillation column as bottom product. This process are effective to remove calcium and magnesium ions in the water.

The other common method is by using nanofiltration (NF). Nanofiltration is one of the most efficient way for water softening. Nanofiltration is a pressure driven-process using a semi-permeable membrane whereby the water molecule will pass through the membrane as permeate and the multivalent cations will be rejected by different mechanism such as size exclusion, electrostatic effects and dielectric exclusion (Labban et al., 2017). However, NF membrane fouling remains as a main challenge to this pressure driven process that lead to flux decline and shorten the membrane lifespan.

1.4. Membrane Distillation

Membrane distillation (MD) is a thermally driven membrane process in which a hydrophobic microporous membrane separates a heated feed solution and a cooled receiving phase. The temperature difference across the membrane create a water vapour gradient, causing water vapour transfer through the pores in the membrane from high vapour pressure to low vapour pressure. The hydrophobic nature of the membrane prevent aqueous solutions to penetrate through the pores due to the high surface tensions, unless a transmembrane pressure higher than the membrane liquid entry pressure (LEP) applied. Therefore, liquid/vapour are formed at the entrance of each pore (zereshki, 2012). The hydrophobic nature of the membrane and low feed pressure are sufficient to prevent the feed solution from penetrating the membrane pores (wetting) and lower the potential of fouling (David et al., 2016). Compared to

pressure driven process, MD process with thermal driven energy is less susceptible to fouling and therefore are much more suitable to be used to softening the hard water.

1.5. Problem Statement

Domestic water hardness varies throughout the world depending of the geography of the land. Living in the hard water area (>180mg/L $CaCO_3$) increased the chances of atopic dermatitis (AD) disease and also increase the skin impairment after exposure to surfactant in contact with the wash products combined with the high calcium content water (Danby et al., 2018). Dealing with hard water problems in cleaning can be nuisance because bathing the soap with hard water leaves a film of sticky soap curd on the skin and may prevent the removal of soil and bacteria (Oram, 2014).

Precipitated calcium carbonate, $CaCO_3$ (PCC) is used in large quantity in paper and pulp industry. PCC used as paper filler and in coating to provide opacity, high brightness and improved quality of printability due to its good ink receptivity (Pöykiö and Nurmesniemi, 2008). When the paper are manufactured, the $CaCO_3$ waste is purged out as wastewater that contributed to hard water because of excessive calcium content in the wastewater. Deinked sludge is generated in paper mills industry producing recycled fibre from recycled paper (Bajpai.P, 2015). Deinking process enables increases of brightness and cleanliness of the material. Froth flotation and wash deinking

process are also used for selective deletion of ink particles, removal of small particles such as $CaCO_3$, clay and kaolin (Bajpai.P, 2015).

Membrane separation process can be used to treat the hard water and remove the small particles from the industry wastewater. Microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) are conventional membrane process that had been used by industry in treating their wastewater before being discharged. However, such membrane are easily fouled by hardness water. Membrane distillation is an emerging thermally driven process that can be used to remove hardness of water. The driving force for the membrane distillation process is given by the vapour pressure gradient generated by the temperature difference between feed and permeate side. Membrane distillation have much more advantages over conventional membrane technology which are relatively lower energy cost as compared to distillation, reverse osmosis and pervaporation, considerable rejection of dissolved, non-volatile species. Membrane distillation also have much lower fouling phenomena as compared to MF, NF, and RO process, lower vapour space, lower operating pressure than pressure-driven process and lower operating temperature as compared to conventional evaporation (Khayet, 2011). Nonetheless, membrane distillation (MD) is susceptible to wetting phenomena induced by cake layer deposition on the membrane surface. The extent of wetting and fouling phenomena is very much related to the operating conditions such as feed concentration as well as hydrodynamics conditions. These studies are scarce but important for the feasibility study of membrane distillation for hardness removal.

1.6. Research Objectives

i. To study the efficiency of the membrane distillation to remove calcium carbonate at different concentration.

ii. To evaluate the effect of flowrate and temperature on the membrane separation performance

iii. To evaluate the fouling phenomena of membrane distillation as a result of wetting by cake layer deposition.

CHAPTER 2

LITERATURE REVIEW

2.1. Hard water produce by industry

Most of the products being produced in industries, use excessive water during their production. In view of this, industry has been trying to preserve water in every aspect possible to ensure water pollution is kept at minimal levels. According to the UN World Water Development Report, 300-500 million tons of heavy metals, solvents, toxic sludge, and other waste accumulate approximately each year from industry. In some developing countries, 70% of industrial waste are dumped into the nature where they pollute the drinking water (Koncagül, 2017).

The pulp and paper industry is one of the heaviest users of water because nearly in every step of the manufacturing process water is used. Pulp and paper mills produce large volume of wastewater and residual sludge. Therefore, more issue in relation with wastewater treatment, discharge, and sludge disposal need to be concerned. Contaminant that presence in the pulp and paper industry waste stream include the filler, absorbable organic halides (AOX), chlorinated organic compounds and chemical oxygen demand (COD) and biological oxygen demand (BOD) contaminants (Gunderson, 2017a).

A wide variety of products are produced by chemical and pharmaceutical industries. These process typically need a large volume of chemical and materials in order to produces chemical products. Therefore, waste water streams generated from this industry contain a lot of ions, contaminant, toxins and organic contents. All these contaminant contribute to the water hardness, therefore all the contaminant

and ions need to be removed and limit the amount of ions in the water before discharge to environment according to the rules and regulation by each country provided. According to Dr Ram Venkatdri, global marketing manager for industrial water in the Energy Group of Pall Corp (Gunderson, 2017b), wastewater stream from chemical and pharmaceutical industry can exhibit a considerable amount of variation in term of volume, quantity, and composition. Therefore plants are using integrated treatment technologies such as membrane technology including microfiltration, ultrafiltration, reverse osmosis, nanofiltration and ion exchange to soften water before being discharged.

2.2. Technology for water softening

There are many technology that can be used to soften the hard water. Technologies such as adsorption, coagulation, precipitation and ion exchange have been applied to remove ions especially fluoride ion from the natural water sources. However, these technologies are unable to produce continuously high quality water suitable for potable purpose due to their limitation in context of removing major ions groundwater especially brackish groundwater (Plattner et al., 2017). Membrane technology, a pressure driven process such as reverse osmosis and nanofiltration are used to soften hard water in order to remove ions and other contaminate from the ground water. Reverse osmosis (RO) can effectively treat hard water from contaminant and ions to produce good quality water but required high electrical energy for even a small scale systems (Pérez-González et al., 2012). Reverse osmosis also has low recovery ratio and the risks of membrane fouling remains a huge challenges (Pérez-González et al., 2012). Nanofiltration on the other hand, can operated at much lower pressure yielding identical permeate (Jadhav et al., 2015).

Nanofiltration can removed monovalent ions to less than 60% as opposed to 90% by RO membranes. Nonetheless, RO is suffer from high operating pressure, low permeate flux and high energy requirement (Alarcón-Herrera et al., 2013).

2.2.1. Ion Exchange

The ion exchange water softener operates by exchanging the hardness minerals that dissolved in water such as calcium and magnesium with the soft minerals such as sodium that contained on the softener resin beads. The sodium gives less damage to the membrane because it does not build up on surfaces as scale deposits (Lord, 2016). The exchange process takes place by passing hard water over the ion exchange resin beads (negatively charged) in a suitable pressure vessel tank. According to Neha Tripathi, ion exchange can lead to calcium sulphate fouling, iron fouling, and other disadvantages. Ion exchange also do not remove microorganism from the feed water but sometimes aid in the bacterial growth because resin beads accumulate organic matter which serves as sources of nutrient for the bacteria (Tripathi, 2017).

According to Irina Levchuk, ion exchange is an efficient process to remove charged organic compound from water (Levchuk et al., 2018). Around 30% to 90% of natural organic matter (NOM) can be removed by using ion exchange treatment from drinking water. A desalination process, LANXESS industry are using combination of RO and ion exchange. To achieve a high water recovery by softening the via selective ion exchanger process. There are many types of ion exchanger for ions removal depends on the process. For instance, chelating resins are able to soften the hard water effectively and this type of ion exchange are often used to soften the concentrate from an RO plant before further RO treatment (Lipnizki et al., 2012).

2.2.2. Nanofiltration (NF)

Nanofiltration is a type of membrane that remove dissolved charged ions under the moderate transmembrane pressure (Sutherland, 2009). A nanofiltration has a pore size around 1.0nm. Nanofiltration removes most organic molecules, nearly all viruses, most of natural organic matter and various type of salts. Nanofiltration also removes divalent ions, appear in hard water, therefore nanofiltration is often used for water softening. Nanofiltration membrane possess a looser structure compared to RO membrane (Jiraratananon et al., 2000). Therefore, NF can be operated at a lower pressure while providing a high permeate flux.

In one of the research, the UF-NF efficiency of seawater desalination are evaluated. NF can achieve higher efficiency in water softening by using UF membrane with smaller MWCO (20kDa) as pre-treatment process (Song et al., 2011). NF membrane has a unique characteristics which selectively separate the divalent or multivalent ions from the monovalent ions. These features make it suitable for water softening. A pilot scale dual-stage NF process designed show high separation performance with high rejection of Ca^{2+} and Mg^{2+} (Su et al., 2015). Furthermore, the dual NF stage process showed good antifouling characteristics (Su et al., 2015).

Even though NF has higher permeation rate, membrane fouling is an inevitable process and become the major problem for NF which lead to reduce productivity, decline in permeates quality, increases energy consumption and treatment cost, and also reduce the membrane lifespan (Aguiar et al., 2018).

2.2.3. Membrane Distillation (MD)

Membrane filtration process which require smaller footprint is an attractive alternative method used to separate the nanoparticle and ions from the wastewater. In membrane distillation (MD), the volatile component in the hot feed solution will evaporate and cross through the hydrophobic membrane and then condense in the permeate side because of the cold temperature. This process result in high purity distillate which is low in ions, nanoparticles and hardness (González et al., 2017). Thermal driven membrane separation such as membrane distillation shows better fouling resistance compared to pressure driven membrane process (Wong, 2016). This is because the particle do not contact the membrane surface directly due to low surface energy of the membrane material. Therefore, membrane distillation is less prone to fouling phenomenon. Membrane distillation can be operated under atmospheric pressure and lower temperature than traditional evaporation process (Mokhtar et al., 2015). Due to its higher surface area, membrane distillation require only low grade thermal energy or waste heat to create the driving force (Khayet, 2011).

Membrane distillation (MD) is an innovative membrane process which is able to remove various type of contaminants. MD provide several benefit such as low operating conditions which will reduce the capital cost. Other than that, MD have important advantages compared to other membrane process which are capable of producing permeate with high rejection of ions, macromolecules, colloids and other volatile component. MD is known to be an energy efficient process than other membrane processes (Boubakri, 2015).

2.3. Direct Contact Membrane Distillation

Direct Contact Membrane Distillation (DCMD) is one of membrane configuration that has been recognized as liquid-liquid separator where feed and permeate are in direct contact with the membrane surfaces and the separation mechanism is based on vapour-liquid equilibrium (VLE) principle (Khayet, 2011). By keeping permeate side much cooler that the feed side, a difference in partial pressure is created across the membrane, therefore the water molecules and other volatile component will be condensed at the permeate side through the membrane pores (Mokhtar et al., 2015).

There are 3 main steps for the water transport through membrane are, formation of a vapour gap at the hot feed solution-membrane interface, transport of the vapour phase through the microporous system membrane, and condensation of the vapour at the cold side membrane-permeate solution interface (Zereshki, 2012).

In direct contact membrane distillation (DCMD), water is used as condensing agent to condense the fluid in the permeate side because water has lower temperature than liquid in the feed side. The liquid in both side of the membrane are in direct contact with the hydrophobic microporous membrane (Zereshki, 2012).

2.4. Membrane Distillation for dissolved suspended solid and hardness removal

Thermal driven membrane distillation process was also found as promising technology for removal of suspended solids and nanoparticle in industry. A research demonstrated by using hydrophobic PTFE membrane for treating dyeing

vat wastewater showed that 90% and 94% of COD and colour removal efficiency were recorded respectively over 48hours of continuous operation (Li, 2018).

DCMD can be employed to separate pure water from aqueous solutions containing non-volatile nanoparticles through the hydrophobic membrane. This work had been demonstrated by Wong who study the efficiency of the MD process in separating TiO_2 nanoparticles (Wong, 2016). The TiO_2 rejection efficiency through the MD process was more than 99% with negligible pore blocking phenomenon being observed. A study perform showed that removal of arsenic by using polyvinylidene fluoride (PVDF) membrane could be achieved. Besides, the removal efficiency of Cl^-, SO_4^{2-}, and Ca^{2+} ions were all higher than 99.90% which indicated that the membrane had no selective rejection of univalent and divalent ions. It also found that removal of arsenic by membrane distillation have higher efficiency compared to pressure driven process such as reverse osmosis and nanofiltration (Qu et al., 2009).

Membrane distillation is an innovative membrane process that have capability to treat the highly concentrated solutions and can be suitable to be used for water treatment. Membrane distillation can be used to treat the oily wastewater. The oilfield produced water contains organic, inorganic fractions and also dispersed oil and mineral compound. Macedonia carried out a study on the efficiency of DCMD in treating the oilfield to produced water (Macedonio, 2014) using polymeric PVDF membranes. The result showed that overall salt rejection factor are more than 99% and total carbon rejection are more than 90% for the membrane distillation performance (Macedonio, 2014). DCMD process with flat sheet hydrophobic PVDF membrane are used to remove boron from natural seawater. Research by Baobakri showed that DCMD process can produce water with high boron removal (90%)

even at high feed concentration (Boubakri, 2015). By using super hydrophobic electrospun naanfibrous membrane (ENMs), DCMD process are able to produce 21.5kg/m^2.hr permeate flux and a stable low permeate conductivity using 30g/L NaCl aqueous solution as feed and a temperature difference of 50°C over a 12 hours of DCMD operations (Li, 2017).

2.5. Membrane Fouling and Scaling by Hardness

Fouling is a complicated phenomenon involves different mechanism such as adsorption, accumulation, or precipitation of organic and inorganic species that take place on the membrane surfaces (Goh et al., 2018). Membrane fouling poses a huge challenge to the reliability of membrane operation. Membrane fouling results in the increased of transmembrane pressure (TMP) to maintain the flux or else permeate flux will decreased if system is operated at constant pressure (Guo et al., 2012). Membrane fouling can be classified as reversible fouling and irreversible fouling. Reversible fouling (including backwashable and non backwashable) occurs due to the cake formation or concentration polarization of materials at the membrane rejection surface (Guo et al., 2012). Membrane with backwashable reversible fouling can be restored through physical washing such as backwashing or hydrodynamic scouring (surface washing), while the non backwashable reversible fouling can be removed by chemical cleaning (Guo et al., 2012). Irreversible fouling occurs by pore plugging and chemisorption on the membrane surface and make the loss of the TMP flux cannot be recovered chemically (Guo et al., 2012). Therefore the membrane that undergo irreversible fouling need to be replaced or go through extensive chemical cleaning.

Scaling refer to the inorganic fouling which is caused by the precipitation or crystallization of inorganic minerals ions such as calcium, magnesium and carbonate sulphate (Karabelas et al., 2017). Membrane scaling occur when the ions in the feed crystalize onto the membrane surface through surface crystallization or bulk crystallization (David et al., 2016). Both process result in decline of permeate flux due to pore blockage. One of the important factor that govern scale formation on the membrane is the availability of nucleation site (Goh et al., 2018). The nucleation and formation of microcrystals that grow over time the make the minerals scale deposited on the membrane surface damage the selective layer and deteriorate the water transport. Concentration polarisation is the main cause that contribute to the salt formation on the membrane surface and cause scaling. Calcium carbonate $CaCO_3$ which can exist as calcium and bicarbonate ions in the industrial water is the most common type of alkaline-based scalant (Piyadasa et al., 2017). Backwashing can be used to remove some of the scalant that deposited on the membrane surface. In some circumstance, backwashing is not favourable due to difficulty of removing the scalants. Addition of antiscalant that are formulated using polyacrylic acid, carboxylic acid, or phosphonates can be used to retard the crystal formation and inhibit the scaling (Goh et al., 2018).

CHAPTER 3

METHODOLOGY

3.1. Chemicals and Materials

The chemicals and materials used in this work are listed in Table 3.1.

Table 3.1 : Chemicals and Materials

Name	Assay	Purpose of use	Manufacturer
Calcium carbonate $CaCO_3$	**-**	Hardness of feed water	Omya AG group
PTFE	-	Membrane for process	Sterlitech Corporation
Hydrochloric acid HCl	87%	To maintain the pH of feed solution	Merck Group

3.2. Equipment

Removal of calcium carbonate is tested using the membrane distillation setup which consists of several equipment as listed in Table 3.2.

Table 3.2: List of Equipment

Equipment	Brand / Model	Purpose of use
Analytical balance	A&D Company Limited (FX-1000)	Weight the permeate water
Hot plate stirrer	Favorit	Mixing the calcium carbonate feed solution
Peristaltic pump	Masterflex L/S	Provide required flowrate and recirculation velocity for feed and permeate liquid during experiment

(Table 3.2 : Continued)

Hot Water Bath	Protech (HC-10)	Heating of feed solution before entering the membrane cell for MD process
Chiller	Huber minichiller	Cooling the permeate water before entering the membrane cell for MD process.
Flowmeter	Dwyer	Used to measure the recirculating velocity of the feed and permeate
Pressure gauge	Unijin (EN837-1)	Used to measure the pressure of water and feed to make sure no pressure build up in the tube.
Lovibond Water Testing AF446 Calcium hardness	Tintometer Group	Used to measure the calcium content in the feed and permeate.

3.3. Overall Experimental Works

Figure 3.1 shows the overall step on how the research are being carried out in general. The experiment start with the preparation of the $CaCO_3$ solution with different concentration. Then the membrane distillation system were set up. Experiment were carried out to investigate the effect of feed concentration, feed flowrate and feed temperature on the DCMD performance. Lastly, the fouling phenomena were studied based on the permeate flux trend.

```
┌─────────────────────────────┐
│   CaCO₃ preparation (0.1g/L- │
│            9.0g/L)           │
└─────────────────────────────┘
              ↓
┌─────────────────────────────┐
│    Membrane Distillation     │
│            system            │
└─────────────────────────────┘
              ↓
┌─────────────────────────────┐
│   Study on effect of feed    │
│ concentration (0.1g/L – 9.0g/L) │
└─────────────────────────────┘
              ↓
┌─────────────────────────────┐
│  Study on effect of feed flowrate │
│   (18.92L/hr – 27.85 L/hr)   │
└─────────────────────────────┘
              ↓
┌─────────────────────────────┐
│   Study on effect of feed    │
│  temperature (60°C - 80°C)   │
└─────────────────────────────┘
              ↓
┌─────────────────────────────┐
│  Study on fouling phenomena  │
│   by flux profile and SEM    │
│            images            │
└─────────────────────────────┘
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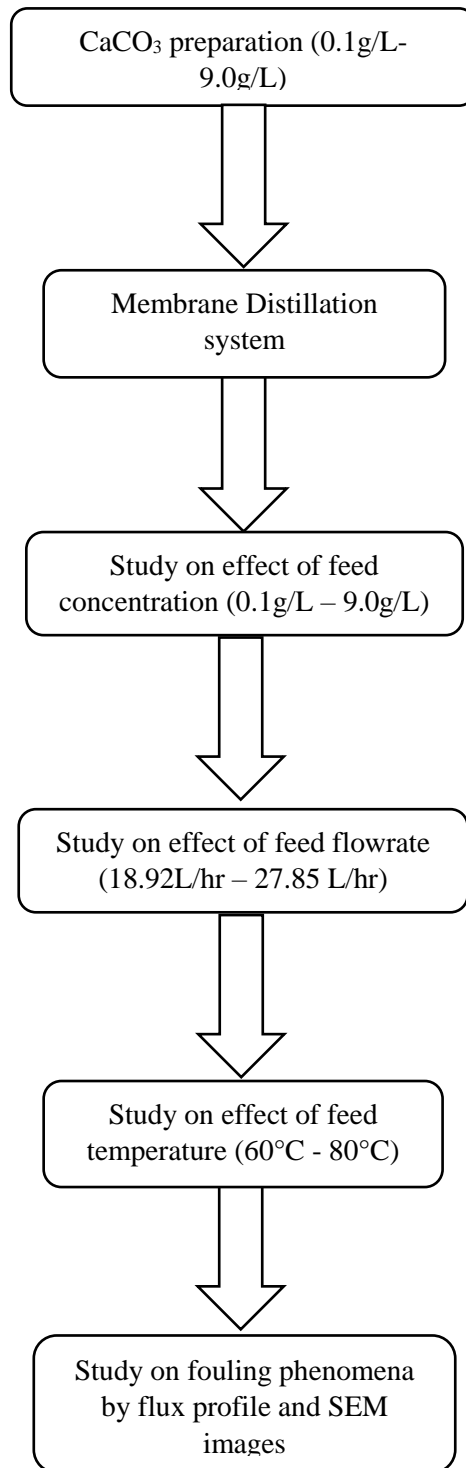
Figure 3.1 Overall Experimental Flowchart

3.4. Feed preparation

Calcium carbonate $CaCO_3$, in powder form, are dispersed in distilled water to prepare the feed solution at concentration of 0.1, 0.5, 1.0, 3.0, 5.0, 7.0, and 9.0 g/L. The feed solution prepared were maintained at pH 4 or lower by adding 5M of HCl. The dissolved $CaCO_3$ solution will be used to study the effect of feed concentration on the membrane flux and solute rejection. The calcium content in the feed solution are measured by using the Lovibond Water Testing AF446 Calcium Hardness Minikit.

3.5. Experimental Setup

The PTFE membrane bought from Sterlitech.Co are maintained in a vertical positon during the whole experiment run. The inlet and outlet flow channel engraved in each of the block at both feed and permeate side. The feed solution was heated to 80°C by placing it in a hot water bath. The feed then continuously pumped to the chamber for separation process and returned to the reservoir by using peristaltic pump. The permeate will continuously recirculated within the cold loop that cooled to the 6°C using a minichiller. The permeate reservoir is a jacketed flask that allows the overflow of excess water as a results of the vapour permeation. The overflow of permeate was continuously weighted on an electronic balance and the data is directly transmitted to the computer. The flux was calculated as the weight of permeate water collected over time and per unit area of the membrane. Pressure of feed and permeate side were monitored by using pressure gauges. While for the flow rates, they were measured using a flow meter. The DCMD system is illustrated in Figure 3.2
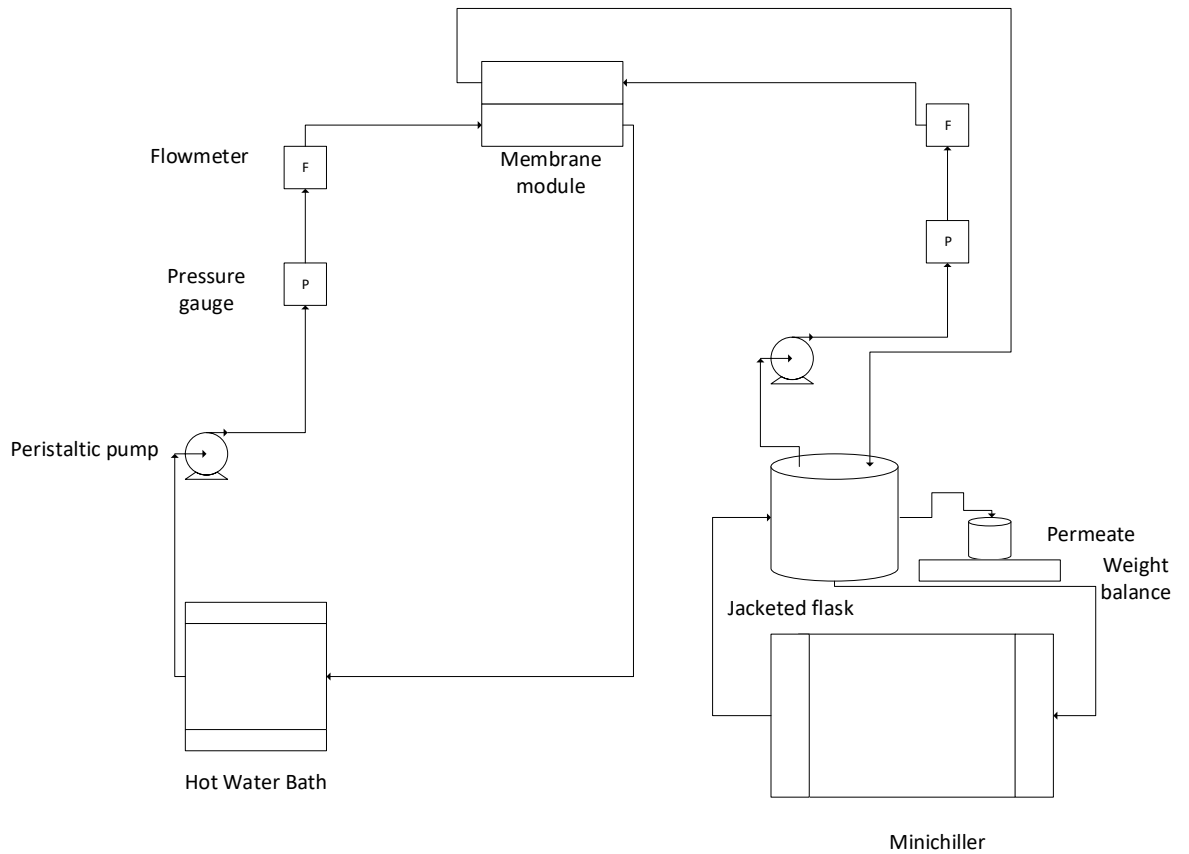
Figure 3.2: Experimental setup

3.6. Effect of feed concentration

The effect of $CaCO_3$ concentration on permeate flux is investigated in range of 0.1g/L to 9g/L. The feed and permeate flowrates are held constant at 26L/hr for both side. The feed and permeate temperature for inlet are maintained at 80°C and 6°C respectively. However, the actual temperature in the chamber are 75°C and 13°C in average for both hot and cold side. The performance of the membrane are evaluated based on the permeate flux and $CaCO_3$ rejection. The calcium content in the feed and permeate are measured by using the Lovibond Water Testing. The permeate flux is calculated by equation:

$$J = \frac{V}{At} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(3.1)$$

Where J is permeation flux (L/m^{2}h), V is permeate volume (L), A is membrane surface area (m^2) and t is time (hr). In this case the membrane area is 0.0042m^2.

Solute rejection is determined by :

$$R = \left(1 - \frac{C_p}{C_f}\right) x \; 100\% \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(3.2)$$

Where R is solute rejection (%), C_p is concentration of solute in the permeate, C_f is concentration of solute in the feed.

3.7. Effect of feed flowrate

The feed flowrate were varied from 18.92L/hr to 27.85L/hr are tested with the feed concentration were held constant at 9.0g/L. The temperature for inlet and outlet are held constant at 80°C and 6°C respectively. The permeate flux and solute rejection was determined by the equation stated in equation (3.1) and equation (3.2)

3.8. Effect of feed temperature

The feed temperature were varied from 60°C to 80°C are tested with the feed concentration 9.0g/L. The feed flowrate were held constant at 26.5L/hr for both hot and cold side. The permeate flux and solute rejection was determined by the equation stated in equation (3.1) and equation (3.2).

3.9. Study of the fouling phenomena

During the experiment, the feed concentration were held constant at 9.0g/L, feed flowrate at 26.5L/hr and temperature hot and cold side at 80°C and 6°C respectively. The flux profile of the membrane over 8 hours were monitored.

3.10. Determination of Calcium content

Calcium content in the feed and permeate streams are determined by using Lovibond Water Testing AF446 Calcium Hardness. 10ml of the sample, 12ml of deionized water and Calcheck tablet are mixed homogenously and then the calcium content will be calculated by Lovibond calculator.

3.11. Deposited cake layer characteristics

Membrane that filter 5.0g/L and 9.0g/L $CaCO_3$ solution are tested with scanning electron microscopy(SEM) to check the deposition of the cake layer on the membrane surface. The surface and cross section of the membrane are scanned to observe the deposition of the Ca^{2+} on the membrane.

CHAPTER 4

RESULT AND DISCUSSION

4.1. Study on Effect of Feed Concentration

Figure 4.1 show the permeate flux against the feed concentrations at 80°C and 26 L/hr feed flowrate. It can be clearly shown from the graph that the permeate flux decreases with increasing $CaCO_3$ feed concentration. The rate of flux decrement is higher at concentration below 3.0 g/L and the flux drop slowed down afterwards up to 9.0 g/L. The 0.1g/L $CaCO_3$ feed concentration show the highest permeate flux 15.11 L/m^2.hr and 9.0g/L $CaCO_3$ feed concentration show the lowest permeate flux 10.6 L/m^2.hr. Question arises here is whether the flux decrement is due to pore blockage, cake deposition or concentration polarization.

High concentration of $CaCO_3$ lead to build-up of polarization layer on the membrane surface. However, high concentration of Ca^{2+} ions will cause the ions precipitate and crystalize on the membrane surface and cause scaling phenomena (Goh et al., 2018). As the polarization layer become thicker, low water molecules can pass through the membrane and cause the permeate flux decline. An analysis shows that by increasing the solute concentration, higher solution viscosity with the will limit the permeate flux at finite pressure differences (Vladisavljević, 1999). High $CaCO_3$ concentration will increase the solution viscosity and induce Ca^{2+} ions deposition on the membrane surface and reduce the permeate flux.