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NOVEL MEMBRANE STRUCTURE DESIGN FOR BIOMASS HARVESTING AND WATER RECYCLING

A Thesis
Presented to
The Academic Faculty

by

Sarasija Cheruvu

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NOVEL MEMBRANE STRUCTURE DESIGN FOR BIOMASS HARVESTING AND WATER RECYCLING

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LIST OF SYMBOLS AND ABBREVIATIONS

cf	Final Concentration
co	Initial Concentration
vf	Final Volume
vo	Initial Volume
DCF	Dynamic Cross-Flow Filter
TFC	Thin-Film Composite
NF	Nanofiltration
PAN	Polyacrylonitrile
PVDF	Polyvinylidenedifluorure
SEM	Scanning Electron Microscopy
FTIR	Fourier Transform Infrared Spectroscopy
DOM	Dissolved Organic Matter
HPSEC	High Performance Size Exclusion Chromatography
PIP	Piperazine
TOC	Total Organic Carbon
COD	Chemical Oxygen Demand
CF	Concentration Factor
VRF	Volumetric Reduction Factor
TMC	Trimesoyl Chloride
AOM	Algogenic Organic Matter

SUMMARY

Sustainable algae biofuel production is rising in demand, and the need to establish an efficient and proper algae harvesting method is extremely essential. Membrane filtration technology seems to be the most promising as a solid-liquid separation process. However, fouling seems to be the major problem for membranes. There is limited research on how to solve the problem of fouling, and cake buildup inside the membranes. A novel membrane design is required to solve the problem of fouling and cake buildup inside the membranes. The objective of this research is to construct a novel two way membrane design for algae biomass harvesting and water recycling. The methods used include culturing algae species, filtering them through the membrane module, and sample analysis for determining the water quality. The results show that the present filtration model had no fouling, or cake buildup as opposed to the previous filtration model. The present model permeate has a very low optical density of 0.007 absorbance at 750 nanometers. This result shows that permeate is completely devoid of algae.

CHAPTER 1

INTRODUCTION

Environmental issues such as global warming and climate change and their impact on human beings have raised a lot of curiosity amongst governing bodies and people worldwide. The root cause of these problems is believed to be usage of fossil fuels, which has played a pivotal role in the increase of greenhouse gas emissions (GHG) such as carbon dioxide and nitrous oxide emissions. Carbon dioxide emissions have been contributing factors to depleted aquatic life as oceans turn acidic by absorbing carbon dioxide from the environment. Also, fossil fuels are extracted by fracking, which could potentially lead to earthquakes and other potential natural disasters. To deal with all these problems, the interest towards developing a more sustainable solution has led to the usage of biofuels extracted from renewable biomasses such as soybean and corn. Soybean and corn take awhile to grow and they also compete with food crops for arable land. Hence, algae cultivation for biofuel production has been seen as a promising technology because algae grow fast, and they do not require huge land space for cultivation. They are clean and renewable sources of energy (Mata et al., 2010). Another interesting aspect about algae growth is that they could be used to remove nitrogen and phosphorus from secondary effluents. Phosphorus from animal wastewater can be used by algae for their growth. In other words, algae grow well on organic matter heterotrophically than autotropically (Van Ginkel., 2014).

In order to be mindful of the sustainable practices in algal biofuels production, National Research Council (2012) wants the harvest water to be recycled which is the

water used for algae harvesting. In addition, U.S. Department of Energy's Bioenergy Technologies Office (2013) has expressed interest in new technologies that recycle water and essential nutrients during algal cultivation. As per the Energy Independence and Security Act of 2007, the demand for water will compete with agriculture crops by the year 2022 with a water footprint of 1000L/L for biodiesel. Water recycling can recover 84% of water after harvesting, while remaining is lost to the environment by means of evaporation or drying (Van Ginkel et al., 2014). Harvest water can be recovered via membrane filtration. Membrane filtration has several advantages compared to other harvesting technologies. In membrane filtration, harvesting efficiency can be more than 99.5%, nutrients will be passed through the membrane while the inhibitors and soluble algal products are removed, and membranes are not as energy intensive as centrifuges. Other harvesting processes require centrifugation as a sub-step for algae concentration; however this is not the case for membrane filtration. Furthermore, membrane filtration does not require any coagulants or chemicals for separation, and hence does not have to deal with downstream problems. In membrane filtration, permeate is collected from the side, while the concentrate is collected from bottom of the membrane module. Membrane filtration has not been scaled up for algae harvesting due to the high operational and maintenance costs from membrane fouling (Van Ginkel et al., 2014). The objective of this present research is to build a novel two way membrane design that solves the problem of membrane fouling. Also, this present membrane design should be able to harvest large volumes of algae, while recycling permeates simultaneously.

CHAPTER 2

LITERATURE REVIEW

In order to harvest algae, there are several solid-liquid separation processes such as centrifugation, gravity sedimentation, air flotation, flocculation, electrophoresis and filtration.

2.1 Algae harvesting

Centrifugation is a mechanical separation method which uses centrifugal force to separate algal biomass and its supernatant based on differences in density. Centrifugation is a quick and simple method in separating the algal biomass from its supernatant effectively, and has shown 80-90% recovery rates, but it has high operational costs for maintenance (Uduman et al., 2010). Some of the other disadvantages include high centrifugal forces that make it a highly energy intensive process.

Gravity sedimentation is another type of mechanical separation technique that can recover supernatant and 1.5% of solids under the influence of gravity with the help of sedimentation tanks and lamella separators. In addition, some of the other advantages include lower operational costs. However, it takes a while for the algae to settle. Also, a large amount of space is required for constructing sedimentation tanks for large-scale production.

Air flotation is a separation technique that involves air or gas to be bubbled in an algal suspension. The air or gas molecules attach to algal solid particles and float to the top of the surface. These floated algal solid particles can be removed easily. In dissolved air flotation, 80-90% of algae can be removed. Some of the drawbacks include the

probability and correct timing of algal cells to interact with the bubbles. For example, solid particles and bubbles float upward only if the interaction takes place between bubbles and solid particles at the same time (Uduman et al., 2010). For air flotation, sometimes chemical flocculants are also used at large-scale; however these chemical flocculants pose difficulties in downstream processing (Christenson et al., 2011). Flocculation is another chemical process that creates larger flocs by aggregating smaller flocs together by adding chemical flocculants like alum and ferric chloride (Pragya et al., 2013). Some of the advantages include being able to remove the organic content in the form of flocs. According to a research study, there has been greater than 90% of algal removal through flocculation (Bilanovic et al., 1988). Some of the disadvantages for flocculation not being used for large-scale production is because large quantities of chemicals are required (W. Zhang et al., 2013). Using large volumes of aluminum and ferric chloride might cause some issues during downstream processing (Sims et al., 2011). Residual ferric and aluminum salts could cause contamination if at all the water is recycled, and could potentially lead to environmental issues (Liu et al., 2013).

In the electrophoresis separation technique, algae get moved by the electric field. Algae are negatively charged, hence they get attached to hydrogen ions because the opposite ions attract. Once algae are bound in aggregates, they can be easily removed in electrophoresis separation technique. The advantages related to this method include cost efficiency, and environmental compatibility. However, this separation method uses up lots of energy, and causes system fouling due to high temperature and power usage (Pragya et al., 2013).

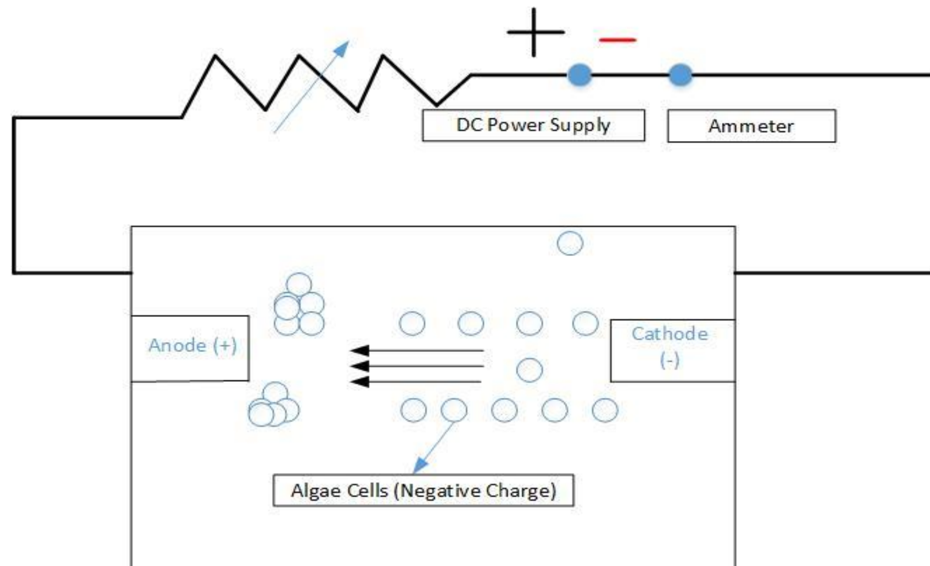

Figure 1: Algal cells moving towards the anode (Uduman et al., 2010)

The above mentioned solid-liquid separation processes have their own advantages and disadvantages, and also require large quantities of water for algae harvesting at industrial scale production. Hence, efficient harvesting method is required for algae biomass production because half of the production cost in algal biofuel production is algae harvesting (Pragya et al., 2013). Inhibitors and organic matter present within the algae must be completely removed as well; otherwise the water will not be usable for further recycling purposes because poor water quality with inhibitors and bacteria will inhibit algal growth. Hence, the need for membrane filtration technology seems to be most promising for removing organic matter, soluble algal products, inhibitors, and microorganisms, while retaining the essential nutrients required for water recycling (Van Ginkel et al., 2014). Table 1 summarizes the different algae harvesting methods with their yields, concentration factor removal, energy usages, advantages and disadvantages.

Table 1: Comparison of different algae harvesting methods (Uduman et al., 2010)

Harvesting Process	**Yield**	**Removal of Concentration Factor**	**Energy Usage**	**Advantages**	**Disadvantages**
Flocculation	22 % Total Suspended Solids	200 - 800	Lesser energy used for slow mixing	Isolating the algae and chemicals together	Contamination problems, separation of chemicals, and expensive flocculants
Centrifugation	12 % Total Suspended Solids	120	High energy usage of $8kWh/m^3$	Supernatant easily separated from algae biomass	High energy requirement, and high operational costs
Gravity Sedimentation	0.5-1.5% Total Suspended Solids	16	0.1 kWh/m^3	Does not have high energy costs	Takes a lot of time
Electroflotation	3% - 5% Total Suspended Solids	300-600	Very high	Cost efficiency	Electrodes to be replaced
Pressure filtration	5-27% Total Suspended Solids	50-245	0.88kWh	Less energy usage, inexpensive, permeate and algae biomass are separated easily	Filters and screens have to be replaced

From Table 1, it can be stated that membrane technology seems to lead the way based on algae biomass recovery rates, low energy rates, and higher number of membrane modules produced at a lower price (Uduman et al., 2010;X.Zhang et al., 2010).

2.2 Water and Nutrients Recycling

Water and nutrients can be reused for algae harvesting after the membrane filtration process. In other words, nutrients like nitrate and phosphate from algae feed tank are transferred into permeate during membrane filtration process while simultaneously removing the inhibitors and contaminants from the cultivated algae. 84% of water can be recovered after algae harvesting (Van Ginkel et al., 2014).

2.3 Membrane Technologies

Filtration membrane separation processes are increasingly rising in importance these days because of the increased production of membranes at a lower cost, and also because they are highly effective in removing algal predators and microorganisms like bacteria, viruses, and other inhibitors from algae. Membranes also retain the essential nutrients for algal growth and water recycle (X. Zhang et al., 2010). In addition, filtration membranes are physical separation processes that do not require any addition of chemicals for further purification (Rossignol et al., 1999; X.Zhang et al., 2010). Filtration involves algal suspension getting passed through the filters, and filters retaining the algal biomass as the filtered permeate goes out of the membrane module. This process is repeated several times until the concentrated form of algae is achieved (Pragya et al., 2013; Uduman et al., 2010).

Filtration types include dead-end flow filtration and cross-flow filtration or tangential flow filtration (Harun et al., 2010). Dead-end filtration is a batch process where

suspension is fed into the membrane module in a batch, and the filtered contents are allowed to stay on the surface of the membrane module until the concentrate is formed. However, the efficiency of filtration might decrease over time as the membrane pores could get blocked with concentrated matter (Munir, 2006). Cross-flow filtration is a continuous process where the algal suspension is fed into the membrane, and the feed is continuously processed into the membrane module (Harun et al., 2010; “Cross-flow micro-filtration", n.d.). It is called cross-flow because the feed flow and the filtration flow make a cross-flow or perpendicular angle together (Munir, 2006). There are various driving forces such as air pressure, vacuum, centrifugal, and gravity that are used to drive algal suspension through the filtration process (Uduman et al., 2010). Cross-flow filtration can be done on microfiltration and ultrafiltration membranes (Rossignol et al., 1999). Ultra filtration membranes rely on isolating particles based on molecular size, and ultrafiltration membranes can retain materials anywhere between 1K to 1000 K molecular weight. Microfiltration membranes removes organisms and particles within 0.025 micrometer to 10.0 micrometer and based on the membrane filter selected (Munir, 2006).

2.4 History of Previous Membrane Designs

Previous research was done comparing 40 kDa polyacrylonitrile (PAN) ultrafiltration membrane with that of polyvinylidenedifluorure (PVDF) microfiltration membrane for algal species *Haslea ostrearia* and *Skeletonema costatum*. The results showed that fouling was the common problem in both the species (Rossignol et al., 1999; X. Zhang et al., 2010). Tangential flow filtration was done on a freshwater phytoplankton by concentrating it 5 to 40 times, and the recovery rate was 70 to 89 percent by using 0.45 micrometer pore size membrane (Petruevski et al., 1994). In a research study,

Chlorella vulgaris and *Phaeodactylum tricornutum* were cultured, and filtered through three PVDF submerged microfiltration membranes made with pore sizes of 9%, 12%, and 15% w/w respectively. The filtration efficiencies were determined by flux-step methods which included determining the critical flux. The critical flux was determined by increasing flux over a period of time, and maintaining the transmembrane pressure at low fluxes, but transmembrane pressures were increased for fluxes that were above the critical flux. This study indicated lower fouling tendencies in comparison with submerged MBRs (Bilad et al., 2012).

Three algal species namely *Phaeodactylum tricornutum*, *Nannochloropsis gaditana* and *Chaetoceros calcitrans* were cultured, and harvested at the end of exponential phases by dynamic filtration method. Dynamic filtration is a method that is used to maximize shear stress and turbulence in the membrane to reduce fouling and concentration, and to increase permeate flux. Rotational system membranes or disks and vibratory systems are design types of dynamic filtration. The Dynamic Cross-flow Filter (DCF) 152/0.14 was used for the experiment. In this study, the design setup for dynamic filtration is a membrane closed with two parallel shafts, and the membrane disks overlapped on each other for rotating at a particular angular speed. During the filtration process, different transmembrane pressures and rotational speeds were used and the permeate was collected inside the shafts and was released out eventually (Rios et al., 2012).

The cross flow filtration was operated on a 2 liters *Chlorella sp*. KR-1 with a transmembrane pressure of 200kPa. Efficiencies of the membranes were determined by comparing PVA-PET membranes, and PVA-PVDF membranes. The concentration

factors were 25 in 3% PVA-PET for 20 hours and 77 in 1% PVA-PVDF for 16 hours. The PVA-PVDF had a higher permeate flux when compared with PVA-PET, suggesting that surface-coated membranes with proper anti-fouling coating could be a possible way to effectively harvest algal biomass (Hwang et al., 2013).

The algal culture *Chlorella pyrenoidosa* FACHB-9 was filtered via microfiltration pore sizes of 0.2, 0.45 and 0.8 respectively, and the ultrafiltration pore sizes included 10000, 20000, and 100000 of molecular weight cutoff. The membrane filtration was done in a batch mode by recycling permeate and retentate into the feed tank. The results of the experiment suggested that the permeate flux rate was similar to microfiltration and ultrafiltration membranes though different pore sizes have been used. Hence, it has been determined that the permeate flux was controlled by fouling layer which acts as the selective layer of the membrane (Sun et al., 2013).

In another experiment, the PVDF membranes were prepared with different PET supports, and the algae filtration was done by cross-flow filtration method. One liter of algae was run at a constant flow rate of 4.5L/min and a cross-flow velocity of 1m/s. The permeate volume and optical density were measured, and retentate values were estimated. The results showed that PVDF membrane (PNSM-1) had an algal retention of 100% and a higher permeate flux of 96 $L/m^2/hr$ compared to a commercial PVDF ultrafiltration membrane of molecular weight cut off 30 kDa (Hwang et al., 2015).

Fouling seems to be the major obstacle in membranes. Fouling happens based on algal cell size, density, and growth phases because extracellular organic matter are excreted specific to algal growth phases. Fouling and cake development can be predicted based on the amount of organic matter released (Babel et al., 2010). According to Babel

et al. (2010) and Rossignol et al. (1999), ultrafiltration membranes have higher filtration efficiency.

The previous membrane design included an ultrafiltration process that was carried out with a hollow fiber PVC membrane with a molecular weight 50 kDa cutout. It was run at a constant pressure of 34.5kPa for concentrating the *Scenedesmus quadricauda* algae. In the experimental setup, the flow rates were recorded for every minute, and the flux decline was calculated (X. Zhang et al., 2010). The objective of this method was to develop an efficient technology for algae harvesting using membrane filtration. Some of the challenges faced with this experimental design were fouling which included buildup of Algogenic Organic Matter (AOM) such as proteins and polysaccharides. The foulants were identified by Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR). Hence, anti-fouling strategies such as air assisted backwash and air scouring were employed to reduce membrane fouling (X. Zhang et al., 2010). Another experiment with the same hollow fiber PVC membrane was carried on *Chlorella zofingiensis* to further investigate membrane fouling. Even after periodical backwashing, *Chlorella zofingiensis*, bacteria and Dissolved Organic Matter (DOM) foulants were harder to remove as they fouled the membrane. To further explore, the DOM was run in High Performance Size Exclusion Chromatography (HPSEC) to further fractionate the DOM components. The results showed carbohydrates fractions were mostly responsible for membrane fouling than proteins (W. Zhang et al., 2013).

2.5 Present Membrane Design

The following Figure 2 shows the present membrane design setup for the experiments. The membrane used was a hollow fiber ultrafiltration membrane module.

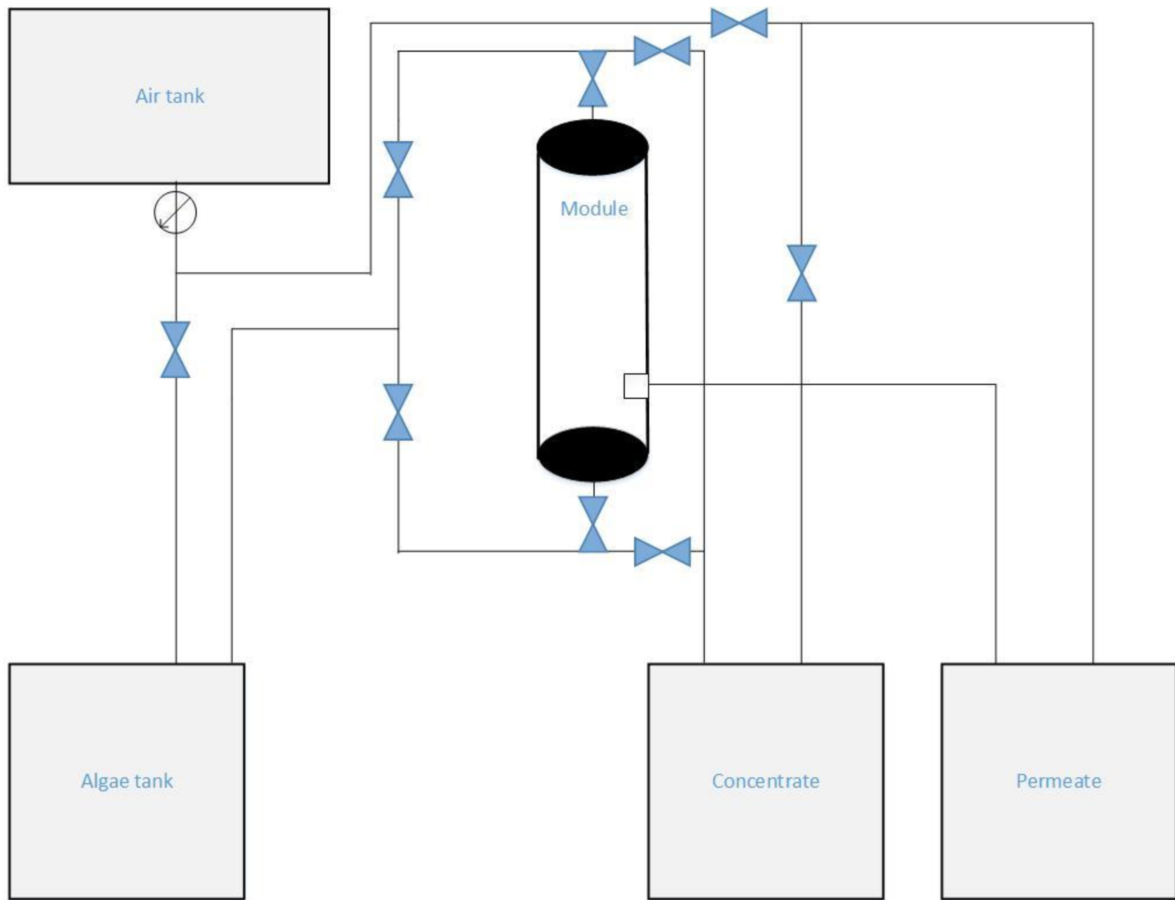

Figure 2: Present membrane filtration design

The previous membrane design model was run in a one-way direction flow from top to bottom of the membrane module (X. Zhang et al., 2010). Some of the challenges encountered for previous design included fouling, and cake getting stuck in bottom and top of the membrane, thereby declining flux flow (W. Zhang et al., 2013; X. Zhang et al., 2010). However, the present design shown in Figure 2 aims to have two ways flow. The cultivated algae were fed into the algae tank. Then, the algae tank was pressurized with air at 5psi. This air pressure enabled algae to move through the membrane module. For the first 15 minutes, algae were moved in the forward flow direction, which took place from top to bottom of the membrane module. The concentrated algae were collected in a concentrate tank, while permeate was collected in the permeate tank. Algae collected

from the concentrate tank were redirected back into the algae feed tank for this process to be continued for 15 minutes in forward flow. Algae flow was switched to reverse flow, which was employed from bottom to top of the membrane module. Algae from the algae feed tank were moved from bottom to top of the membrane module for 15 minutes again. The concentrated algae and permeate were collected in their respective tanks just like the way they were collected in the forward flow. This two way design creates a shear force that attempts to push and remove the cake and foulants struck inside the membrane module. After 15 minutes of forward flow and 15 minutes of reverse flow, there was air scouring done in both directions for 1 minute. After air scour, the filtration process was continued until the maximum permeate was achieved from the algae. The membrane module was cleaned with deionized water after filtration to keep the membrane clean.

CHAPTER 3

MATERIALS AND METHODS

3.1 Materials

Algae species such as *Nannochloropsis oculata* KA32 and *Chlorella kessleri* have been cultured. Then, these algae species were used for further filtration in the hollow fiber membranes.

3.1.1 Algae Culturing

Seawater algae species, *Nannochloropsis oculata* strain KA32 and fresh water algae species *Chlorella kessleri* were obtained from Georgia Institute of Technology, Atlanta. They were initially cultured in 800 milliliters (mL) columns for a week, and were later on moved to 15 Liters (L) panels for seven days in Georgia Institute of Technology, Atlanta. The growth media used for *Nannochloropsis oculata* KA32 was F/2 media, and for *Chlorella kessleri* was BG11. The columns and panels were treated as photobioreactors by exposing light to the columns and panels, and were aerated with 2% CO_2. The concentration of *Nannochloropsis oculata* KA32 in the 15 L panel at the time of culturing was 1.8 g/L, and the concentration of *Chlorella kessleri* in the 15 L panel was 0.6 g/L. The difference in concentration is seen because *Nannochloropsis oculata* KA32 being a seawater algal species has a higher density than *Chlorella kessleri*, which is a freshwater algal species.

3.1.2 Membranes Information

The ultrafiltration membrane used was hollow fiber membrane modules (LU8A-4A), which was made of PVC. They were provided by Litree Co. (Hainan, China). The

membrane had 50 kDa MWCO (~0.01 μm in pore size), 0.125 m^2 filtration area, and was hydrophilic in nature. Also, the hollow fiber membranes were 0.25 m long, and the inner diameter was 1.0 mm and the outer diameter was 1.66 mm (X. Zhang et al., 2010).

Interfacial polymerization technology was used for making the active skin layer of the Thin-Film Composite (TFC) Nanofiltration (NF) hollow fiber membrane. The PS/PVC membrane was made by using the 2.0 w/v% of piperazine (PIP) with 1.0 w/v% of NA_3-PO_4 as the acid acceptor, and these were extruded into the lumen side of the ultrafiltration hollow fiber membrane for about 10 minutes,and then the excess solution was drained and air-dried with nitrogen. The PIP surface was immersed in an organic phase solution with 0.5 wt% Trimesoyl Chloride (TMC) in n-hexane for about 50 seconds, resulting in polyamide active skin layer over the PS/PVC membrane surface. The hollow fiber membrane was cured at 70 ^{o}C for 10 minutes to allow further polymerization. Then, the fabricated composite NF hollow fiber membrane was rinsed with DI water for 30 minutes, and was later on stored in 1.0wt% $NaHSO_3$ (Wei et al., 2013).

3.2 Methods

3.2.1 Filtration Process

After culturing algae for seven days in 15 L panels, 3800 mL of algae were sampled for the ultra filtration process. The ultrafiltration process starts with air pressurizing the algae tank at constant 5psi, and then algae were moved from the membrane module to the concentrate tank. Once algae were filled in the concentrate tank, they were re-circulated back into the algae tank. Hence, it is a continuous system. This filtration process was done for 15 minutes in the forward flow direction, and then was

switched for 15 minutes in the reverse flow direction. Meanwhile, permeate was collected simultaneously in the permeate tank. Air scouring was done after reverse flow to clean any membrane foulants and cake struck in the membrane module. This filtration process was repeated till the maximum permeate was achieved. After permeate was obtained from the ultrafiltration process, sample analyses were done for determining the water quality. After sample analyses, permeate from the ultrafiltration membrane was again circulated into the nanofiltration membrane module to further obtain a higher rejection rate. The nanofiltration permeate method was done by using laboratory cross-flow filtration appartatus, and each nanofiltration membrane module consisted of 8 hollow fibers with an effective area of 24 cm^2 approximately. Before testing, the hollow fiber membranes were under 0.5MPa pressure for 1 hour with DI water to ensure that the membrane was in a steady state. Once, this was done, the ultrafiltration permeate was run in the nanofiltration module at 0.4 MPa and $25.0 \pm 1.0\ ^{o}C$ (Wei et al., 2013).

3.2.2 Sample Analysis

Permeate and concentrate samples were further processed with the following sample analyses to determine the permeate water quality.

1. Filtration volumes

The initial volume of the algae prior to the filtration process were measured, and after the filtration, permeate and the concentrate volumes were measured. Based on this, the Concentration Factor (CF) and the Volumetric Reduction Factor (VRF) have been calculated.

CF = cf/co, where cf is final concentration and co is initial concentration.

VRF = vo/vf, where vo is initial concentration, and vf is final concentration.

2. Dry weights

Dry weights on algae samples were measured on a daily basis to keep track of the algae concentration. First, the filters were pre-conditioned in a muffle furnace for a day, and then the next day, the filters were weighted out. Filters were placed on a dry weight vacuum machine. Then, small volume of algae cultivated sample, and the concentrated sample were added on top of the filters. On top of this, 10 ml of 31.5g/L of ammonium formate was added to ensure that the algae solution goes through the filters. Then, after it has been vacuumed, the filters were transferred to the drying oven for a day. Then, the filters were put in the desiccator for the filters to be in room temperature. After 30 minutes in the desiccator, the filters were weighed out on a mass balance to determine dry weight measurement. Dry weights were done on concentrated algae sample obtained right after filtration, and algae sample right before filtration to determine the algae concentrations.

3. Optical Density

The algal species before and after passing through the filtration membrane were measured for optical density at 750 nanometers. The optical densities of algae samples in the panels were measured on a daily basis to keep track of the algal growth using the spectrophotometer.

4. Zeta potential

The zeta potential was measured right after a day of seed culturing in the panels, and also was measured right before the algae were filtered. The algae sample was filled into the vial, and placed in the zetameter to measure the zeta potential.

5. Nutrients

A sample of algae after cultivation was filtered through the 0.2 microfilter, and this sample was compared with the permeate sample from the membrane filtration. Then the samples were run on ion-exchange chromatography to compare the nitrogen and phosphorus nutrient values between the cultivated samples and the permeate samples. This was done to see if the nutrients were recycled in the permeate even after membrane filtration.

6. Total Organic Carbon (TOC)

The Total Organic Carbon (TOC) is a measure of the permeate quality. The permeate samples were run on a TOC analyzer machine. The algae cultivation samples before filtration were centrifuged and the supernatants were taken to measure the TOC. The TOC of the ultrafiltration permeate and the nanofiltration permeates samples were done to see which harvesting method has a better permeate quality. Glucose solution standards ranging from 0ppm to 10ppm concentrations were used as standards.

7. Chemical Oxygen Demand (COD)

For the Chemical Oxygen Demand (COD), the standard solutions were prepared for 0mg/L, 500 mg/L, 750 mg/L, 1000 mg/L and 1500 mg/L. The algae centrifuged supernatant samples, ultrafiltration and nanofiltration permeate samples were measured for COD as well. After sample preparation, samples were placed in a pre-heated digester block for 2 hours at 150 degrees Celsius. Once done, the digester block was switched off. The samples were further cooled for 30 minutes in the dark. Once, samples were removed from the dark, the percent transmittance was measured in a spectrophotometer. Finally a graph was plotted to determine the concentration of the samples.

8. Color

The color measurements were done on algae feed tank samples, concentrates, and permeates. The optical density was measured by spectrophotometer at various wavelengths for color determination.

9. pH

The pH was measured on algae panels till the filtration day. In addition, algae samples before and after filtration were measured.

CHAPTER 4

RESULTS AND DISCUSSION

The sample analyses were done to determine permeate quality of the filtration processes. This section covers all the data, and results obtained from this two way membrane design model.

4.1 Results

Nannochloropsis oculata KA32 and *Chlorella kessleri* were grown in 15 Liters (L) panels. The following figure shows optical density of *Nannochloropsis oculata* KA32 versus time in days to show the *Nannochloropsis oculata* KA32 growth curve.

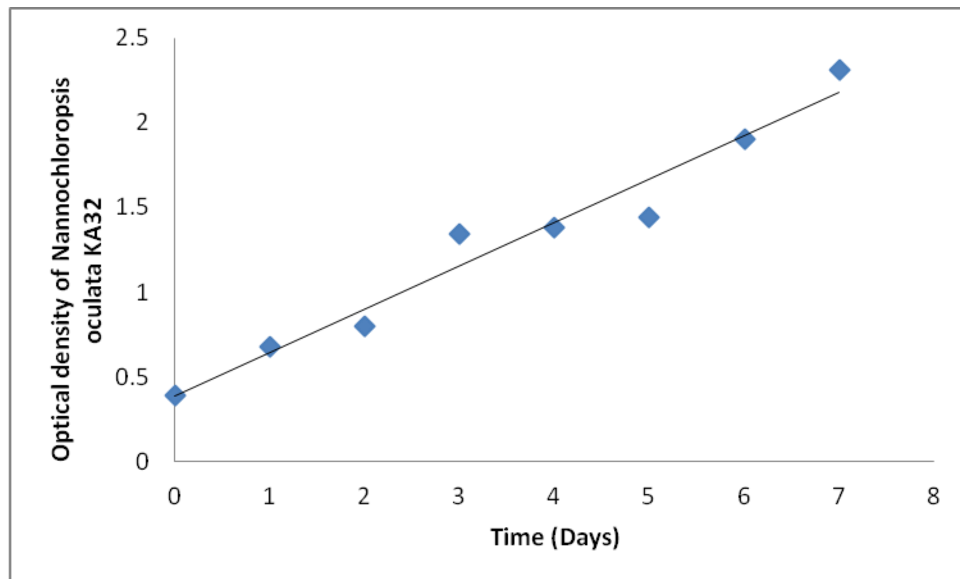

Figure 3: Optical Density of *Nannochloropsis oculata* KA32 vs. Time

From the graph above, the growth of *Nannochloropis oculata* is presented in linear form. The optical density at 750 nanometers (nm) versus time in days was plotted.

The growth curve has been monitored till seven days. Figure 4 shows the optical density of *Chlorella kessleri* versus time to show the *Chlorella kessleri* growth curve.

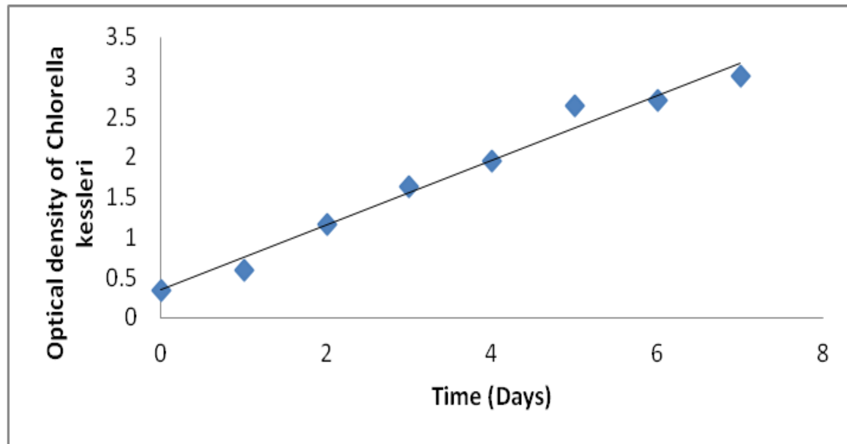

Figure 4: Optical density of *Chlorella kessleri* vs. Time

From the graph above, the growth of *Chlorella kessleri* is presented in linear form. The optical density at 750 nm versus time in days is plotted. The growth curve has been monitored for seven days similar to *Nannochloropsis oculata* KA32. The growth conditions for the algae species included their respective growth media, light exposure to the panels, and CO_2 aeration. Figure 5 shows the *Nannochloropsis oculata* KA32 pH versus time.

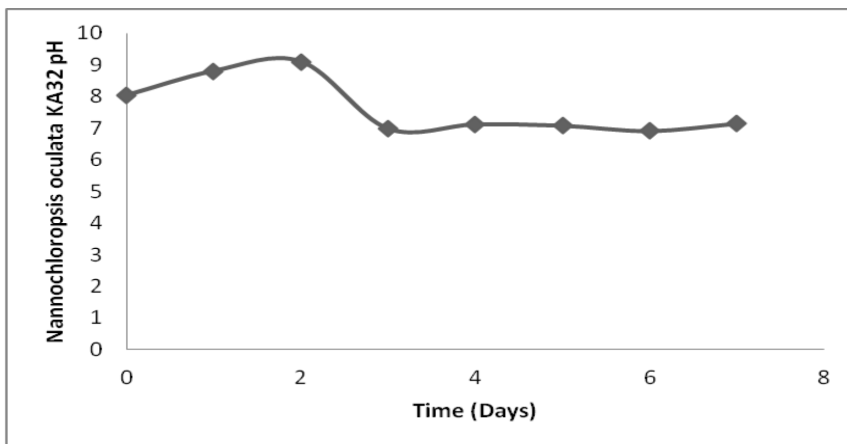

Figure 5: *Nannochloropsis oculata* KA32 pH vs. Time

The graph above shows the *Nannochloropsis oculata* KA32 pH increasing and decreasing and remaining constant over a period of time. The following figure shows *Chlorella kessleri* pH versus time. *Nannochloropsis oculata* KA32 algae feed tank had a pH of 7.14 before filtration. After filtration, *Nannochloropsis oculata* KA32 permeate pH was 8.21, showing an increase in pH. The following Figure 6 shows *Chlorella kessleri* pH versus time graph.

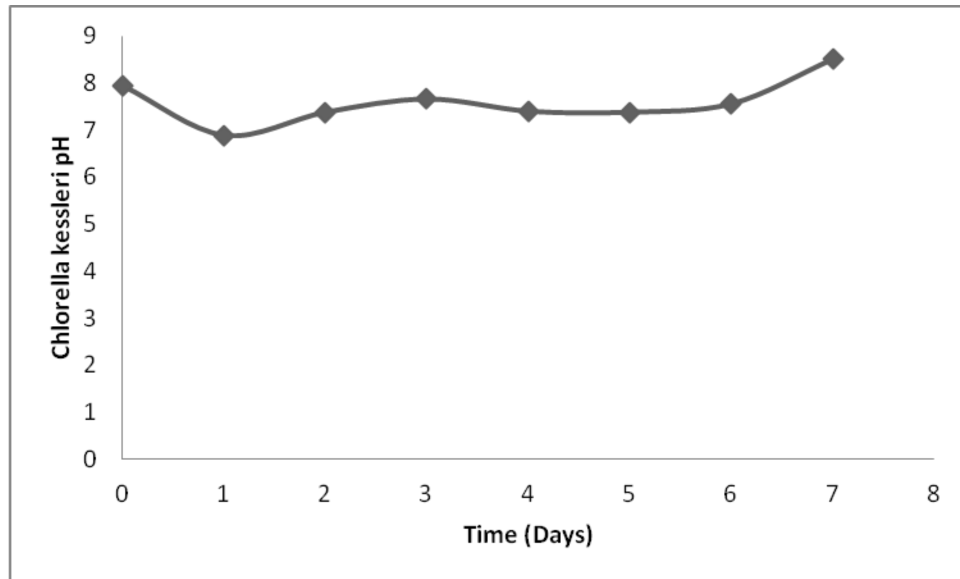

Figure 6: *Chlorella kessleri* pH vs. Time

Figure 6 initially shows *Chlorella kessleri* pH decreasing and increasing while remaining constant over a period of time. The pH was monitored to see if the pH will vary or not for both the species. The pH was almost similar for both species. Table 2 shows Total Organic Carbon (TOC) done on the centrifuged algae samples, ultrafiltration permeates, and nanofiltration permeates. TOC is the main indicator for measuring water quality. TOC of the ultrafiltration permeate and nanofiltration permeate were compared with TOC of the centrifuged algae supernatant. This was done to see the separation

efficiency of the membrane filtration harvesting method versus a centrifuge harvesting method.

Table 2: Total Organic Carbon

Sample Name	**Centrifuged Supernatant of algae tank (mg/L)**	**Ultrafiltration (mg/L)**	**Nanofiltration (mg/L)**
Nannochloropsis oculata KA32	77	114	85
Chlorella kessleri	64	120	68

Table 2 shows the Total Organic Carbon (TOC) of the *Nannochloropsis oculata* KA32 and *Chlorella kessleri* samples. The TOC of the nanofiltration permeate was almost equivalent to TOC of the centrifuged algae supernatant. These TOC results further show that membrane filtration is on par with centrifuge in terms of separation efficiency. So, membranes can be used for harvesting and they are not as highly energy intensive as centrifuges.

Table 3 shows the Chemical Oxygen Demand (COD) done on *Nannochloropsis oculata* KA32 and *Chlorella kessleri* algae species. The Chemical Oxygen Demand (COD) is another indicator for determining permeate quality. The COD was done on the centrifuged algae tank sample, and the ultrafiltrations permeate samples to determine the separation efficiency as well.

Table 3: Chemical Oxygen Demand

Sample Name	**Centrifuged supernatant of algae tank (mg/L)**	**Ultrafiltration permeate (mg/L)**
Nannochloropsis oculata KA32	1574	1334
Chlorella kessleri	318	32

From the above table for Chemical Oxygen Demand (COD), it can be observed that ultrafiltration permeate COD was much lesser than the centrifuged algae supernatant for *Nannochloropsis oculata* KA32 and *Chlorella kessleri* as well. This shows that the ultrafiltration membrane permeate has higher separation efficiency than a centrifuge. The following Table 4 shows the zeta potential of algae right after 1 day of seed culturing, and 1 day before filtration for the two algae species. The zeta potential is measured in this case to determine the stability of the algae molecules. If the zeta potential is too high positively or negatively, then the molecules will repel each other ("Zeta potential an introduction in 30 minutes", n.d.). The zeta potential was done on both algae species, *Nannochloropsis oculata* KA32 and *Chlorella kessleri* to determine the surface charge of the two algae species. Table 4 shows zeta potential of both algae species being negatively charged.

Table 4: Zeta Potential

Sample Name	Zeta Potential (my)
Nannochloropsis oculata KA32 (one day after seed culturing)	-14.8
Nannochloropsis oculata KA32 (Before filtration)	-8.94
Chlorella kessleri (one day after seed culturing)	-22.7
Chlorella kessleri (Before filtration)	-23.2

The zeta potential measurements were done one day after seed culturing and also before filtration. According to Table 4, zeta potential was neither too high nor too low. Hence, the algae molecules will not repel each other ("Zeta potential an introduction in 30 minutes", n.d.). The following Table 5 shows the filtration volumes of algae species, *Nannochloropsis oculata* KA32, and *Chlorella kessleri*. From Table 5, it can be seen that the Concentration Factor (CF) is much higher for *Chlorella kessleri* than *Nannochloropsis oculata* KA32 despite using the same sample volume for filtration. *Nannochloropsis oculata* KA32 being a seawater species has a higher density than *Chlorella kessleri*, which is a freshwater species. This could be the reason why the concentration factor was a little bit lower in *Nannochloropsis oculata* KA32 than *Chlorella kessleri.* The filtration was carried till maximum permeate was achieved from the algae species.

Table 5: Filtration Comparison

Sample Name	**Initial volume (mL)**	**Concentrate (mL)**	**Permeate (mL)**	**Volumetric Reduction Factor (VRF)**	**Concentration Factor (CF)**	**Runs**
Nannochloropsis oculata KA32	3800	51	3655	1.04	74.5	143
Chlorella kessleri	3800	31	3634	1.05	122.6	202

The following Table 6 shows *Chlorella kessleri* algae tank, and permeate sample measurements at various nanometers to determine color of the algae species. The color was measured for optical density at different wavelengths by using a spectrophotometer. The color was measured to see the permeate quality. *Chlorella kessleri* algae tank optical density was very high around 1.976 at 750 nm. However after ultrafiltration, permeate had 0.007 optical density, which means that permeate was almost closer to zero. Nanofiltration permeate had 0.002 optical density, which is even closer to zero. This optical density measurement shows that permeate is completely devoid of algae. The green color of algae is not visible in the permeate visually to further state that membrane filtration has enabled the permeate to be completely clear and free of algae.

Table 6: *Chlorella kessleri* Color

Sample	Absorbance at 630 nm	Absorbance at 645 nm	Absorbance at 663 nm	Absorbance at 665 nm	Absorbance at 750 nm
Algae Tank	2.184	2.054	2.236	2.444	1.976
Ultrafiltration Permeate	0.001	0	0.001	0.002	0.007
Nanofiltration Permeate	0.004	0.003	0.003	0.003	0.002

Table 7 shows the *Nannochloropsis oculata* KA32 color readings. The color procedure was carried out in the same way as it was carried out for *Chlorella kessleri*. The *Nannochloropsis oculata* KA32 had a higher optical density around 2.392 at 750 nm, while the *Nannochloropsis oculata* KA32 ultrafiltration permeate was around 0.009 and 0.007 for nanofiltration permeate. These results shows that even *Nannochloropsis oculata* KA32 permeates were almost close to zero, hence being devoid of algae.

Table 7: *Nannochloropsis oculata* KA32 Color

Sample	Absorbance at 630 nm	Absorbance at 645 nm	Absorbance at 663 nm	Absorbance at 665 nm	Absorbance at 750 nm
Algae Tank	2.886	2.73	2.938	3.094	2.392
Ultrafiltration Permeate	0.015	0.015	0.016	0.012	0.009
Nanofiltration Permeate	0.008	0.002	0.008	0.005	0.007

According to the data, *Nannochloropsis oculata* KA32 had a higher optical density in terms of algae tank, and permeates than *Chlorella kessleri*. This is because *Nannochloropsis oculata* KA32 being a seawater species has higher density than fresh water species, *Chlorella kessleri*. It can be observed from both the color tables above,

that the algae tank has a higher absorbance at 750 nm, however the ultrafiltration and nanofiltration permeate have lower absorbance almost close to zero, showing that the permeate is clear and free of algae. Table 8 shows *Nannochloropsis oculata* KA32 nutrients comprising of Nitrogen and Phosphorus. The *Nannochloropsis oculata* KA32 algae tank contains 20.2 N mg/L and 4.13 P mg/L, whereas *Nannochloropsis oculata* KA32 permeate has 21.2 N mg/L and 0.748 P mg/L. This shows that algae tank had less Nitrogen intake compared to the end effluent permeate. The Phosphorus had higher Phosphorus intake in the algae tank, but was lower in the end effluent permeate.

Table 8: *Nannochloropsis oculata* KA32 Nutrients

Sample Name	**N mg/L**	**P mg/L**
Nannochloropsis oculata KA32 algae tank	20.2	4.13
Nannochloropsis oculata KA32 ultrafiltration permeate	21.2	0.748

Similarly, the following Table 9 shows the *Chlorella kessleri* nutrients comprising of Nitrogen and Phosphorus. The Nitrogen intake in the algae tank for *Chlorella kessleri* was low compared to effluent permeate. The Phosphorus intake in the algae tank was a bit lower in the effluent permeate compared to the *Chlorella kessleri* algae tank. Hence, the nutrients have been recycled from algae tank to the permeate for both *Chlorella kessleri* and *Nannochloropsis oculata* KA32.

Table 9: *Chlorella kessleri* Nutrients

Sample Name	N mg/L	P mg/L
Chlorella kessleri algae tank	187.57	0.028
Chlorella kessleri ultra filtration permeate	194.97	0.0306

4.2 Mass-Balances

Table 10 shows *Nannochloropsis oculata* KA32 mass balance. The whole purpose of a mass balance is to see if inputs equal outputs in a system.

Table 10: *Nannochloropsis oculata* KA32 Mass Balance

	Algae Feed Tank	**Permeate**	**Concentrate**	**Amount recovered**
Volume	3.8L	3.655 L	0.051 L	98%
Nitrogen	76.8 mg	77.5 mg	-	100%
Phosphorus	15.6 mg	2.7 mg	-	17%
Dry weights	26600 mg	-	5457 mg (74.5 CF)	21%
TOC	293 mg centrifuged supernatant	417 mg filtered sample	-	42% (Removal)
COD	5981 mg centrifuged supernatant	4876 mg filtered sample	-	18% (Removal)

Table 10 shows mass balance on volume, dry weights, nutrients, TOC and COD. Mass is calculated by multiplying concentration and volume. In this case the system is a filtration membrane module. The mass balance is done to see if the algae have been

harvested through the membrane filtration module. From Table 10, it can be seen that dry weights before entering the system were 26600 mg and 5457 mg of biomass as they were exiting the system with a concentration factor (CF) of 74.5. This shows that algae harvesting has been accomplished. The COD of the centrifuged algae supernatant was much higher than the ultrafiltration permeate, showing that membrane filtration is much better than centrifugation. Most of the permeate has been recovered in terms of volume showing that water or permeate can be recycled back into the system. Nitrogen has been recovered in the permeate from the algae tank. However, Phosphorus was much lower in the permeate than the algae tank for *Nannochloropsis oculata* KA32 because Phosphorus could have been used up by the algae species. The following Table 11 shows *Chlorella kessleri* mass balance.

Table 11: *Chlorella kessleri* Mass Balance

	Algae Feed Tank	**Permeate**	**Concentrate**	**Amount recovered**
Volume	3.8 L	3.634 L	0.031 L	96%
Nitrogen	712.8 mg	708.5 mg	-	99%
Phosphorus	0.11 mg	0.11 mg	-	100 %
Dry weights	15200 mg	-	4740 mg (122.6 CF)	31%
TOC	243 mg centrifuged supernatant	436 mg filtered sample	-	79% (Removal)
COD	1208 mg centrifuged supernatant	116 mg filtered sample	-	90% (Removal)

Table 11 shows *Chlorella kessleri* algae tank dry weight was 15200 mg. Dry weights for *Chlorella kessleri* concentrate was 4740 mg with a concentration factor of 122.6. The COD values are much lesser in ultrafiltration permeates than the COD values for centrifuged algae supernatant. The TOC is almost similar to centrifugation in terms of separation efficiency, showing that membranes have almost the same water quality separation efficiency as centrifuges. The final volume collected for *Chlorella kessleri* was 3634 mL, showing that most of the water or permeate has been recovered. The Nitrogen has been recovered in the permeate from the algae feed tank. Phosphorus has maintained the same nutrient concentration showing that the nutrients have been recycled for *Chlorella kessleri*.

CHAPTER 5

CONCLUSION AND FUTURE WORK

The ultrafiltration and nanofiltration combined together have produced a very clear permeate as they have removed inhibitors and contaminants from the algae. Permeate is also devoid of algae for both algae species, hence it could be reused for further algae cultivation purposes. The problem of inlet membrane fouling has been solved through this present two way membrane filtration system. Dry weights results show that algae have been harvested. Next step for future research would be to find out the permeability coefficient, so that it can be scaled up for commercial use. In other words, there should be a commercial membrane system that integrates ultrafiltration and nanofiltration in one design. Water recycling feasibility and inhibitor removal have to be further investigated. Finally, there should be water quality requirements for algae biomass water recycling.

APPENDIX

STANDARDS

This appendix shows the standards for Total Organic Carbon, Chemical Oxygen Demand, and Nutrients.

Total Organic Carbon

The following Table 12 shows the Total Organic Carbon standards for glucose concentrations ranging from 0 ppm to 10 ppm of glucose.

Table 12: Total Organic Carbon Glucose Standards

Glucose Concentration (PPM)	**TOC (mg/L)**
0 ppm glucose	0.23
2 ppm glucose	1.01
4 ppm glucose	1.55
6 ppm glucose	2.64
8 ppm glucose	3.06
10 ppm glucose	3.80

Chemical Oxygen Demand

The following Table 13 shows the Chemical Oxygen Demand standards ranging from 0 mg/L to 1000 mg/L.

Table 13: Chemical Oxygen Demand Standards

Concentration (mg/L)	**Transmittance (%)**
0	100%
250	77.40%
500	61.50%
750	47.00%
1000	37.50%

Nutrients

The following Table 14 shows the *Nannochloropsis oculata* KA32 nutrient standards for Nitrogen and Phosphorus dilutions ranging from 1x to 100 x.

Table 14: *Nannochloropsis oculata* KA32 Nutrients Standards

Sample Name	**N mg/L**	**P mg/L**
Nannochloropsis oculata KA32 100x	1.80	2.66
Nannochloropsis oculata KA3210x	18.04	26.65
Nannochloropsis oculata KA32 5x	36.08	53.30
Nannochloropsis oculata KA32 1x	180.39	266.49

The following Table 15 shows Chlorella kessleri nutrient standards for Nitrogen and Phosphorus dilutions ranging from 1x to 100 x.

Table 15: *Chlorella kessleri* Nutrients Standards

Sample Name	**N mg/L**	**P mg/L**
Chlorella kessleri 100x	0.90	2.16
Chlorella kessleri 10x	9.01	21.62
Chlorella kessleri 5x	18.02	43.24
Chlorella kessleri 1x	90.10	216.19

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