EFFECT OF TEMPERATURE TOWARDS MEMBRANE FOULING BY MICROALGAE ALGAL ORGANIC MATTER

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EFFECT OF TEMPERATURE TOWARDS MEMBRANE FOULING BY MICROALGAE ALGAL ORGANIC MATTER

by

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LIST OF ABBREVATION

AOM	Algal Organic Matter
bEPS	Bound Extracellular Polymeric Substance
EDX	Energy Dispersive X-Ray Analysis
EPS	Extracellular Polymeric Substance
HA	Humic Acid
IOM	Intracellular Organic Matter
MD	Membrane Distillation
MF	Microfiltration
NOM	Natural Organic Matter
PP	Polypropylene
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidene Fluoride
RO	Reverse Osmosis
SEM	Scanning Electron Microscope
sEPS	Soluble Extracellular Polymeric Substance
TEP	Transparent Exopolymer Particles
UF	Ultrafiltration

KESAN SUHU TINGGI KEATAS PENYISIKAN MEMBRAN DISEBABKAN BAHAN ORGANIK MIKROALGA

ABSTRAK

Alga marin menghasilkan bahan organik algal (AOM) yang didapati menjadi penyebab terjadinya penyisikan dalam proses membran. Banyak kajian menunjukkan bahawa alga, menyebabkan pelepasan AOM yang signifikan ke dalam air secara ekstraselular dan intraselular melalui lisis sel. Membran penyulingan (MD) adalah teknologi baru yang didorong oleh termal yang memiliki banyak potensi dalam penyahgaraman, perawatan air dan air sisa, dan aplikasi lain. Keupayaan MD untuk pelbagai aplikasi telah diperbaiki berkat kemajuan dalam reka bentuk membran dan penggunaan sumber tenaga alternatif. Penyisikan membran, sebaliknya, masih menjadi isu utama yang melanda kestabilan jangka panjang MD. Dalam kajian ini, AOMs, yang merupakan bahan polimer ekstraselular larut (sEPS) dan EPS terikat (bEPS) dua spesies bentik (*Amphora coffeaeformis*dan *Navicula incerta*) terdedah kepada julat suhu untuk merangsang proses membran dan membran PP gentian geronggang direndam selama proses pemanasan untuk mengkaji kesan fouling membran pada suhu tinggi. EPS spesies diatom bentik diekstraksi dan dicirikan dengan menggunakan analisis colourimetric di mana untuk analisis karbohidrat, kaedah asid fenol-sulfurik digunakan untuk mengukur kepekatan karbohidrat dan untuk analisis protein, kaedah asid bicinchoninic (BCA) digunakan untuk menentukan kepekatan protein. Pencirian EPS dilakukan setelah alga dituai pada suhu bilik dan terdedah kepada suhu 60 °C, 70 °C dan 80 °C selama 8 jam. Begitu juga, membran direndam semasa proses pemanasan dan dikumpulkan selepas pemanasan untuk pencirian. Kajian ini akan membantu dalam menentukan ciri EPS yang dilepaskan oleh sel alga pada suhu yang lebih tinggi semasa

proses MD. Apabila suhu yang terdedah kepada EPS meningkat dari suhu bilik hingga 60°C, kepekatan protein dalam bEPS meningkat dari 340.74 ± 33.10µg/g menjadi 343.27 ± 32.03µg/g untuk *N. incerta* dan 279.75 ± 88.78µg/g menjadi 338.89 ± 119.51µg/g untuk *A. coffeaeformis*. Kepekatan protein bEPS tertinggi 375.58 ± 51.58µg/g untuk *N. incerta* diperoleh pada 80°C dan untuk *A. coffeaeformis* tertinggi 338.89 ± 119.51µg/g diperoleh pada 60°C. Untuk sEPS tren berbeza antara spesies dengan peningkatan suhu di mana kepekatan protein tertinggi 356.41 ± 185.16µg/g untuk *A. coffeaeformis* diperoleh pada suhu bilik dan untuk *N. incerta* tertinggi 321.59 ± 68.89µg/g diperoleh pada 60°C. Kepekatan karbohidrat dalam sEPS dan bEPS berbeza pada suhu yang berbeza pada spesies yang berbeza dan tidak dapat digeneralisasikan untuk setiap spesies alga. Walau bagaimanapun, kepekatan karbohidrat tertinggi di *N. incerta* untuk kedua-dua sEPS dan bEPS diperoleh pada suhu 70°C dengan nilai 679.30 ± 230.46µg/g dan 883.69 ± 51.70µg/g . Bagi *A. coffeaeformis*, kepekatan karbohidrat tertinggi dalam sEPS dan bEPS masing-masing adalah 310.194 ± 38.31µg/g pada 70°C dan 540.56 ± 232.79µg/g pada 28 °C. Lebih-lebih lagi, dari analisis membran, sudut kontak berkurang apabila suhu meningkat untuk EPS kedua-dua spesies. Sudut sentuhan untuk membran yang direndam dalam sEPS dan bEPS *A. coffeaeformis* dikurangkan masing-masing sebanyak 17% dan 59% apabila suhu meningkat dari suhu bilik hingga 80 °C. Untuk membran yang direndam dalam sEPS dan bEPS *N. incerta*, sudut kontak dikurangkan masing-masing sebanyak 29% dan 72% apabila suhu meningkat dari suhu bilik hingga 80 °C. Perbandingan antara gambar SEM menunjukkan bahawa bEPS menyumbang penyisikan yang lebih teruk berbanding dengan sEPS. Selanjutnya, peningkatan suhu meningkatkan penyisikan membran untuk kedua-dua sEPS dan bEPS. Secara keseluruhan, komposisi protein dalam EPS larut dan

EPS terikat pada suhu yang berbeza kemungkinan akan menentukan tahap penyisikan dalam operasi MD.

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ABSTRACT

Marine algae produce algal organic matter (AOM) which were found to be the cause in membrane fouling. Many studies shown that algae, cause significant releases of AOM into water extracellularly and intracellularly through cell lysis. Membrane distillation (MD) is a new thermally-driven technology that has a lot of potential in desalination, water and wastewater treatment, and other applications. The viability of MD for various applications has been improved thanks to advancements in membrane design and the utilisation of alternate energy sources. Fouling of membranes, on the other hand, is still a key issue that plagues MD's long-term stability. In this study, AOMs, which are soluble extracellular polymeric substance (sEPS) and bounded EPS (bEPS) two benthic species (*Amphora coffeaeformis* and *Navicula incerta*) were exposed to a temperature range to stimulate membrane processes and hollow fire PP membranes were soaked during the heating process to study the effect on the membrane fouling at high temperatures. The EPS of benthic diatom species were extracted and were characterized by using colourimetric analysis where for carbohydrate analysis, the phenol-sulphuric acid method was used to measure the carbohydrate concentration and for protein analysis, the bicinchoninic acid (BCA) method was used to determine the protein concentration. The characterization of the EPS was done after the algal were harvested at room temperature and exposed to temperatures 60°C, 70°C and 80°C for 8 hours. Similarly, the membranes were soaked during the heating process and collected after the heating for characterization. This study will help in determining the characteristic of EPS released by algal cells at a higher temperature during the MD

processes. When the temperature exposed to the EPS increased from room temperature to 60°C, the protein concentration in bEPS increased from 340.74 ± 33.10μg/g to 343.27 ± 32.03μg/g for *N. incerta* and 279.75 ± 88.78μg/g to 338.89 ± 119.51μg/g for *A. coffeaeformis*. The highest bEPS protein concentration of 375.58 ± 51.58μg/g for *N. incerta* was obtained at 80°C and for *A. coffeaeformis* highest of 338.89 ± 119.51μg/g was obtained at 60°C. For sEPS the trends were different between the species with the increasing temperature where the highest protein concentration of 356.41 ± 185.16μg/g for *A. coffeaeformis* was obtained at room temperature and for *N. incerta* highest of 321.59 ± 68.89μg/g was obtained at 60°C. The carbohydrate concentration in sEPS and bEPS varies at different temperatures in different species and cannot be generalized for every algal species. However, the highest carbohydrate concentration in *N. incerta* for both sEPS and bEPS were obtained at 70°C with values 679.30 ± 230.46μg/g and 883.69 ± 51.70μg/g respectively. For *A. coffeaeformis*, the highest carbohydrate concentration in sEPS and bEPS were 310.194 ± 38.31μg/g at 70°C and 540.56 ± 232.79μg/g at 28°C respectively. Moreover, from the membrane analysis, the contact angle reduces as the temperature increases for EPS of both species. The contact angle for membrane soaked in sEPS and bEPS of *A. coffeaeformis* reduced by 17% and 59% respectively when temperature increased from room temperature to 80°C. For membrane soaked in sEPS and bEPS of *N. incerta*, the contact angle reduced by 29% and 72% respectively when temperature increased from room temperature to 80°C. The comparison between SEM images showed that bEPS contributes more severe fouling compared to sEPS. Furthermore, increasing the temperature increases the fouling of the membrane for both sEPS and bEPS. Overall, the compositions of protein in the soluble EPS and bound EPS at different temperatures will likely dictate the severity of fouling in MD operations.

CHAPTER 1

INTRODUCTION

1.1 Background

Global water shortage and the lack of clean water have become critical problem worldwide. One of the solutions to this problem is seawater desalination where the freshwater supply can surpass the supply from the hydrological cycle (Jiang et al., 2020). Statistics done by International Desalination Association shows that a total of over 18 214 water desalination plant have been installed in more than 150 countries where the productions have achieved up to 90 million m3/day (International Desalination Association, 2020). The method which is widely used currently is reverse osmosis (RO) with multi-stage flash distillation (MSF). However, the common problem with this method is that this process is very complex and difficult to be scaled down for remote areas (Jiang et al., 2020). The best alternative to this method is membrane distillation (MD). MD uses membrane separation which is thermally driven based on the vapour pressure difference. Thus, resulting in lower energy consumption, smaller space requirement, and higher effluent quality which makes it a suitable technology for seawater desalination in remote areas (Liu et al., 2019).

Besides, the improvement of MD achieved to the point where up to 100% salt rejection and permeability have been achieved. Membrane fouling is a major problem after long operational hours due to the deposition of algal organic matter such as extracellular polymeric substance (EPS). At high temperatures, bacteria can also excrete EPS which adhere to the membrane surfaces promoting the fouling process. This membrane fouling reduces the permeate and productivity quality that leads to a higher plant operating and maintenance cost. Moreover, an additional cost will be required for

the pre-treatment, membrane replacement due to a shortened lifespan, and membrane cleaning processes (Goh et al., 2018).

1.2 Problem Statement

In order for the membrane distillation to work effectively the fouling has to be reduced. Many studies have been done on the fouling of membrane in membrane processes to identify the effect of algal organic matter on the membrane. Researches (Her et al., 2004; Jiang et al., 2020; Y. Zhang & Fu, 2018) showed that algal organic matter played a major role in fouling of the membrane in low-pressure membrane processes. Jiang et al.(2020) and (Tijing et al., 2015), showed that organic matter causes organic fouling which leads to the formation of conditioning film. DOC. Other researches (Weiwei Huang et al., 2014; Ly et al., 2017; Merle et al., 2016; X. Zhang et al., 2013), showed that the hydrophilicity of AOM causes the formation of the cake-like layer on membrane surface due to pore blocking. Besides, a study was done by Armbrecht et al.(2014), Winn-jung Huang et al.(2007) and Jackson(1990) on AOM found that TEP in algal organic matter also causes fouling. The previous study done by (Liu et al., 2019) showed that at a higher temperature the fouling was more significant which reduced the normalized flux (NF) of the membrane.

In another study done by (Jiang et al., 2020) increasing the temperature of MD causes temperature polarization and microbial community succession which leads to a higher membrane fouling. From all these studies and research, very few studied how temperature affects the algal organic matter in MD membrane fouling. By studying the temperature effect on AOM, the most efficient parameter for MD operation can be identified and fouling mitigation can be studied. In this study, 2 strains of benthic diatoms will be subjected to high temperatures where their compositional changes and

the fouling extensiveness to the polypropylene hollow fibre membrane will be studied in this project.

1.3 Objectives

The objectives for this experiment are:

i. To study the extensiveness of fouling of the membrane that are exposed to the algal organic matter at different temperature
ii. To identify the type of fouling on the membrane used where the presence of microalgae are prominent
iii. To identify the steps to prevent fouling on the membrane where the presence of microalgae are prominent

CHAPTER 2

LITERATURE REVIEW

2.1 Membrane Distillation

Membrane distillation is a relatively new process that replaces the conventional separation methods such as reverse osmosis and distillation. This method is cost-efficient and energy-saving which recently becomes an attractive alternative for conventional methods. The major advantages of using MD separation processes are it requires lower operating pressure and temperature than conventional separation processes which are pressure-driven such as reverse osmosis (RO) (Lawson & Lloyd, 1997).

The temperature of the solution not required to heat up till the boiling point and membrane properties such as mechanical properties are less demanding in MD (Alkhudhiri et al., 2012). This translates into a lower operating cost of equipment and increased process safety. MD theoretically can achieve 100% rejection of macromolecules, ions, cells, colloids, and other involatile materials due to the vapour-liquid equilibrium working principle. Besides, MD equipment is smaller because of the thick pore volume of the microporous membrane which supports the vapour-liquid contact. Where else the conventional distillation method relies on high-pressure vapour velocities to provide efficient vapour-liquid contact. The chemical interaction in MD is reduced between the membrane and contact solution. (Lawson & Lloyd, 1997). The MD process also requires a relatively larger pore size membrane compare to other separation processes which result in lower fouling (Alkhudhiri et al., 2012).

Alternative sources such as solar energy can be used to power MD processes which are more cost-effective (Alkhudhiri et al., 2012). Membrane distillation is a process that is thermally driven where hydrophobic membranes are used to separate the

hot feed solution and cold water stream and allow the evaporation of water due to temperature difference (Manawi et al., 2014). It has benefits compared to other MD is also able to utilize heat from geothermal heat, and waste heat for the separation of high-quality clean water from contaminated water (Bogler & Bar-Zeev, 2018).

2.2 Membrane Distillation Configurations

There are four main configurations of MD processes as shown in Figure 2.1 which are Direct Contact Membrane Distillation (DCMD), Air Gap Membrane Distillation (AGMD), Sweeping Gas Membrane Distillation, and Vacuum Membrane Distillation (VMD) (Kiss & Kattan Readi, 2018).

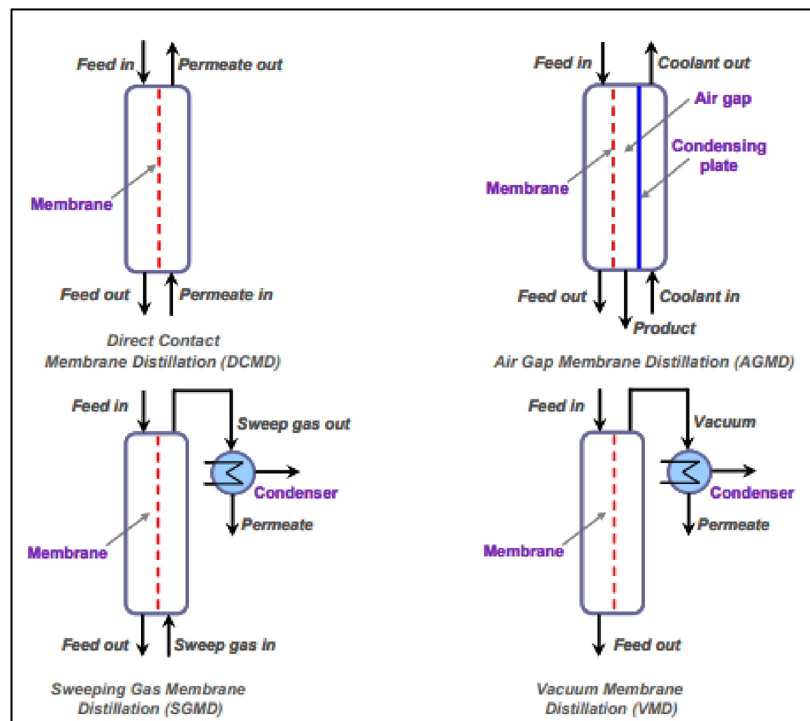

Figure 2.1 Conventional membrane distillation configurations. Adapted from Kiss & Kattan Readi (2018)

In DCMD, the hot solution will be in direct contact with the hot membrane surface and the evaporation occurs at the feed-membrane surface. Due to the vapour pressure difference across the membrane, the vapour will be transported to the permeate

side and condenses in the membrane module (Kiss & Kattan Readi, 2018). Due to the hydrophobicity of the membrane, the feed cannot pass through the membrane and only vapour exist inside the membrane pores. DCMD is the simplest MD configuration and largely implemented in desalination processes. However, the drawback of using DCMD is the conduction through the membrane results in heat loss higher than another MD configuration (Alkhudhiri et al., 2012).

In AGMD, there is a permeate gap that is occupied with stagnant air lies between a cooling walling and the membrane. Similar to the DCMD, the hot solution will be in direct contact with the hot membrane surface. The vapour will pass through the air gap and condenses over the membrane modules cold surface. The air gap will help in reducing the heat lost by increasing the conductive heat transfer resistance (Alkhudhiri et al., 2012). AGMD can be used to remove volatile components from feed solutions since the permeate fluid will not be in direct contact with the membrane (Kiss & Kattan Readi, 2018).

SGMD is also known as air stripping where an inert gas is used to sweep the vapour from the permeate side to condense outside the membrane module (Alkhudhiri et al., 2012). The gas barrier is similar to AGMD but since the inert gas is not stationary hence it enhances the mass transfer rate. SGMD is commonly used to remove volatile components from an aqueous solution. The drawback of SGMD is it requires a larger condenser because a small amount of permeate diffuses in a large amount of sweep gas (Kiss & Kattan Readi, 2018).

Lastly, in VMD a vacuum is created in the permeate side of the membrane by using a pump to suck out the vapour passing through the membrane and condensing it outside of the module (Alkhudhiri et al., 2012). This has a major advantage where the conduction heat loss can be negligible (Khayet, 2011). Unlike in pervaporation, the

wetting in the VMD membrane is avoided. The VMD is used to remove organic compounds from aqueous solutions (Kiss & Kattan Readi, 2018).

According to Khayet (2011), a membrane should satisfy ten requirements before the application in MD operations. In short, the membrane can be single or multi-layered with at least one layer made from a porous and hydrophobic

material, the membrane should have pore size distribution as narrow as possible to avoid the penetration of permeate, the tortuosity factor should be small, porosity should be as high as possible, the thickness should be optimum, thermal conductivity should be small as possible, high fouling resistance material, good thermal stability, excellent chemical resistance and long life (Khayet, 2011).

The common membrane used for MD is hydrophobic membranes made from polymers such as polyvinylidene fluoride (PVDF), polypropylene (PP), polytetrafluoroethylene (PTFE) and polyethylene (PE). A study done by Al-Obaidani et al.(2008) showed that membranes physical properties such as thermal conductivity have a large impact on the permeate flux and thermal efficiency. From Figure 2.2 we can see that membranes with higher thermal conductivity coefficient display lower thermal efficiency and lower permeate flux (Al-Obaidani et al., 2008).

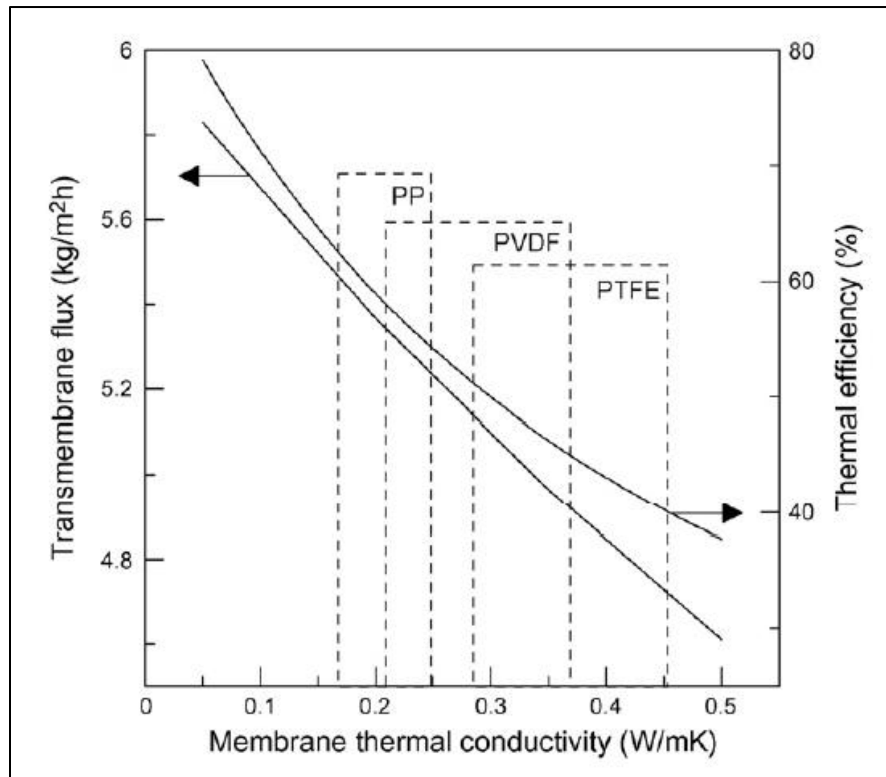

Figure 2.2 Membrane thermal conductivity effects on simulated DCMD permeate flux and thermal efficiency (Al-Obaidani et al., 2008)

MD membrane modules can come in many forms which are flat plate module, hollow fiber and spiral wound. Flat plate modules are commonly used, and cleaning is relatively easy. Hollow fiber membranes consist of tubular capillaries which are small. However, these membranes have a high potential for fouling. Spiral wound modules consist of spacer and membrane wrapped around a collection tube. Spiral wound modules and hollow fiber modules are cost-efficient due to greater membrane areas (Warsinger et al., 2015).

2.3 Membrane Distillation Fouling

MD membrane faces a similar challenge faced by membrane-based separation system which is membrane fouling. Fouling is the accumulation of unwanted particles or materials on the membrane surface with an associated detriment of function

(Warsinger et al., 2015). Classical DLVO theory describes the forces of interaction between the membrane surface and the foulants (Derjaguin & Landau, 1993). DLVO theory states that the summation of the electric double layer forces and the van der Waals forces is the net particle-surface interaction (Tijing et al., 2015).

A fouling laying causes an increase in thermal and hydraulic resistance (Hamzah et al., 2019). This layer reduces the temperature gradient across the membrane causing the increase in temperature polarization which results in a lower driving force (Hsu et al., 2002). The main four factors are affecting the fouling formation which are the foulant characteristics, feedwater characteristics, operating conditions and the properties of the membrane (Tang et al., 2011). However, when it comes to fouling on the membrane surface, the main factors will the kind of foulants, their properties and concentration present in the feed water (Tijing et al., 2015).

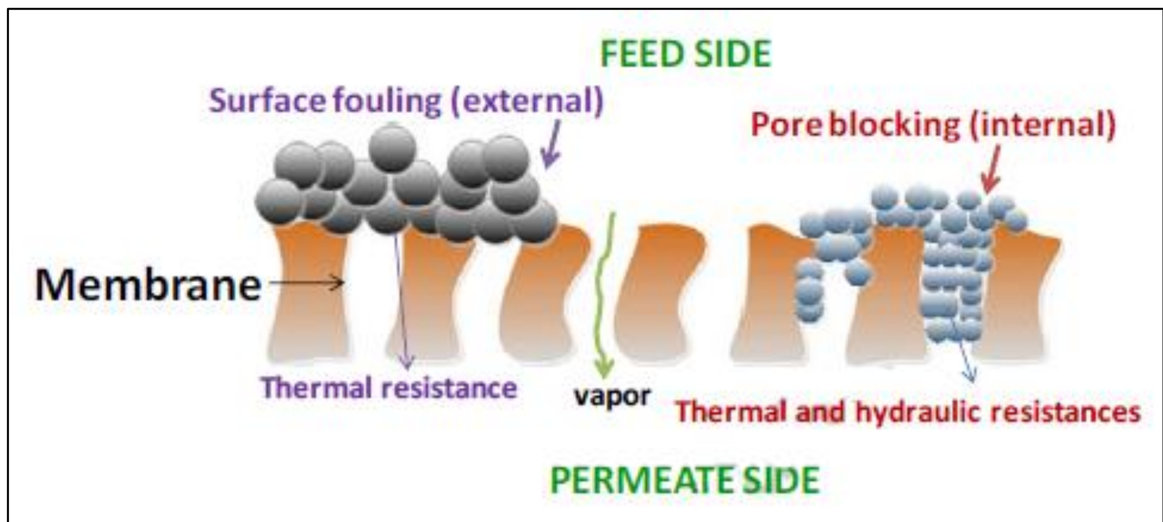

Figure 2.3 Two types of membrane fouling: Surface fouling (external) & Pore blocking (internal). (Knyazkova & Maynarovich, 1999)

Fouling can be divided into two types which are external surface fouling and pore blocking fouling (internal fouling) as shown in Figure 2.3 (Knyazkova & Maynarovich, 1999). External fouling occurs when foulants build up in a gel or cake-

like layer in the outer feed side of the membrane while pore-blocking occurs when the foulants are formed inside of the membrane pore by partial or complete blocking of the pore (Zhu & Nyström, 1998). Pore blocking is irreversible since it degrades the membrane while external surface fouling is reversible and can be cleaned by chemicals or backwashing (Hoek et al., 2008).

There are three main groups of fouling materials which are inorganic fouling, organic fouling, and biological fouling (Meng et al., 2009a). The deposition of colloidal inorganic particle and precipitation of hard mineral salts causes inorganic fouling or also known as scaling. Crystallization can either be heterogenous if crystal nucleate on the surface of the membrane or homogenous if crystals nucleate in the bulk. Organic fouling is caused by the deposition of organic matters (OM) such as humic acid (HA), proteins and polysaccharides.

There are few types of bulk organic matter in the interest of drinkable water treatment which are natural organic matter (NOM) which mainly consists of HA substances derived from leaching of vegetable debris and algal organic matter (AOM) which consist of extracellular and intracellular macromolecules and cellular debris (Amy, 2008). Organic fouling occurs when high molecular weight organic molecules such as natural organic matters (NOMs) and transparent exopolymer particles (TEP) undergo deposition, reaction, and interactions with the membrane surface (Goh et al., 2018). Organic molecules are released by aquatic organisms and bacteria when exposed to a high temperature which increases the biofilm-forming effect. Biological fouling occurs due to microbial organisms such as fungi, bacteria, and algae.

Fouling such as biofouling, organic fouling, and inorganic fouling can take place simultaneously depending on membrane nature, feed water quality, and operating

conditions (Goh et al., 2018). Besides, fouling has a great impact on the membrane permeability, membrane effectiveness and the life of the membrane.

2.4 Biofouling of membrane distillation

Biofoulings occur due to the accumulation of biological species and their growth on the membrane surfaces. This affects the membrane permeability which reduces productivity and causes operational problems. Microorganisms are the main biological species involved in biofouling. However, comparing to other membrane processes such as MF, UF and RO less fouling can be expected in MD since the operating temperature is high and the high salinity limits the growth of microorganisms. Even though microorganisms can't withstand high temperature there are certain bacteria species that can survive and grow in extreme conditions causing biofouling (Tijing et al., 2015). Gryta (2002) studied the growth of microorganism on MD membrane using DCMD where he found that the most common growth of microorganism using different membranes were fungi and bacteria (Gryta, 2002).

There are three stages in the formation of biofilm. The first stage is the formation of conditioning film. The biofilm-forming process begins with the nutrients substance from the feed solution and organic matter released by dead microorganisms such as bacteria cells attaching to the membrane surface promoting the formation of cake layer or known as conditioning film (Liu et al., 2019). This is where organic fouling plays the main role whereas mentioned above organic matters releases soluble microbial (SMP) and secreted extracellular polymeric substance (EPS) which accumulate on the membrane surfaces due to permeate drag and gravity force forming the conditioning film (Jiang et al., 2020). The conditioning film consists of lipids, polysaccharides, HA, and proteins (Tijing et al., 2015).

Then, the attachment of survived bacteria to the organic conditioning film begins and starts to grow. Then following an irreversible attachment of these bacteria the biofilm develops into a multi-layered biofilm structure which compromises dead and living cells encased in a protective matrix of self-produced EPS (Bogler & Bar-Zeev, 2018). After the colonization of the survived organisms, the next stage will be microbial succession and further attachment of organic matter.

Lastly, it enters the last stage where a stage and gradually mature biofilm formed successfully on the MD membrane (Liu et al., 2019). Figure 2.4 shows a simple schematic diagram of the biofilm formation process. The formation of biofilm in the membrane surface might induce membrane wetting due to the release of amphiphilic EPS from microorganisms. Amphiphilic EPS contains both hydrophilic and lipophilic properties which decrease the hydrophobicity of the membrane leading to salt leakage from the feed side to distillate side. Similar to organic fouling, the formation of biofilm can partially or completely block the pores of the membrane causing a reduction in diffusive transport (Liu et al., 2019). The temperature polarization of the membrane will increase when the pores are completely blocked by a hydrodynamically stagnant membrane (Gryta, 2008).

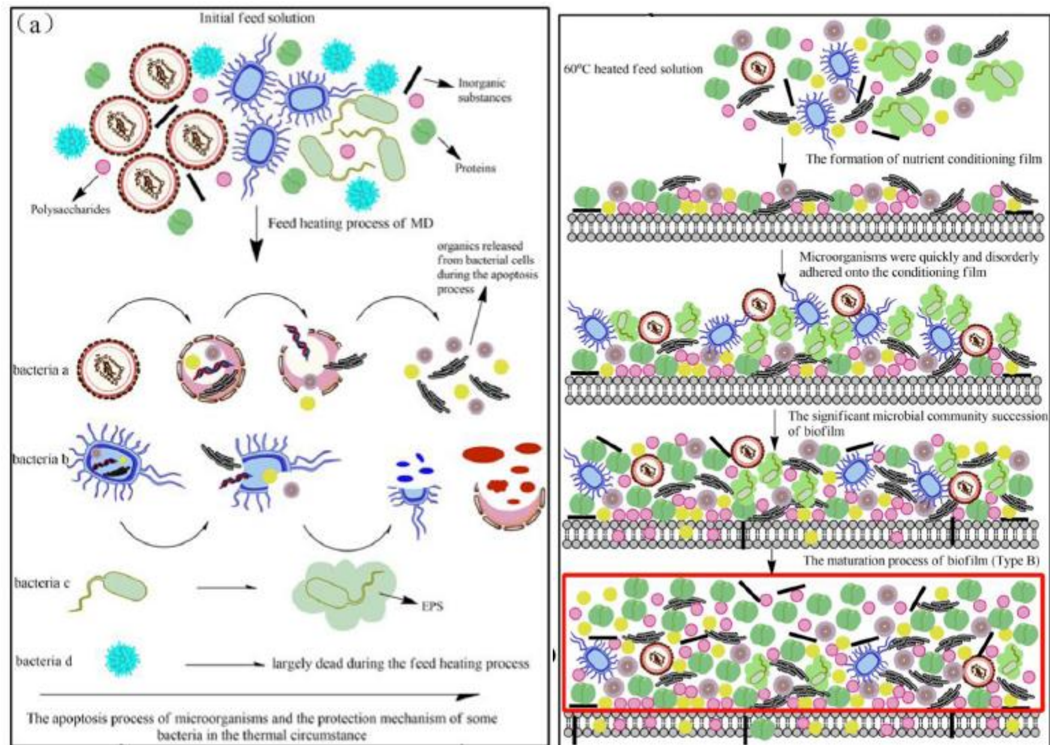

Figure 2.4 Schematic diagram of biofilm formation: (a)Feed solution heating (b)Biofilm formation process (Liu et al., 2019)

2.5 Algal / Algogenic organic matter (AOM) as biofoulants

The feed water for water desalination processes using MD is usually taken from the sea, lakes and reservoir. Microalgae are diverse in the group of prokaryotic and eukaryotic organisms. These microalgae have a wide range of tolerance to temperature, salinity, pH and nutrients (Y. Zhang & Fu, 2018). The water from these places is abundant with microalgae since they are the primary producers where they produce organic matter and undergo photosynthesis and serve as a food source for freshwater organisms (Her et al., 2004). However, an excessive amount of microalgae or algae bloom can cause severe problem to the water where it will be polluted by nutrients such as phosphate and nitrogenous compounds (Loza et al., 2014).

Algae blooms are usually compromised of blue-green or green algae or both together. This might also lead to eutrophication which harms the aquatic ecosystem and

threats to humans as well. Algae blooms or high amount of algae will reduce the transparency of the water while blocks the sunlight which functions as an important factor for photosynthesis for aquatic plants. As a result, the oxygen content in the water will deplete causing the death of photosynthetic and aquatic organisms.

Membrane processes such as MD, MF and UF are known for their ability to remove colloidal particles and pathogenic microorganisms. Although, these membrane processes can filter these particles however the fouling of algae reduces the membrane permeability due to their accumulation or formation of cake-like substance as discussed on the biofouling topic above. The composition of algal suspension is mainly composed of excreted metabolic products, algal cells and debris which can cause fouling in all kind of membrane processes including MD (Rickman et al., 2012). Cell debris are particle that are smaller in size than the pores of the membrane that can cause pore blocking. Most of the study done on the algal fouling was on based on MF, UF and NF and very few were available on algal fouling on MD. However, from the studies on other membrane processes, we can study how and what affect the fouling of the membranes.

Now let's look more in detail about the algal cells and AOM present in the microalgae suspensions. WEHR (2007) estimated that the amount of microalgae species are around 1-10 million. They come in various sizes and shapes such as ellipsoids, needles and spheres (Ozkan & Berberoglu, 2013). Since MD only allows vapour through the membrane the penetration of these microalgae should not be a worry but the formation of the cake-like layer or biofilm. Various studies have shown that algal have a large influence on the flux decline and fouling of membranes. Nearly all the species of microalgae produce organic matters either by enzyme-catalyzed reactions for their growth or due to adverse environmental effects such as limitation of nutrients and

unfavourable environment such as salinity, pH and temperature (Y. Zhang & Fu, 2018). AOM can also increase when the cell rupture due to self-disruption or any other external action (Pivokonsky et al., 2006).

The major components of AOM are proteins, polysaccharides, humic acids and low molecular weight acids. Algae releases AOM into the water intracellularly by cell lysis which is intracellular organic matter (IOM) and extracellularly which extracellular organic matter (EOM) (Her et al., 2004). Besides, there is a special class of AOM which is transparent exopolymer particles (TEP) that is formed either by aggregation of dissolve precursor released during the metabolic process of algal cells or releasing during cell breakage (Passow, 2002; Passow et al., 2001).

Extracellular polymeric substances (EPS) fall under EOM. They are defined as "extracellular polymeric substances of biological origin that participate in the formation of microbial aggregates" (GEESEY & GG, 1982). EPS is a general term for different classes of EOM components such as protein, polysaccharides, lipids and other polymeric substances (Kidoue et al., 1980). EPS can either in bound or soluble which divides it further into two categories which are bound EPS (bEPS) and soluble EPS (sEPS/SMP). Bound EPS are located outside of the cell surface containing protein, humic acids, lipids, nucleic acids and polysaccharides (Meng et al., 2009b). Soluble EPS are released from metabolic processes which are also known as substrate-utilisation-associated products (UAP), and decay of biomasses which is known as biomass-associated products (BAP) (Barker & Stuckey, 1999; Laspidou & Rittmann, 2002).

AOM growth can be divided into 4 phases which are lag phase, exponential phase, stationary phase and death phase (Ly et al., 2017). Huang et al.(2007) experimented with three cyanobacteria species where all of them produced a high

amount of AOM at exponential phase compared to stationary phase at lower at stationary phase. Pivokonsky et al. (2006) showed that the growth phase linearly increased regardless of algal species for the exponential and stationary phase. Li et al (2011) reported for AOM extracted from *M. aeruginosa,* the IOM values were highest in the total dissolved organic carbon (DOC) under exponential phase which proves the statement by Huang et al.(2007).

Many researchers found that AOM in algal suspension is largely composed of hydrophilic DOC (Her et al., 2004; Weiwei Huang et al., 2014; Ly et al., 2017; Merle et al., 2016; Xiaolei Zhang et al., 2013). Weiwei Huang et al.(2014) studied the AOM from five algae containing cyanobacteria, green algae and diatoms where the hydrophilic fraction for all the species was above 60% and was the largest portion of the DOC. Similarly, Her et al. (2004) obtained up to 78.6% of the hydrophilic fraction of AOM using cyanobacteria. Hydrophilicity plays a major part in membrane fouling. The hydrophilic fraction of AOM mainly composed of proteins and polysaccharides (Lee et al., 2006). The hydrophilic interaction of these components such as dipole-dipole attraction and hydrogen bonding to the hydrophobic membrane surface will cause the formation of the cake-like layer due to the pore blocking (Her et al., 2004; Y. Zhang & Fu, 2018). (Her et al., 2004; Jiang et al., 2020; Y. Zhang & Fu, 2018)

Besides, hydrophobic components can also cause fouling by strong hydrophobic interaction with the hydrophobic membrane of MD. The molecular weight distribution varied with the type of algal species (Her et al., 2004; Weiwei Huang et al., 2014; Ly et al., 2017; Merle et al., 2016; Xiaolei Zhang et al., 2013). The large molecular weight molecules in AOM were protein and polysaccharide while the smaller ones were acids and humic-like substance (Y. Zhang & Fu, 2018).

Transparent exopolymer particles (TEP) are highly sticky and flexible in nature (Passow, 2002). This stickiness of TEP causes the accumulation and absorption of other materials such as microorganisms mainly bacteria, trace metals and other AOM components in the feed water to the MD forming aggregation (Armbrecht et al., 2014; Winn-jung Huang et al., 2007; Jackson, 1990). This leads to the formation of a conditioning film that contributes to biofouling.

Hence, from the studies done by many researchers, we can see that there are many factors in how the AOM affect membrane fouling. The main causes of fouling were the accumulation caused by TEP causing the forming of cake-like layer, hydrophilicity and hydrophobicity of membrane which causes the pore blocking and high molecular weight components such as protein and polysaccharide, lower molecular components such as humic acids which both are major components of AOM. Figure 2.5 shows how different the composition of AOM affects the fouling of the membrane (Y. Zhang & Fu, 2018). However, most of this research is based on low-pressure membrane distillation such as UF, NF and RO. Therefore, it is important to study the effect of microalgae organic matters on the fouling of MD, to study whether the effects of algal organic matter are similar or different from the other membrane processes. This is crucial in setting the parameters of the MD process such as temperature and membrane properties.

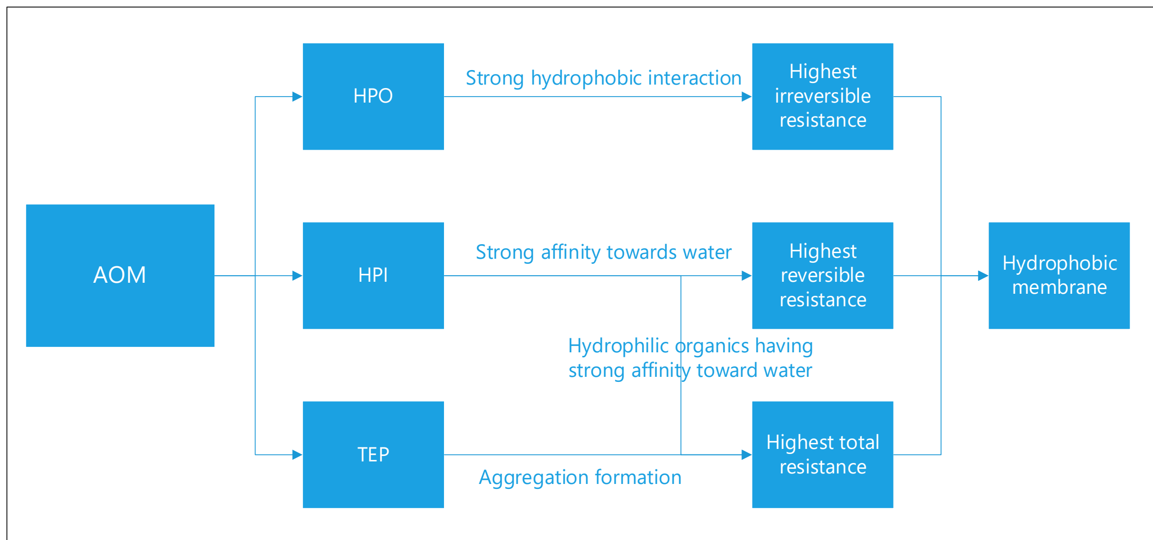

Figure 2.5 Compositions of AOM in membrane fouling (Y. Zhang & Fu, 2018)

2.6 Temperature effects toward algal organic matter

Most of the study on AOM were done to study the membrane fouling in different low-pressure membranes and very few studies were done on the temperature effect on AOM. However, the study on the temperature from these researchers (Araújo & Garcia, 2005; Chu et al., 2015; Lan et al., 2015; Tan et al., 2014; Wolfstein & Stal, 2002; Zhao et al., 2015) were at lower temperatures (20°C-40°C) which did not suit the study of this paper since MD operation occurs at a much higher temperature (60°C-80°C). Nevertheless, there are many studies on the influence of feed temperature on membrane fouling and the composition of the microbial community on the membrane surfaces which can be very much related to the AOM (Bogler & Bar-Zeev, 2018; Jiang et al., 2020; Krivorot et al., 2011; Liu et al., 2019).

In the study done by Liu et al.(2019), the influence of feed temperature on membrane fouling and the composition of the microbial community on the PTFE membrane was studied at two different temperatures which are 40 °C and 60 °C. The study found out that at temperature 40°C the normalized flux declined slowly by 35.1% which is lower than at 60 °C where the declines of normalized flux were faster and

declined by 69.4%. The declining trend in the initial stage for both the temperature was similar but then a more severe decline was observed at 60°C. At 60 °C, the organic and inorganic matter were higher in concentration than in 40°C.

This might be due to the release of EPS (AOM) of algal. Cell rupture of algal occurs due to external action such as high temperature (Pivokonsky et al., 2006). This was proven by comparing the EEM fluorescence spectra obtain for both the temperature where the peak which represents protein-like substances and humid-acids showed a higher peak in 60°C (Liu et al., 2019). This resulted in a thicker and denser conditioning film / cake-like layer to be formed at 60°C due to the accumulation of EPS on the membrane surfaces by permeate drag and gravity force forming the conditioning film (Jiang et al., 2020). Thus, causing biofouling that leads to a more severe and higher flux decline rate.

Similar results were obtained in the study done by Bogler & Bar-Zeev (2018) where increasing feed temperature of 47°C, 55°C, and 65°C on biofilm growth and MD performance were studied. Increasing the temperature resulted in reduced normalized flux especially at 55°C where there was a 78% decline in the flux. This might be due to the Anoxybacillus sp. bacteria found in the feed water which grows optimally at that temperature. Besides, salts were found in the distillate when MD operating at temperature 55°C and 65°C over the duration of 3 days. This is due to the membrane wetting which impaired the rejection of salts and other non-volatile contaminants which usually caused by amphiphilic EPS which decrease the hydrophobicity of the membrane leading to salt leakage (Liu et al., 2019). The study found that at temperature 65°C most of the membrane pore was covered with a continuous layer of EPS which was secreted due to heat shock in the feed solution. The shock causes the release of AOM such as

EPS due to the cell lysis or rupture of algal organic matters (Bogler & Bar-Zeev, 2018; Pivokonsky et al., 2006).

Krivorot et al (2011) studied on the effect of temperature regime on biofouling in the membrane. DCMD was run in 3 sets which are 40°C cross flow, 40°C parallel flow and temperature cycling from 70°C to 40°C. All the DCMD membrane formed biofilm consisting of components of AOM. The protein and DNA contents were higher when DCMD was run at 40°C compare to the temperature cycling from 70°C to 40°C. This temperature cycling method is usually found in dairy industries where it is used to kill microorganisms (Knight et al., 2004). This suggests that during the temperature cycling the microorganism in DCMD died and as a result, the attachment to the biofilm will be reduced leading to lower biofouling of the membrane. However, the study of AOM on temperature cycling is not available and further study has to be done.

Thus, we can conclude that the study on the effect of temperature on AOM and how it affects the membrane is lacking and more studies should be done. MD desalination solution provides areas such as rural where the accessibility of clean water is difficult with safe and drinkable water. Hence, it is important since these studies will improve the efficiency of the MD process and allow more investors to invest in these technologies.

CHAPTER 3

METHODOLOGY

Figure 3.1 shows the activity of the research.

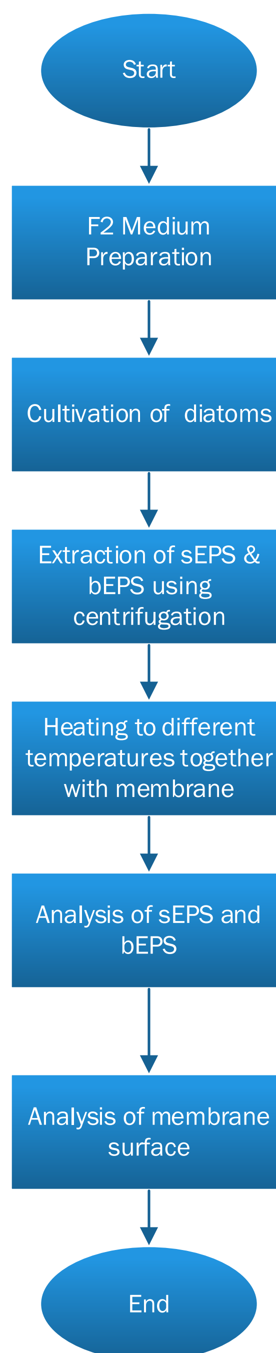

Figure 3.1 Methodology flow chart

3.1 Cultivation of diatoms

The algae diatoms that used for this project will be *Amphora coffeaeformis* (UTEX 2983) and *Navicula incerta* (UTEX 2044). The diatoms then will be cultivated in 2l batch cultures in sterilized f/2 medium. F/2 mediums were sterilized by autoclaving for 20 min under 121°C. Cell count was done beforehand using a hemocytometer (Neubauer chamber) under the light microscope (BX-51, Olympus, Japan) to ensure the same amount of cells are cultured for both cells. The diatoms were cultivated for 2 weeks under an aseptic condition where the cultures were incubated in 24 hours artificial lighting (1500lx) at 25 ± 2°C. Aeration is provided to provide oxygen and CO_2 by bubbling atmospheric air (filtered through Midisart 0.2 µm PTFE membrane filter, Sartorius, Germany) (Merle et al., 2016). F/2 medium is a widely used seawater medium for growing marine algae especially diatoms (Robert R, L, 1975).

3.2 Fresh and dry weight of cell

To obtain the fresh and dry weight of cell the algal suspensions have to centrifuged twice. First, the algal suspension from the cultivation will undergo centrifugation twice to obtain the fresh and dry weight. The 50ml of the solution for each culture was centrifuged at 8500rpm for 15minutes to obtain the supernatant (soluble EPS,sEPS). Then, the supernatant was removed by pipetting it from the top fraction of the centrifuging tube. The residual algae were mixed with 50ml distilled water and centrifuged again at 8000rpm for 10minutes. The distilled water washes out any leftover sEPS in the residual algae. The distilled water fraction is then pipetted and removed to obtain the fresh weight of the sample. Before the centrifugation, the mass of centrifuging tube was measured. The fresh samples were then placed in the oven at

55°C till completely dried and constant dry mass was obtained. This method was done 3 times and the average weight was calculated.

3.3 Extraction of sEPS and bEPS

In order to obtain the sEPS and bEPS centrifugation method will be used. The algal suspensions were divided into 36 centrifuging tubes each containing 50ml of the solution for each culture. Similar to the weight obtaining method, the 50ml algal suspensions have been centrifuged first at 8500rpm for 15min to extract the sEPS. Then, the remaining bEPS was mixed with 25ml of NaCl solution. These extracts were kept in the fridge at 3°C before the heating process. (Yan et al., 2017; Zhao et al., 2015).

3.4 Heating the sEPS and bEPS with the PP hollow fibre membrane to different temperatures

The centrifuged sEPS and bEPS were heated with PP hollow fibre membrane (0.2 μm pore size, Membrana, Germany). to a different temperature to study the effect of AOM temperature on membrane fouling. The PP hollow fibre membrane was cut into 2 pieces of 1.5cm and 2 pieces of 3cm and placed in the beaker of the extracts. The smaller membrane was used in the contact angle analysis where else the longer membrane was used for SEM analysis. SEPS extracts separated into 4 beakers containing 450ml of the extract. One beaker of sEPS extract was left at room temperature as a control for the study. The other 3 beakers were using a hot plate magnetic stirrer for 8 hours at temperatures of 60°C, 70°C and 80°C. Similarly, for the bEPS, the extracts were separated into 4 beakers each containing 225ml of the extracts where one beaker was left at room temperature as control and the remaining were heated at temperatures similar to the sEPS extracts. After the heating, the extracts and the soaked membranes were collected back into the centrifuging tube and kept in the fridge

at a temperature of 3°C prior to any analysis. Three replicates were done for each species.

3.5 Analysis of Carbohydrate and Protein

3.5.1 Carbohydrate Analysis

For the carbohydrate analysis, the extracts were first centrifuged at 8500rpm for 15min. 1ml of supernatant from the centrifuged extracts were pipetted and added with 0.5ml phenol (0.5%) and 2.5 ml of concentrated sulphuric acid (97%). The solutions were let to sit for 10 min before being placed into a water bath at a temperature of 30°C for 15min. The solutions were covered with parafilm to avoid any evaporation. Then the solutions were cooled to room temperature and the carbohydrate contents were read using the Ultraviolet-visible spectroscopy at a wavelength of 490nm. The readings were taken 3 times and averaged.

3.5.2 Protein Analysis

The protein analysis was done by first centrifuging the extracts at 8500rpm for 15min. Then, 0.05ml of supernatant was extracted and mixed with 1ml of BCA working reagent. Once mixed, the solutions were heated at 37°C for 30min and let to cool to room temperature. The solutions were covered with parafilm to avoid any evaporation. The solutions were then placed in Ultraviolet-visible spectroscopy and readings for protein analysis were taken at wavelength 562nm. The readings were taken using small and large cuvette 3 times and averaged.