

FABRICATION OF TiO_2 -EMBEDDED PVDF MEMBRANES AND THEIR APPLICATION IN ALGAE MEMBRANE BIOREACTOR SYSTEMS

A Thesis

presented to

the Faculty of the Graduate School

at the University of Missouri-Columbia

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

By

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December 2013

APPROVAL

The undersigned, appointed by the dean of the Graduate School, have examined the thesis entitled

FABRICATION OF TIO₂-EMBEDDED PVDF MEMBRANES AND THEIR APPLICATION
IN ALGAE MEMBRANE BIOREACTOR SYSTEMS

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a candidate for the degree of master of Science,

and hereby certify that, in their opinion, it is worthy of acceptance.

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ACKNOWLEDGEMENTS

First and most importantly, I would like to express my thanks to my advisors Dr. Zhiqiang Hu and Dr. Baolin Deng, in the Department of Civil and Environmental Engineering for all the time and effort they dedicated in providing me with constant guidance, numerous advices and generous encouragement and support throughout my graduate studies.

I also need to extend my gratitude to Dr. Christine Costello in the Department of Bioengineering for being my graduation thesis committee, her guidance will always been appreciated.

I would like to extend my thanks to PhD candidate Jun Yin, also in the Department of Civil and Environmental Engineering for sharing his expert experience in membrane technology and general lab work aspects. Also, my I am grateful for having known and been working with all my wonderful colleagues from both Dr. Deng and Dr. Hu's group throughout these years, especially for Tianyu Tang, Shengnan Xu, Shashikanth Gajaraj, Chiqian Zhang, Peng Wan, Qi Shen, Jialiang Guo, Jingjing Dai whose cooperation and help really carried me.

At last, I want to thank my parents for being my backbone and harbor through this two years of study and the first twenty five years of my life.

TABLE OF CONTENTS

APPROVAL	i
ACKNOWLEDGEMENTS	ii
LIST OF TABLES	v
LIST OF FIGURES	vi
ABSTRACT	viii
CHAPTER ONE.....	1
LITERATURE REVIEW	1
1.1. Microalgae and Algae Cultivation.....	1
1.1.1. Microalgae	2
1.1.2. Additional Benefits of Microalgae Cultivation	5
1.1.3. Cultivation Conditions	5
1.2. Microalgae for Wastewater Treatment.....	7
1.2.1. Advances in Algae-based Wastewater Treatment.....	8
1.3. Promising of Algae-based MBR for Wastewater Polishing and Water Reuse.....	9
1.4. Membrane Technology.....	10
1.4.1. Membrane Materials	12
1.4.2. Membrane Modules	13
1.4.3. Membrane Fouling	17
1.4.4. Membrane Fouling Mechanisms	18
1.4.5. Membrane Fouling Control.....	22

CHAPTER TWO	27
METHODOLOGY	27
2.1. Membrane Modification and Module Fabrication.....	27
2.1.1. Membrane Fabrication materials.....	27
2.1.2. Fabrication of PVDF/PVDF+TiO ₂ Hollow Fiber Membranes.....	28
2.1.3. Assembly of PVDF/PVDF+TiO ₂ Hollow Fiber Membrane Modules	30
2.2. Algal Cultivation	31
2.3. High-density Algae MBR System Set-up.....	33
CHAPTER THREE	39
RESULTS AND DISCUSSION	39
3.1. High-density algae cultivation	39
3.2. Nitrogen and phosphorus removal by algae.....	40
3.3. Invasion of filamentous species during algae MBR operation	41
3.4. Membrane fouling monitoring and resistance change before and after cleaning.....	45
3.5. Hollow Fiber Membrane Characterization by SEM and EDS Analysis.	48
CHAPTER FOUR.....	52
DISCUSSION	52
CHAPTER FIVE	54
CONCLUSION.....	54
REFERENCES	56

LIST OF TABLES

Table 1. A comparison of land use and biofuel productivity between microalgae and other biodiesel feedstocks (Mata et al. 2010).....	3
Table 2. Classification of membrane processes (Van Der Bruggen et al. 2003).	11
Table 3. Models developed to describe membrane fouling (modified after (Meng et al. 2009)).	19
Table 4. Membrane modification methods.(Pinnau et al. 1999).....	25
Table 5. Membrane fabrication parameters.	29
Table 6 Hollow fiber membrane module parameters.....	31
Table 7. Bold's basal medium (Bold 1949).	32
Table 8. Chemical composition of the feeding solutions.	33
Table 9. Operating conditions of the high-density algae MBR systems.	34
Table 10. Recovery of membrane total resistance after membrane cleaning.....	46
Table 11. Reversible and irreversible resistance calculation after cleaning.....	46
Table 12. Permeance recovery calculation after cleaning.....	47

LIST OF FIGURES

Figure 1. Plate-and-frame design for the separation of helium from natural gas (Stern et al. 1965).....	14
Figure 2. Tubular Membrane Configuration for ultrafiltration from Koch Membrane Systems Inc. (Courtesy Koch Membrane Systems Inc.).....	15
Figure 3. Spiral membrane module configuration and its cross section view (Courtesy from Koch Membrane Systems Inc.).....	16
Figure 4. Diagram of hollow fiber membrane module (Courtesy Pall Corporation.).....	17
Figure 5. A schematic of membrane fouling due to: (a) pore blockage, (b) and cake layer formation (Meng et al. 2009).....	18
Figure 6. Fabricated hollow fiber membranes.	29
Figure 7. Two hollow fiber membrane module designs, complex design (top) and simple design (bottom).	30
Figure 8. Experimental set-up of two parallel high-density algal MBR systems.....	34
Figure 9 Biomass concentration monitoring for high-density algae cultivation in two identical bioreactors: MBR#1 (●), and MBR#2 (●).....	39
Figure 10. Influent (■) and effluent NO ₃ ⁻ -N concentrations of the high-density algae cultivation systems: MBR#1 (●), and MBR#2 (●).....	40
Figure 11. Influent (■) and effluent phosphorus concentrations of the high-density algae cultivation systems: MBR#1 (●), and MBR#2 (●).....	41
Figure 13. Settling of contaminated algae mix, (1) algae suspension right after string, (2) at 1 min settling, (3) at 1 min 40 s settling.	43
Figure 14. Change in algae floc size during the study period.....	44
Figure 15 Fluorescence light source spectrum for algae cultivation tested by Ocean Optics PC2000 PC plug-in Spectrometer.	44

Figure 16. The change in total membrane resistance during the study period between the two types of membranes, PVDF (●) and PVDF+TiO₂ membranes (●).....45

Figure 17. SEM images of the surfaces of (a), (c) clean PVDF hollow fiber membranes; (b), (d) clean PVDF+TiO₂ membranes.....48

Figure 18. SEM images of the surfaces of (a), (c) fouled PVDF hollow fiber membranes; (b), (d) fouled PVDF+TiO₂ membranes after 112 days of operation.49

Figure 19. SEM images of the surfaces of (a), (c) cleaned PVDF hollow fiber membranes; (b), (d) cleaned PVDF+TiO₂ membranes after complete cleaning.50

FABRICATION OF TiO₂-EMBEDDED PVDF MEMBRANES AND THEIR APPLICATION IN ALGAE MEMBRANE BIOREACTOR SYSTEMS

Weiming Hu

ABSTRACT

Polyvinylidene difluoride (PVDF) membranes with and without TiO₂ (5% by mass) were fabricated and applied for high-density algae cultivation in membrane algae bioreactors (MBR). Microalgae species *Chlorella Vulgaris* was cultivated in the MBR systems fed with artificial wastewater at a target solids retention time (SRT) of 25 days. Under steady-state conditions, the MBR systems had an average algae biomass concentration of 2350 mg/L (COD unit) with simultaneous removal of about 78% of phosphorus and 34% of nitrogen from wastewater. The anti-fouling characteristics of membranes were evaluated based on the measurement of intrinsic, reversible and irreversible resistances, and the scanning electron spectroscopy (SEM) study. Total resistance of TiO₂-embedded membranes was 65% lower than the control (membranes without TiO₂ impregnation) during 90 days of operation. This research demonstrated that embedding TiO₂ into the PVDF membranes resulted in membranes with better antifouling properties for high-density algae cultivation.

CHAPTER ONE

LITERATURE REVIEW

1.1. Microalgae and Algae Cultivation

The emission of greenhouse gases including carbon dioxide (CO₂), nitrous oxide (N₂O), and methane (CH₄) is increasing with the growth of global economy which could lead to an average global temperature increase of 3.6 °C (IEA 2012). Greenhouse gases emissions can also contribute to other environmental problems. For instance, oceans as one of the biggest consumer of CO₂ absorb approximately 30% of CO₂ emitted by human activities each year, and absorption of CO₂ in oceans will lower the pH of water, which can cause the loss of aquatic life and further damage the marine ecosystem. In 2006 alone, the amount of CO₂ emissions to the atmosphere were 29 Gt, and the estimated removal of CO₂ by natural environment was about 12 Gt (EIA 2006). Hence, mitigation strategies are required to remove excess CO₂. Finding the solution toward the use of clean and renewable energy sources that produce less greenhouse gases is now one of the most important and challenging issues facing human societies.

Many renewable energy options are being studied and each has a different degree of success and challenges for implementation. These options include biofuel, solar energy, wind, and geothermal applications. For global warming control, techniques such as carbon sequestration have been proposed. Biofuel production development has shown rapid growth globally, because of its potential for reducing greenhouse gases and achieving energy security (IEA 2007). Most common biofuels are biodiesel and bioethanol, both of which can replace fossil fuels such as diesel and gasoline.

The traditional feedstocks for biodiesel production are vegetable oils or animal fats. Low-cost feedstock fats such as non-edible oils, used cooking oils, animal fats and grease can be used to produce biodiesel, however the available quantities are not enough to match the demand for biodiesel production today (Mata et al. 2010). New biodiesel production methods are constantly been sought, among which microalgae biomass production as a source of raw material for biodiesel has drawn increasing interest in recent years.

1.1.1. Microalgae

Microalgae are microscopic in size, and are commonly found in freshwater and marine systems. They have different forms depending on the species. While some are unicellular, others are in chains or in groups. The sizes of microalgae range from a few micrometers to a few hundred micrometers. With their capability of oxygen photosynthesis, microalgae in oceans produce approximately half of the oxygen in the atmosphere while they utilize greenhouse gas – carbon dioxide for growth (Leach 1992).

Microalgae have higher biomass productivity than plant crops in terms of land area required for cultivation. Hence, they are predicted to have lower cost per yield using traditional oxidation ponds (Benemann et al. 1977). For instance, switchgrass is one of the fastest growing terrestrial crops, but it can convert no more than 1 W/m^2 solar energy to biomass energy, which is only 0.5 % of total solar energy ($200 - 300 \text{ W/m}^2$) received at a typical mid-latitude region. Microalgae, on the other hand, are able to convert solar energy into biomass with efficiencies of 10- 20% or even higher (Huntley et al. 2007), thus could reduce the land area required for cultivation.

Table 1. A comparison of land use and biofuel productivity between microalgae and other biodiesel feedstocks (Mata et al. 2010)

Plant source	Seed oil content (% oil by wt in biomass)	Oil yield (L oil/ha year)	Land use (m² year/kg biodiesel)	Biodiesel productivity (kg biodiesel/ha year)
Corn/Maize (<i>Zea mays</i> L.)	44	172	66	152
Hemp (<i>Cannabis sativa</i> L.)	33	363	31	321
Soybean (<i>Glycine max</i> L.)	18	636	18	562
Jatropha (<i>Jatropha curcas</i> L.)	28	741	15	656
Camelina (<i>Camelina sativa</i> L.)	42	915	12	809
Canola/Rapeseed (<i>Brassica napus</i> L.)	41	974	12	862
Sunflower (<i>Helianthus annuus</i> L.)	40	1070	11	946
Castor (<i>Ricinus communis</i>)	48	1307	9	1156
Palm oil (<i>Elaeis guineensis</i>)	36	5366	2	4747
Microalgae (low oil content)	30	58,700	0.2	51,927
Microalgae (medium oil content)	50	97,800	0.1	86,515
Microalgae (high oil content)	70	136,900	0.1	121,104

Table 1 compares the biodiesel production efficiencies between microalgae and other oil rich crops (Peterson et al. 1998, Callaway 2004, Reijnders et al. 2008, Abou Kheira et al. 2009, Atabani et al. 2012). Although for some oil rich plants the oil contents are similar to that of microalgae there are significant variations in the overall plant biomass productivity, oil yield and biodiesel

productivity. Furthermore, in terms of land use, microalgae have an advantage because of their higher biomass productivity and oil yield.

In order to quantify the environmental performance of algal biofuels, life cycle assessments (LCA) of algal biofuels have been explored. Campbell (Campbell et al. 2011) conducted a comparative LCA study to compare biodiesel production from algae with canola and ULS (ultra-low sulfur) diesel, and in that study comparisons of greenhouse gas (GHG) emissions (g CO₂-eq per t km) and costs (¢ per t km) are given. Algae GHG emissions (27.6–18.2) compare very favorably with canola (35.9) and ULS diesel (81.2). But costs were not so favorable for algae and ranged from 2.2 to 4.8, compared with canola (4.2) and ULS diesel (3.8). Among all the algal biofuel production stages, including algal culture production, algal culture harvesting, algal culture dewatering, and transesterification or in some cases anaerobic digestion (Singh et al. 2011), the algal dewatering is the most energy consuming stage. For example, Lardon reported that dewatering and hexane extraction could account for 90% of the total process energy (Lardon et al. 2009). In another research (Sills et al. 2012), the energy demands (MJ/MJ Biofuel) of processes coupling dry extraction methods (centrifugation, thermal drying, hexane extraction) were compared with those coupling wet extraction methods (belt filter press, hydrothermal liquefaction, hydrotreatment), and the results demonstrated that dry extraction processes have high energy demands sometimes exceed 0.5 or 1.0 MJ/MJ biofuel (centrifugation, thermal drying), while wet extraction methods like belt filter press (0.1 MJ/MJ biofuel) are much more energy efficient. The energy return on energy invested (EROI) for biofuel production was also reported considering different algal biofuel productivities (low, base and high productivity), and the data demonstrated that base or high productivity processes coupling wet lipid extraction are likely more likely to have a EROI value over 1.0 MJ energy produced/MJ energy input.

1.1.2. Additional Benefits of Microalgae Cultivation

Microalgae provide feedstock for several different kinds of renewable fuels such as biodiesel, methane, ethanol, and hydrogen. Unlike regular diesel products that emit both SO₂ and SO₃ (Corro 2002), biodiesel produced from microalgae contains no sulfur so it has no emission of SO₂. While it has just as good performance as petroleum diesel, biodiesel from algae also emits less CO (-49%) and hydrocarbons (-67%) comparing to diesel (Delucchi 2003).

Microalgae cultivation removes CO₂ from industrial flue gases and produces biomass at the same time (Wang et al. 2008). Algae biomass debris after lipid extraction can be further utilized to produce ethanol, methane, animal feedstock, or fertilizer due to its high N, P concentrations (Wang et al. 2008). Microalgae also have the potential to provide many other valuable products. These products include fats, polyunsaturated fatty acids, oil, natural dyes, sugars, pigments, antioxidants, high value bioactive compounds, and other fine chemicals (Raja et al. 2008)

1.1.3. Cultivation Conditions

In natural environments, microalgae utilize three essential components for growth: sunlight, CO₂ and nutrients.

Lighting is one of the most important factors controlling algal growth. Most commercial microalgae production lines use natural sunlight as a light source because it is free (Janssen et al. 2003). One limitation for this approach is that it is strongly influenced by availability of natural light due to diurnal cycles, seasonal and even weather related variations. In order to ensure sufficient light contact, fluorescent lamps are used in many pilot scale algae cultivation systems (Muller-Feuga et al. 1998).

Three forms of CO₂ are available for algal growth: CO₂ from the atmosphere, CO₂ dissolved in water (in the form of bicarbonate) and CO₂ emission from industries (Wang et al. 2008). Algae can be tolerant to CO₂ at the concentration as high as 15% (Huntley et al. 2007).

Other nutrients required for microalgae production include macronutrients such as nitrogen, phosphorus, sulfur, calcium, magnesium, sodium, potassium and chloride; micronutrients such as iron, boron, manganese, copper, molybdenum, vanadium, cobalt, nickel, silicon and selenium (Suh et al. 2003).

Continuous mixing is important and necessary for large-scale algae cultivation, which helps enhance light utilization efficiency, promotes gas exchange, improves nutrient distribution and reduces thermal stratification in algae ponds or photobioreactors (Bosca et al. 1991). Otherwise, accumulation of microalgae cells in the corners of bioreactors will occur and bring negative impacts such as deterioration of cells and unwanted anaerobic decomposition. Therefore, either mechanical stirring or gas feeding, or in some cases both are commonly used.

Productivity of algae increases with increasing temperature until it reaches optimum temperature, above which algal productivity starts to reduce due to enzymatic inhibition at high temperatures (Sheehan et al. 1998). The optimal temperature for algae growth varies between algae species and depends on nutrient or light conditions. However, normally the optimum temperature is in the range of 28 to 35 °C (Soeder 1985).

The pH of growth media affects algae growth, partially because it changes the bio-availability of CO₂ for photosynthesis and the availability and uptake of nutrients (García et al. 2000). The water pH affects algal productivity by changing alkalinity and ionic composition of medium, algae-bacteria interactions because of changes in microbial activity and the efficiency of CO₂ supply

(Heubeck et al. 2007, Park et al. 2010, Craggs et al. 2011). By consuming CO_2 and HCO_3^- in water, algal photosynthesis can increase pH up to 11 (Park et al. 2010). The increase in pH can enhance both ammonia N removal via ammonia volatilization and phosphorus removal through phosphorus precipitation with ferric, calcium and magnesium ions (García et al. 2000). However, a high pH environment can actually inhibit algae growth. For instance, free ammonia concentration of 34 and 51 mg/L at pH of 9.5 reduced algal photosynthesis of *Scenedesmus obliquus* by 50% and 90%, respectively (Azov et al. 1982). The productivities of *Chaetoceros* sp. and *Chlorella* sp. were reduced by 22% when pH increased from 8 to 9 (Weissman et al. 1988).

1.2. Microalgae for Wastewater Treatment

Wastewater is a good source for algae cultivation. It usually contains NH_4^+ , NO_3^- , PO_4^{3-} and organic matter, which can be utilized as nutrients by algae for their growth. Since the first use of microalgae for wastewater treatment (Oswald et al. 1957), many species of microalgae have been found to effectively grow in wastewater while removing nutrients simultaneously (Chong et al. 2000, Patel et al. 2012, Abou-Shanab et al. 2013). However, due to the difficulties in growth under low temperature and potential competition between bacteria and algae, the applications of algae in wastewater industry are relatively minor.

With more stringent effluent limitations, many wastewater treatment facilities are required to remove nutrients through advanced wastewater treatment. Nitrogen and phosphorus, can cause eutrophication, a significant environmental problem. Eutrophication is a phenomenon where a substantial increase of phytoplankton is triggered by introducing excess nutrients into water body, causing depletion of oxygen in water and eliminating aquatic life or species (Banens et al. 1998). In conventional wastewater treatment processes, nitrogen can be removed by nitrification and

denitrification while phosphorus is removed through both chemical precipitation and activated sludge sorption (Hoffmann 1998). As a result, nitrogen in water can be completely removed through denitrification, and phosphorus removal through these wastewater treatment processes is not easily recoverable.

Microalgae are an alternative solution to remove and recover nitrogen, phosphorus (Tam et al. 1994) and heavy metals (Ahluwalia et al. 2007) for wastewater treatment while offering other benefits. For instance, oxygen production associated with algal photosynthesis increases the dissolved oxygen (DO) concentrations in wastewater, which can reduce the need for mechanical aeration and further reduce the cost of the treatment process (Mallick 2002). Algae-based wastewater treatment processes do not generate chemical sludge byproducts, and for most cases the recovered nitrogen and phosphorus in algae can be reused either as fertilizer or animal feedstock (Wilkie et al. 2002).

1.2.1. Advances in Algae-based Wastewater Treatment

One of the commonly used algae-based wastewater treatment systems is called High-Rate Algal Ponds (HRAP), which are shallow oxidation ponds that facilitate algal growth. These HRAP systems are usually designed as circular channels with brush mixing to ensure algae suspension and CO₂ transfer in wastewater. The HRAP systems can achieve high-level removal of contaminants such as BOD, TSS, nitrogen, phosphorus and metals for both municipal and agricultural wastewater (Fallowfield et al. 1985, Picot et al. 1991). But the issue related to efficient and cost-effective harvest of microalgae biomass has been a major limitation of HRAPs (Molina Grima et al. 2003). Algae biomass harvesting is challenging because of: (1) low biomass concentration in the HRAP systems (typically around 500 g/m³); (2) suspended mixed liquor that

is difficult to form large flocs; (3) small cell size (5-20 μm). There are various harvesting methods developed for algae biomass collection including centrifugation, sedimentation, air flotation assisted with chemical flocculation. All these techniques are generally costly for large-scale algae cultivation and harvesting.

Membrane technology has advantages over conventional cultivation and biomass separation methods. First of all, high-density algae cultivation becomes possible through the use of membrane bioreactor (MBR) operation. Second, membrane filtration does not require additional chemicals such as coagulants, which will simplify biomass processing and make it easy to reuse water after filtration (Rós et al. 2012). Third, membrane filtration processes can achieve more complete recovery of algae biomass (Babel et al. 2000), and it will not cause significant damage to cell structure. Most importantly, when compared to conventional dewatering methods, such as centrifugation and thermal drying, membrane filtration is a relatively lower-energy consuming method for algae harvesting (Uduman et al. 2010).

1.3. Promising of Algae-based MBR for Wastewater Polishing and Water Reuse

Problems associated with clean water scarcity have been growing as a global issue in the past decades. There are 1.2 billion people lacking access to safe drinking water. About 2.6 billion people have little or no sanitation and millions of people are dying each year because of water-transmitted diseases (Montgomery et al. 2007). Additionally, a growing number of new pollutants are contaminating water bodies these days due to human activities.

As the effluent water quality after wastewater treatment needs to meet more and more stringent regulation permits, many conventional water treatment systems are facing a significant challenge (Visvanathan et al. 2000). The effluent water quality from conventional facilities is highly

dependent on the hydrodynamic conditions in the sedimentation tank and the sludge settling properties. In order to achieve excellent water quality, sedimentation tanks with large volume are required to ensure adequate separation performance, which cannot be applied to facilities with space limitation.

In order to face these challenges associated with water scarcity and water contamination, the applications of membrane technology for water treatment and water reuse have been especially attractive because membrane processes offer many advantages over conventional water treatment processes.

1.4. Membrane Technology

Membranes are commonly used for separation, allowing for a feeding stream to be split into two separate fractions: concentrated fraction and permeated fraction (Van Der Bruggen et al. 2003). This separation process can selectively retain particles and dissolved components at one side of the membrane depending on their properties such as size, shape and charge. The classification of membrane processes is based on several criteria, such as pore size of the membrane, retained particle size or molecular weight and the pressure exerted on the membrane surfaces (Table 2).

Table 2. Classification of membrane processes (Van Der Bruggen et al. 2003).

	Microfiltration (MF)	Ultrafiltration (UF)	Nanofiltration (NF)	Reverse Osmosis (RO)
Permeability (l/h.m ² .bar)	>1,000	10-1,000	1.5-30	0.05–1.5
Pressure (bar)	0.1-2	0.1–5	3–20	5–120
Pore size (nm)	100-10,000	2-100	0.5-2	<0.5
Rejection				
Monovalent ion	-	-	-	+
Multivalent ion	-	-/+	+	+
Small organic compounds	-	-	-/+	+
Macromolecules	-	+	+	+
Particles	+	+	+	+
Separation mechanism	Sieving	Sieving	Sieving	Diffusion
Applications	Clarification, Pretreatment, Removal of bacteria	Removal of macromolecules, bacteria, viruses	Removal of ion and small organics	Ultrapure water, desalination

Note: “+” and “-” in table meaning “Yes” and “No” respectively.

Compared to other types of membranes, microfiltration (MF) membranes have the largest pores ranging from 0.1 μm to 10 μm . MF membranes can provide a relatively higher permeability to reach a larger flux at lower pressure. As the filtration processes guarantee the removal of particles larger than the pore size of the membrane, the MF membrane is an ideal barrier for the removal of suspended solids, colloids and most of microorganisms.

Ultrafiltration (UF) membranes have smaller pores ranging from 2 nm to 100 nm. Since the pores are smaller, the permeability of UF membranes is significantly lower than that of MF membranes. The pore size of UF membranes determine their ability to remove some dissolved organic compounds with large molecular weights from water.

Nanofiltration (NF) membranes have pore sizes even smaller than UF membranes, with their pore sizes around 1 nm. The pore sizes of UF membranes make them suitable for removing smaller

molecules dissolved in water. NF membranes can also have surface charges caused by ionizable groups, such as carboxylic or sulfonic acid groups, on membrane surfaces (Van Der Bruggen et al. 2003). The surface charges associated with these functional groups introduce the effect of Donnan exclusion, which causes ion rejection from charges on the membrane surfaces. The Donnan exclusion effect provides nanofiltration membranes an additional selective rejection on soluble components smaller than membrane pore sizes (Schaep et al. 1998).

Reverse osmosis (RO) membranes are really dense membranes without predefined pores. As water has to follow a tortuous pathway through the membrane to reach the permeate side, RO membranes can remove the smallest molecules such as salts and monovalent ions (Greenlee et al. 2009). RO membrane filtration can generate extremely pure permeate during the filtration process, although the drawback of RO membrane filtration is associated with the extremely high-energy cost.

1.4.1. Membrane Materials

Three basic requirements for a reliable membrane are: high selectivity, high permeability and mechanical stability. To meet all these criteria, organic polymers are the most commonly used materials for conventional pressure-driven membrane processes (Ter Meulen 1992).

Materials often used for microfiltration applications are the hydrophobic polytetrafluoroethylene (PTFE), poly (vinylidene fluoride) (PVDF), polypropylene (PP), polyethylene (PE), and hydrophilic materials like cellulose esters, polycarbonate (PC), poly sulfone/poly (ether sulfone) (PSf/PES), polyamide (PA) and polyetheretherketone (PEEK). Microfiltration membranes are prepared through sintering, track-etching, stretching or phase inversion techniques. Ultrafiltration membranes must be prepared through the phase inversion technique, and commonly used materials are polysulfone/poly (ether sulfone)/sulfonated polysulfone, poly (vinylidene fluoride),

polyacrylonitrile, cellulose acetate, polyimide/poly (ether imide), aliphatic polyamide, and polyetheretherketone (Van Der Bruggen et al. 2003). Nanofiltration membranes are made of aromatic polyamide, polysulfone/poly (ether sulfone)/sulfonated polysulfone, cellulose acetate, or poly (piperazine amide). Reverse osmosis membranes can be made of cellulose triacetate, aromatic polyamide or interfacial polymerization of polyamide and poly (ether urea).

In this research, all the membranes are manufactured using poly (vinylidene fluoride) (PVDF) as a base material because PVDF has excellent chemical stability, thermal stability and good mechanical strength (Bonyadi et al. 2009). PVDF membranes are also known to have high permeability and high separation efficiency (Baker 2012). Nonetheless, its higher hydrophobic nature results in more rapid membrane fouling by biomolecules and organic matter (Zhang et al. 2009).

1.4.2. Membrane Modules

Industrial membrane plants are equipped with thousands of square meters of membrane in order to process large quantities of water. Before membranes are implanted in membrane plants, manufactures pack membranes in a variety of ways to reach desired process efficiency. Such ways of packing membranes are called membrane modules (Baker 2012).

The increasing technology development since the 1960s has greatly promoted the production of low-cost membrane modules. After decades of development, there are three membrane modules that are commonly used for commercial membrane products: plate-and-frame, tubular and hollow fiber modules.

Plate-and-frame modules are one of the simplest and oldest types of membrane modules. The plate-and-frame modules proposed in 1965 is shown in Figure 1 (Stern et al. 1965).

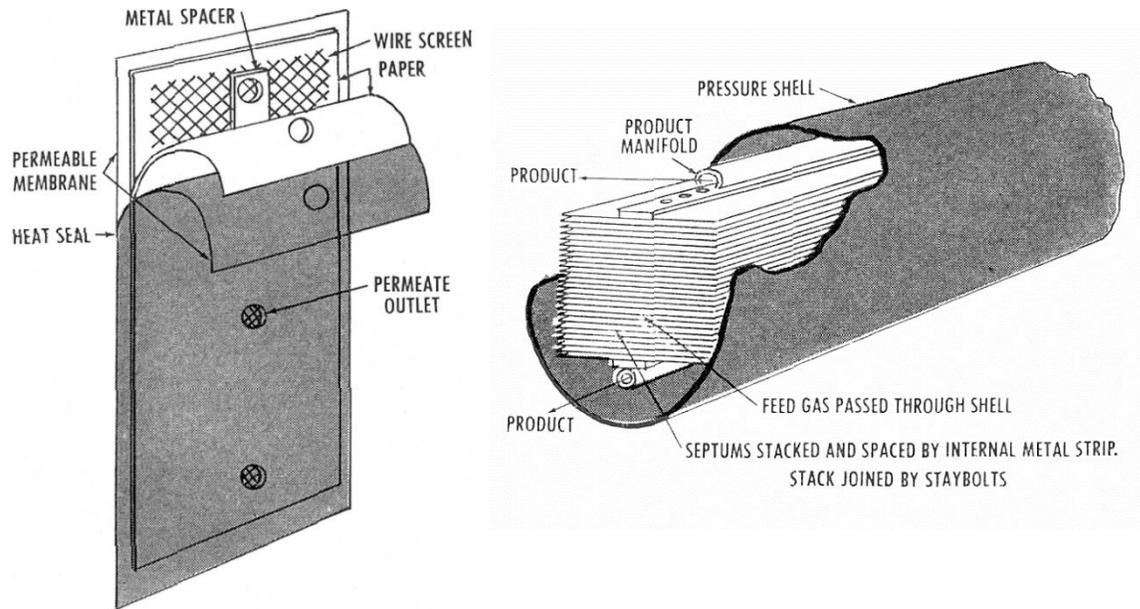


Figure 1. Plate-and-frame design for the separation of helium from natural gas (Stern et al. 1965).

In plate-and-frame modules, permeable membranes are fixed on frames made of different materials. Membrane, feed spacers and product spacers are layered together, and the feed mixture is forced across the membrane surface to achieve the desired separation. The cost of plate-and-frame modules is higher than other alternatives, which limits its applications. Plate-and-frame modules are now used mainly in electrodialysis systems and a small number of reverse osmosis and ultrafiltration applications (G ünther et al. 1996).

Tubular membrane modules (Figure 2) are normally used in ultrafiltration applications. The tubes consist of porous paper or fiberglass materials with membrane formed inside the tubes. A typical tubular membrane module is presented in Figure 2.

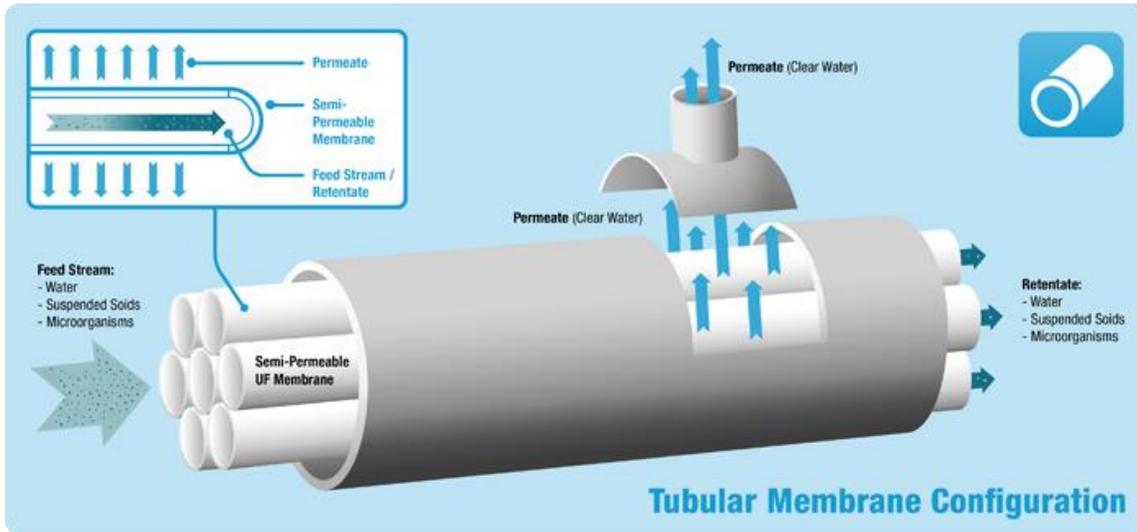


Figure 2. Tubular Membrane Configuration for ultrafiltration from Koch Membrane Systems Inc. (Courtesy Koch Membrane Systems Inc.).

Spiral wound membrane modules are constructed by using simple flat membranes in the form of a “pocket” containing two membrane sheets separated by a highly porous support plate (Meares 1994). Several pockets are wound around a tube to create tangential flow geometry and to reduce membrane fouling. A typical design of spiral wound membrane module configuration is shown in Figure 3 together with cross section diagram.

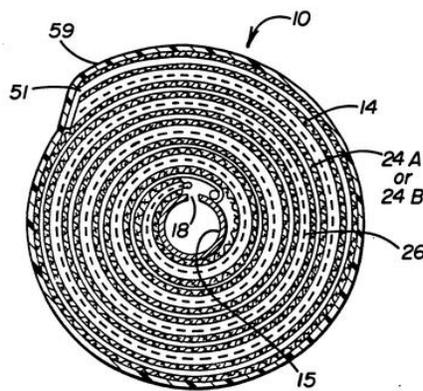
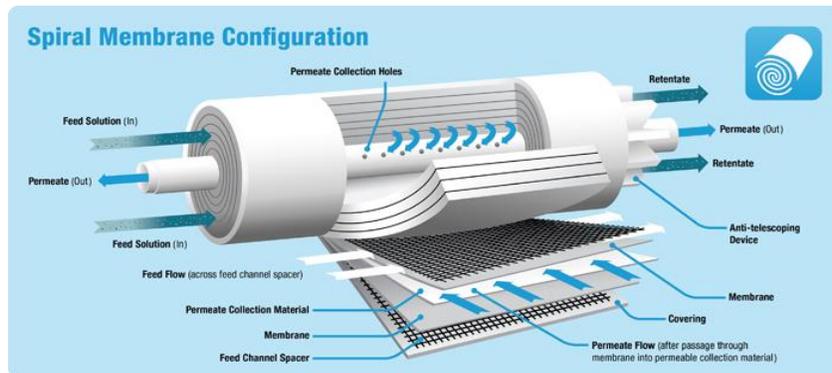


Figure 3. Spiral membrane module configuration and its cross section view (Courtesy from Koch Membrane Systems Inc.).

Hollow fiber membrane modules consist of an assembly of fibers with skin separation layers, and more open matrix helping to withstand pressure gradients and maintain structure integrity (Zeman 1996). Hollow fiber membrane modules can contain larger quantities of fibers in one module if needed. As a result, hollow fiber modules can pack in a very large surface area within an enclosed volume thus greatly increase the efficiency of separation process. A schematic of a typical hollow fiber membrane module is presented in Figure 4.

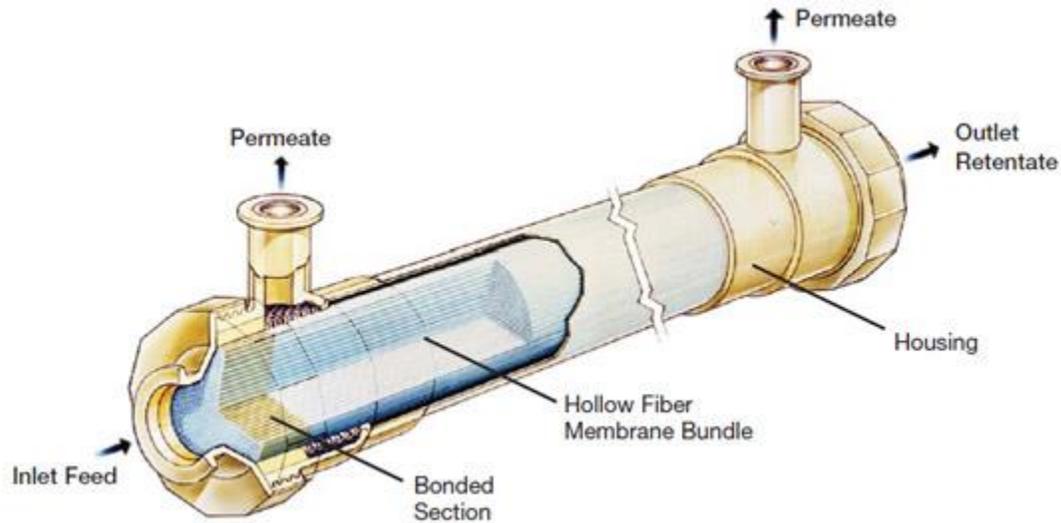


Figure 4. Diagram of hollow fiber membrane module (Courtesy Pall Corporation.).

1.4.3. Membrane Fouling

While there are numerous advantageous of MBR over conventional activated sludge treatment processes, cost is one major drawback limiting the applications of MBR systems. Fortunately, since the commercialization of membrane processes has become more successful over the past years, the costs of membrane modules have decreased dramatically (From Over \$ 100/M² to < \$ 50/m²) (Judd et al. 2011). Now the main contribution of overall MBR operating cost is associated with membrane fouling abatement. Membrane fouling can cause problems leading to the rise of operating costs in many different ways such as reducing lifespan of membranes. It also requires frequent cleaning/maintenance on membranes which also cause high energy consumption (e.g., via aeration) for fouling mitigation (up to 70% of the total energy costs for the unit) (Verrecht et al. 2008).

1.4.4. Membrane Fouling Mechanisms

Membrane fouling is a phenomenon when solute or particles deposit on membrane surfaces or inside membrane pores resulting in decrease in membrane performance.

As demonstrated in Figure 5, membrane fouling can be attributed to both membrane pore blockage caused by smaller particles or colloids and cake layer formation on membrane surfaces. In between, cake layer formation has been identified as the predominant membrane fouling component (Lee et al. 2001).

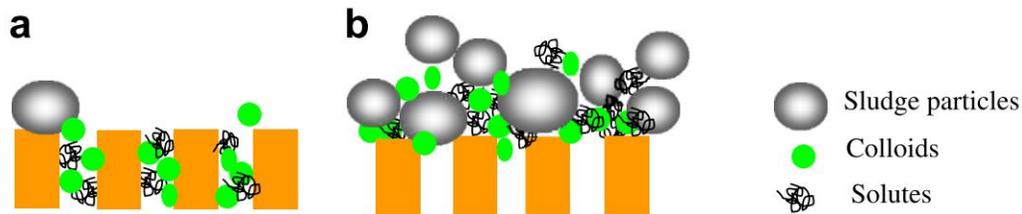


Figure 5. A schematic of membrane fouling due to: (a) pore blockage, (b) and cake layer formation (Meng et al. 2009).

In order to predict and measure fouling resistance, many researchers have developed models to express the relationship between operating conditions and membrane fouling. Some of these established expressions are listed in Table 3.

A number of fouling factors have been identified affecting membrane filtration, which can be classified into four categories: membrane materials, biomass characteristics, feeding water characteristics, and operating conditions (Le-Clech et al. 2006). The interaction between all these factors and fouling is extremely complex. Major fouling factors such as extracellular polymeric substances (EPS), soluble EPS or sometimes referred to as (SMP) and hydrodynamic conditions are discussed below.

Table 3. Models developed to describe membrane fouling (modified after (Meng et al. 2009)).

Application	Expression	Remarks
Classical Cake Filtration (Shimizu et al. 1993)	$J = \frac{\Delta P}{\mu(Rm + \alpha C_{MLSS})}$	J is membrane flux (L/m ² h), ΔP is TMP, C _{MLSS} is the biomass concentration (mg/L), m is sludge viscosity (mPa s), α is specific cake resistance (m/kg).
Concentration Polarization (Ishiguro et al. 1994)	$J = a + b \log(\Delta C_{DOC})$	C _{DOC} is the differential DOC concentration between the activated sludge and the permeate (mg/L).
Cross-flow MBR (Krauth et al. 1993)	$J = J_o \exp\left(\frac{kR_e(C_{MLSS} - C_{MLVSS})}{C_{MLVSS}}\right)$	MLSS is sludge concentration (kg/m ³), MLVSS is volatile sludge concentration (kg/m ³), k is a constant related with TMP, Re is Reynolds number. J ₀ is the initial membrane flux (L/m ² h).
Submerged MBR (Nagaoka et al. 1998)	$R_t = R_m + \alpha m$	The accumulation, detachment and consolidation of EPS on the membranes were considered. m is EPS density on the membrane surface (kg/m ²)
Submerged MBR (Meng et al. 2006)	$R_f = 2.25 \exp(MLSS \times 9 \times 10^{-5}) + 0.111EPS - 1.99 \times 10^{-2}PSD - 3.20$	R _f is the fouling resistance, EPS is the bound extracellular polymeric substances (mg/g-MLSS), PSD is mean particle size (μm).
Submerged MBR (Lee et al. 2002)	$R_t = R_m + \alpha m, \quad m = \frac{k_m(V_p X_{TSS})}{A}$	This model is used to describe membrane fouling. Where A is specific resistance of accumulated mass (m/kg), m is accumulated mass on the membranes (kg/m ²), A is membrane area (m ²), V _p is permeate volume (m ³), X _{TSS} is total suspended solids, k _m efficiency of cross-flow velocity, ranging from 0 to 1.
Submerged MBR (Liu et al. 2003)	$K = (8.93 \times 10^7) \times C_{MLSS}^{0.532} J^{0.376} U_a^{-3.05}$	K is the increasing rate of filtration resistance (1/(m h)), X is sludge concentration (mg/L), J is membrane flux (L/m ² h), U _{Lr} is observed cross-flow velocity of the tap water in the membrane zone (m/s).
Resistance in Series (Field et al. 1995)	$R_t = R_m + R_c + R_f, J = TMP/(\eta R_t)$	η =dynamic viscosity of the permeate; R _t is total resistance; R _m intrinsic membrane resistance; R _c reversible resistance; R _f irreversible fouling resistance

EPS are considered one of the predominant factors causing membrane fouling (Meng et al. 2009). EPS are organic molecules secreted by microorganisms into the environment, e.g., proteins, polysaccharides, nucleic acids, lipids, humic acids (Staudt et al. 2004). EPS are mostly composed of polysaccharides and proteins, which contribute to 50% to 90% of the total organic matter in biofilms (Guo et al. 2012). There are two forms of EPS, bound EPS and soluble EPS. Soluble EPS are sometimes referred to as SMP, which can be defined as a group of organic compounds that are released into solution from microbial metabolism and decay (Barker et al. 1999). Bound EPS have been reported not only as the major sludge floc components but also key membrane foulants in MBR systems. The bound EPS concentration has a close relationship with the specific cake resistance: as bound EPS concentration increased, specific cake resistance increased (Cho et al. 2005). Some researchers subcategorized bound EPS into loosely bound EPS and tightly bound EPS, and proved that fouling resistance was mainly caused by loosely bound EPS instead of tightly bound EPS (Ramesh et al. 2006).

Due to the complex nature of MBR systems, membrane fouling can hardly be attributed solely to bound EPS. The contribution of soluble EPS has also drawn much attention recently. Because of their soluble property, soluble EPS can accumulate on membrane surfaces as well as penetrate into membrane pores, which result in the poor filterability of the sludge suspension. Geng showed that the floc size distribution and the amount of soluble EPS in mixed liquor were the most important properties that influenced the fouling, while the bound EPS was not directly related to fouling. Iritani (Iritani et al. 2007) reported that soluble EPS is the controlling factor in membrane fouling. Rosenberger (Rosenberger et al. 2006) also reported that the difference in soluble EPS content between two identical MBR systems had an impact on membrane performance. Soluble EPS or SMP were also the major reason causing membrane fouling in algae MBR systems (Henderson et

al. 2008, Huang et al. 2012). These results suggest that soluble EPS has significant impact on membrane fouling, and the soluble EPS concentration and composition could determine fouling propensity.

In an MBR operation, although biofouling and organic fouling mainly govern membrane fouling, inorganic fouling along with deposition of cells and cell debris on membrane surfaces also happens during membrane filtration. Ognier (Ognier et al. 2002) reported severe CaCO_3 fouling in a MBR using a ceramic ultrafiltration membrane module, and found that high alkalinity of the activated sludge (pH = 8-9) can trigger the precipitation of CaCO_3 . Wang (Wang et al. 2008) observed that cake layer can be formed by a combination of organic and inorganic substances such as Mg, Al, Ca, Fe, which facilitates the formation of the cake layer. In addition, inorganic fouling is not easily recovered even after chemical cleaning (You et al. 2006). A number of cations and anions are typically present in MBR systems, such as Ca^{2+} , Mg^{2+} , Al^{3+} , Fe^{3+} , CO_3^{2-} , PO_4^{3-} and OH^- , and high concentrations of these inorganic salts are mainly responsible for inorganic fouling (Shirazi et al. 2010). This is likely due to the fact that dissolved salts are normally concentrated 4-10 times causing high concentrations exceeding the solubility at the membrane surfaces (van de Lisdonk et al. 2000).

As one of the most important operating parameters of MBR systems, solids retention time (SRT) is also identified as the main parameter affecting EPS concentrations (Lu et al. 2001), although there is contradictory information in the literature. Some researchers found that EPS concentration in bioreactors increases as SRT increases (Kimura et al. 2009), thus leading to an increase of membrane fouling. Ahmed (Ahmed et al. 2007), however, reported that as SRT decreased from 60 to 20 days, the bound-EPS per unit of biomass increased, and consequently, the specific cake resistance increased. Jinsong (Jinsong et al. 2006) reported that the polysaccharide concentration

in the supernatant was about 100% higher for the SRT of 10 days than that for 30 days, and their long term experiments also showed more severe membrane fouling for the SRT of 10 days than that of 30 days. Hence, it appears that appropriate SRT range needs to be identified for membrane fouling control.

Hydraulic retention time (HRT) is another important operating factor that has strong impact on membrane fouling. Meng (Meng et al. 2007) reported that low HRT resulted in high EPS concentration, high mixed liquor suspended solids (MLSS) concentration and sludge viscosity, and these factors had negative effect on membrane fouling. Chae (Chae et al. 2006) showed that as HRT decreased from 10 to 4 h, EPS concentrations increased and the average sludge particle size increased, leading to reduced settling of the sludge and increased membrane fouling. Cho (Cho et al. 2005) also found that short HRT and high flux condition resulted in the acceleration of membrane fouling.

Aeration affects both the size of sludge flocs and membrane fouling as well. On the one hand, aeration can reduce sludge attachment to membrane surfaces. On the other hand, too high aeration will break sludge flocs thus facilitating the release of soluble EPS, colloids and solutes, which could become major membrane foulants. Size of air bubbles also affects the fouling (Fane et al. 2005) as fouling control was noticeably improved by using smaller nozzle with smaller bubbles.

1.4.5. Membrane Fouling Control

Membrane fouling control strategies have been intensively studied for years. Currently available methods can be categorized into three groups: hydraulic control, chemical control and biological control.

Increase of aeration intensity within a certain range have been demonstrated to help increase the permeability of membranes (Psoch et al. 2006), and the removal of cake layer resistance (Chang et al. 2003). In addition, periodic backwashing helps maintain high flux and extend the membrane operation period by reducing membrane resistance (Psoch et al. 2006).

A common practice for chemical fouling control is the use of flocculants and coagulants. Aluminum or iron-based coagulants are most commonly used to neutralize negatively charged flocs and colloids which allows them to flocculate with each other by electrostatic attraction, and therefore, reduces chance for organic matter to attach on membrane surfaces (Zhang et al. 2008). Other chemicals were also tested as additives. Activated carbon has been applied in MBR systems to remove EPS (Ying et al. 2006), thus reducing fouling (Aun Ng et al. 2006). A membrane fouling reducer (MFR) which is a cationic polymeric material was also proven to enhance permeate flux in MBR systems (Yoon et al. 2006) by increasing the cake layer porosity and reducing soluble EPS concentrations (Hwang et al. 2007). Chemical enhanced backwashing is another approach for chemical fouling control. Finally, ozone backwashing was found to be highly effective in membrane fouling control (Kim et al. 2007).

Various biological fouling control methods have also been explored. As the most important operating parameter, SRT has great impact on membrane fouling. Although there is continued debate about the role of SRT in membrane fouling, it appears that a relatively long SRT is preferred, as both bound & soluble EPS concentration will decrease which can reduce fouling (Liang et al. 2007). Other biological factors are important too. MLSS/viscosity and food/biomass are two ratios that have impact on fouling behavior. When MLSS/viscosity ratio drops, the permeate flux could increase due to increase of membrane total resistance (Li et al. 2007), In addition, the decrease of

food/biomass ratio will reduce membrane fouling resistance largely due to the long SRT operation (Trussell et al. 2006).

1.4.6. Membrane Fouling Control through Membrane Modification

Membrane fouling is greatly influenced by the hydrophobic and electrostatic interactions between organic matters in water and membrane surfaces. Hydrophilic materials, in general, have a strong affinity to water, which results in faster dissolution in water, as these materials readily attract water or adsorb water. Hydrophobic materials, on the other hand, are water repelling and they have limited ability to absorb water. For membrane separation purposes, hydrophilic materials such as citric acid (CA) and polyacrylonitrile (PAN) are preferred because of their excellent fouling resistance (Li et al. 2008). However, hydrophilic membranes are less resistant to chemicals, temperature, and biological degradation and their limitations become apparent during long time operations. On the contrary, hydrophobic materials such as PES, PS or PVDF have generally higher physical and chemical stability. Therefore, even though their antifouling performances are not as good as hydrophilic materials, they are also popularly used in membrane industry. These hydrophobic materials are often blended with hydrophilic polymers, such as polyvinylpyrrolidone (PVP), to make it more hydrophilic for fabrication of membrane products. The PS and PES materials are commonly used for UF membranes and as a support for composite RO membranes. Meanwhile, typical hydrophobic materials such as PTFE (Teflon), PVDF, polyethylene (PE), and polypropylene (PP) are commonly used for MF membranes (Li et al. 2008).

The development of high performance membranes involves selection of suitable materials and formation of desired membrane structures. It is necessary to modify the membrane to enhance the membrane performance. The main purposes of membrane modification are: 1) to increase

membrane flux or selectively, 2) to increase membrane hydrophilicity and reduce membrane fouling, and 3) to increase chemical resistance. Some of the techniques used for such modifications are listed in Table 4.

Heat treatment was the first reported method for membrane modification. Zsigmondy demonstrated that pore size of nitrocellulose membrane could be decreased by hot water or steam treatments (Bachmann Juen,1922).

Table 4. Membrane modification methods.(Pinnau et al. 1999)

Modification method	Goal	Application
Annealing		
heat-treatment	elimination of membrane defects	RO, GS, UF
solvent treatment	control of pore size	RO, GS, UF
Solvent-exchange	elimination of membrane defects	GS, UF
Surface coating	elimination of membrane	GS
	improvement of fouling resistance	RO,NF,UF
Chemical treatment		
fluorination	improvement of flux and selectivity	GS
cross-linking	improvement of chemical resistance	UF
pyrolysis	improvement of flux and selectivity	RO, GS, PV

Plasma treatment has been utilized in membrane surface modification by a number of researchers. Kim (Kim et al. 2002) treated PS membrane using oxygen plasma treatment which changed PS membrane surface from hydrophobic to hydrophilic and thus reduced fouling. Yu (Yu et al. 2005)

applied NH_3 plasma treatment on polypropylene membrane surfaces and found that fouling on treated membranes was lower resulting in better flux recovery after cleaning. CO_2 plasma treatment on PS membrane surfaces (Wavhal et al. 2005) also successfully changed the surfaces to hydrophilic with excellent antifouling property. While the plasma treatment processes have advantages, they can only modify the membrane at very shallow depth. Hence, it is difficult to use for large-scale production (Yu et al. 2007).

CHAPTER TWO

METHODOLOGY

2.1. Membrane Modification and Module Fabrication

2.1.1. Membrane Fabrication materials

One goal of this research was to modify PVDF membrane by incorporating titanium dioxide (TiO₂) nanoparticles into PVDF membrane to increase the hydrophilicity of polyvinylidene fluoride (PVDF) membranes and to introduce photocatalytic property. PVDF was selected as a major polymer for membrane fabrication in this research due to its high purity, physical strength, and chemical resistance to solvents, acids, bases and heat. PVDF has been used as a common material in membrane industry. PVDF with an average molecular weight of 180,000 Dalton was obtained in the form of white beads (Sigma-Aldrich).

Polyvinylpyrrolidone (PVP), made from monomer N-vinylpyrrolidone, was used as an additive to increase hydrophilicity and porosity of PVDF membrane with desired anti-fouling property. The average molecular weight of PVP was 10,000 Da, which was obtained from Sigma Aldrich.

Titanium dioxide (TiO₂) nanoparticles are a well-known photocatalytic material, as they can be activated under irradiation of UV light or in some cases, visible light. In this research, TiO₂ nanoparticles were *AEROXIDE TiO₂ P25* (EVONIK INDUSTRIES, AG) with an average primary particle size of 21 nm, and specific surface area (BET) of 50 ±15 m²/g.

N-Methyl-2-pyrrolidone (NMP, anhydrous, 99.5%, Sigma Aldrich) was used as a solvent in membrane fabrication. NMP is a slightly yellowish liquid that is miscible with water. It was

selected as solvent because PVDF has high solubility in NMP and NMP/PVDF has high mutual affinity to promote mixing.

2.1.2. Fabrication of PVDF/PVDF+TiO₂ Hollow Fiber Membranes

The casting solution for PVDF hollow fiber membrane fabrication was prepared as follow: PVDF (3.2 g) was dissolved in NMP (15.8 g) with PVP (1 g) as an additive in a closed glass bottle. The solution was then magnetically stirred at 60 °C for 6 hours. Finally, the casting solution was left to cool and stand for 8 hours to eliminate bubbles in the solution.

Both PVDF and nano-TiO₂ modified PVDF (labeled as PVDF+TiO₂ thereafter) hollow fiber membranes were prepared through the phase inversion method. Casting solution was pumped by nitrogen cylinder at 35 psi, and DI water as bore liquid was pumped at the speed of 0.8 ml/min. Both casting solution and bore liquid were pumped simultaneously through a spinneret, which had outer diameter (OD) of 1000 μm and inner diameter (ID) of 600 μm. Coagulation occurred when nascent fiber was immersed in a coagulation bath using tap water as a coagulant. Fiber was later collected by a spinning wheel collector, and cut into lengths of 30 cm after rinsed with DI water for 2 hours. Detailed parameters of hollow fiber membrane fabrications are listed in Table 5.

Table 5. Membrane fabrication parameters.

Spinneret OD/ID	1.0 mm/ 0.6 mm
Spinneret temperature (°C)	25
Spinning solution	PVDF/PVP/NMP
Concentration (wt%)	16/5/79%
TiO ₂ concentration (wt%)	5%
Membrane pore size (nm)	20
Dope solution flow rate (mL/min)	1.2
Bore fluid composition	DI water
Bore fluid flow rate (mL/min)	0.8
Range of air-gap distance (cm)	0
Coagulant	Tap water
Coagulant temperature (°C)	25
Washing bath	Tap water
Washing bath temperature (°C)	25
Take-up speed (cm/min)	450

Fabricated PVDF and PVDF+TiO₂ hollow fiber membranes had uniformed inner and outer diameter with smooth surface (Figure 6).

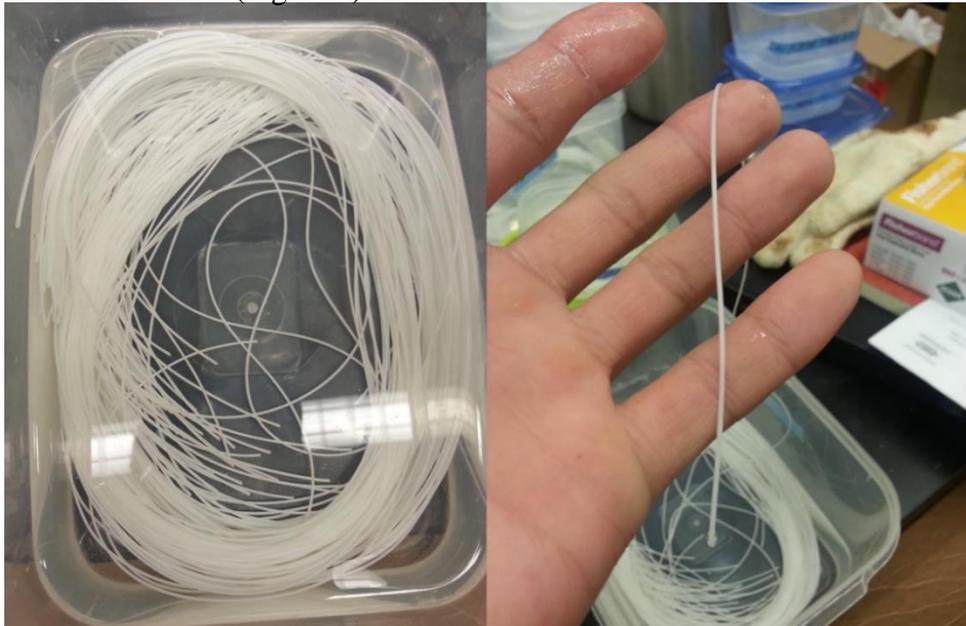


Figure 6. Fabricated hollow fiber membranes.

2.1.3. Assembly of PVDF/PVDF+TiO₂ Hollow Fiber Membrane Modules

Two types of hollow fiber membrane modules (Figure 7) were developed and evaluated in this research. The first module fabrication was more complex (Figure 7, top panel) with air supply and air bubbling functions. Both PVDF and PVDF+TiO₂ hollow fiber membranes were assembled. Air bubbling was supplied through an inlet on the top of the module channeled to the bottom of the central pillar. When air was supplied, air bubbles exited from the bottom and through brushing hollow fiber membranes surfaces thus reducing algae deposition onto the membrane surface. However, modules with the first design had leaking problems due to incompatible parts, so a second type of design was made as presented in Figure 7 (bottom panel), this design was more simplistic in design, assembly and maintenance, but modules made with this design did not include the function of incorporated air bubbling, so air supply was provided by adding tubes to channel air right under membrane modules.

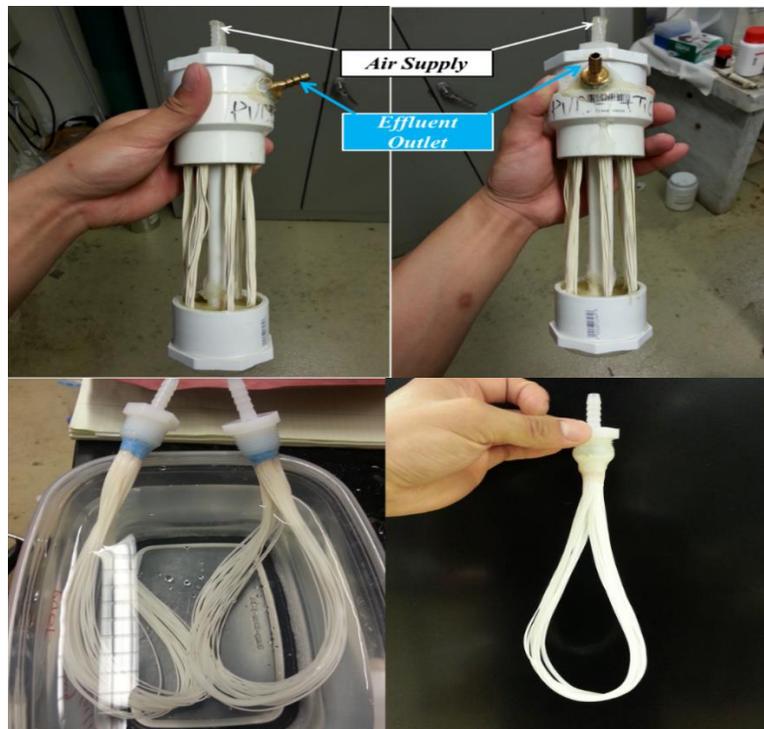


Figure 7. Two hollow fiber membrane module designs, complex design (top) and simple design (bottom).

Detailed parameters for each design are listed in Table 6.

Table 6 Hollow fiber membrane module parameters.

Design	HFM Amount	HFM Fiber Diameter (mm)	HFM Length (cm)	Total surface area (cm²)
Simple	40	1	28	352
Complex	120	1	15	570

2.2. Algal Cultivation

The algae species used for the high-density algal MBR system was *Chlorella Vulgaris* (Item 152075) purchased directly from the Carolina Biological Supply Company.

Bold's Basal Medium (Bold 1949) was used for algae cultivation before algae seed was applied in the algae MBR system. The components of the medium are listed in Table 7.

Table 7. Bold's basal medium (Bold 1949).

Component	1 Liter Stock solution	added quantity below per liter of medium	Molar concentration in the final Medium[¶]
<u>Major Stock Solutions</u>			
NaNO ₃	25.00 g L ⁻¹ dH ₂ O	10 mL	2.94 x 10 ⁻³ M
CaCl ₂ • 2H ₂ O	2.50 g L ⁻¹ dH ₂ O	10 mL	1.70 x 10 ⁻⁴ M
MgSO ₄ • 7H ₂ O	7.50 g L ⁻¹ dH ₂ O	10 mL	3.04 x 10 ⁻⁴ M
K ₂ HPO ₄	7.50 g L ⁻¹ dH ₂ O	10 mL	4.31 x 10 ⁻⁴ M
KH ₂ PO ₄	17.50 g L ⁻¹ dH ₂ O	10 mL	1.29 x 10 ⁻³ M
NaCl	2.50 g L ⁻¹ dH ₂ O	10 mL	4.28 x 10 ⁻⁴ M
<u>Alkaline EDTA Stock Solution</u>		add 1 mL of this solution per liter of medium	
EDTA anhydrous	50 g L ⁻¹ dH ₂ O		4.28 x 10 ⁻⁴ M
KOH	31 g L ⁻¹ dH ₂ O		1.38 x 10 ⁻³ M
<u>Acidified Iron Stock Solution</u>		add 1 mL of this solution per liter of medium	
FeSO ₄ • 7H ₂ O	4.98 g L ⁻¹ dH ₂ O		4.48 x 10 ⁻⁵ M
H ₂ SO ₄	1.0 mL		
<u>Boron Stock Solution</u>		add 1 mL of this solution per liter of medium	
H ₃ BO ₃	11.42 g L ⁻¹ dH ₂ O		4.62 x 10 ⁻⁴ M
<u>Trace Metal Stock Solution</u>		add 1 mL of this solution per liter of medium	
ZnSO ₄ • 7H ₂ O	8.82 g L ⁻¹ dH ₂ O		7.67 x 10 ⁻⁵ M
MnCl ₂ • 4H ₂ O	1.44 g L ⁻¹ dH ₂ O		1.82 x 10 ⁻⁵ M
MoO ₃	0.71 g L ⁻¹ dH ₂ O		1.23 x 10 ⁻⁵ M
CuSO ₄ • 5H ₂ O	1.57 g L ⁻¹ dH ₂ O		1.57 x 10 ⁻⁵ M
Co(NO ₃) ₂ • 6H ₂ O	0.49 g L ⁻¹ dH ₂ O		4.21 x 10 ⁻⁶ M

Artificial wastewater was used as a feed solution with components listed in Table 8. K₂HPO₄ and NaNO₃ were used as sources for phosphorus and nitrogen, respectively. Different concentrations of P and N were provided in the feed to study nutrient removal efficiencies under different nutrient concentrations.

Table 8. Chemical composition of the feeding solutions.

Component	Concentration (mM)
K ₂ HPO ₄	4-11
NaNO ₃	3-9
NaCl	0.43
NaHCO ₃	1
MgSO ₄	0.3
CaCl ₂ .2H ₂ O	0.17
EDTA disodium salt dehydrate	0.01
FeCl ₃	0.01
FeCl ₂ .4H ₂ O	Fe ²⁺ =0.01 mM
MnSO ₄ .H ₂ O	Mn ²⁺ = 0.02 mM
(NH ₄) ₆ Mo ₇ O ₂₄ .4H ₂ O	Mo ₇ O ₂₄ ⁶⁻ = 0.001 mM NH ₄ ⁺ = 0.006 mM
CuSO ₄	Cu ²⁺ =0.005 mM
ZnSO ₄ .7H ₂ O	Zn ²⁺ =0.006 mM
NiSO ₄ .6H ₂ O	Ni ²⁺ =0.001 mM

2.3.High-density Algae MBR System Set-up

Two bench-scale algae membrane bioreactors (Figure 8) were set up in parallel to study both the antifouling performance of TiO₂ imbedded PVDF hollow fiber membrane and the wastewater treatment/polishing performance in the high-density algae cultivation.

Two reactors were operated in duplicate under the same operating conditions as listed in Table 9. Each reactor had a total volume of 4 L with a hydraulic retention time (HRT) and a target solids retention time (SRT) of 0.5 d and 25 d, respectively. Membrane fouling was monitored by setting recording the change in transmembrane pressure through pressure gauges at constant flux (1×10^{-5} m/s).

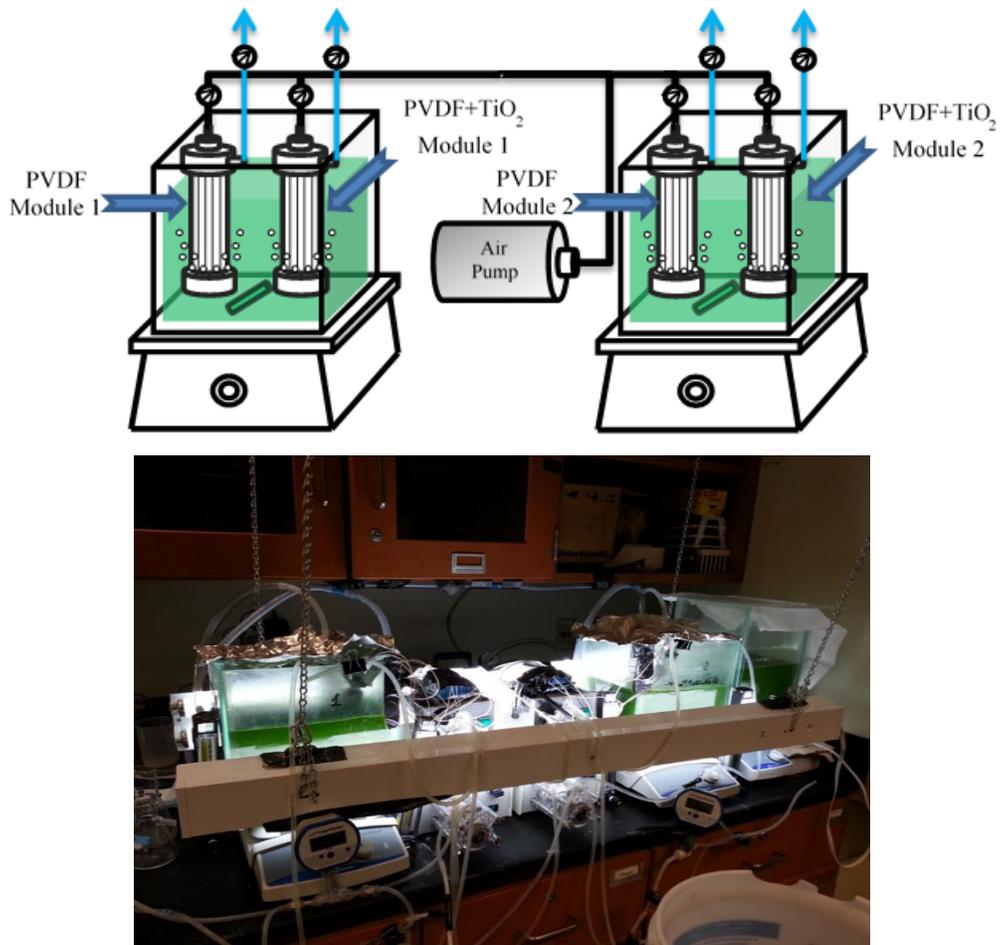


Figure 8. Experimental set-up of two parallel high-density algal MBR systems.

Table 9. Operating conditions of the high-density algae MBR systems.

Tank Volume	4 L
Temperature (°C)	20°C
pH	8-9
Hydraulic Retention Time (HRT)	0.5 day
Solids Retention Time (SRT)	25 day
Biomass wastage	166 ml/day
Feeding Water	Synthetic Wastewater

Each reactor was equipped with one PVDF hollow fiber membrane and one PVDF+TiO₂ hollow fiber membrane. Light was provided for algae growth by placing two 40W T12 fluorescent light bulbs in the front and back of the bioreactor, resulting in a light intensity of 121 $\mu\text{mol}/\text{m}^2/\text{s}$ at the surface of the mixed liquor. The bioreactors were well mixed through magnetic mixing at 600 rpm while intermittent air bubbling (on and off, cycling every 6 h) was provided by an air pump at 40 LPM.

2.4. Membrane resistance in series model

A number of theoretical methods have been developed to describe the membrane fouling phenomena, among which, the simplest and most commonly used one is called resistance in series model (Field et al. 1995). According to this model, a relationship between permeate flux (J), transmembrane pressure (TMP) and membrane resistance can be expressed in the following equation:

$$J = TMP / (\eta \times R_t) \quad (1)$$

Where TMP is the transmembrane pressure ($N\ s\ m^{-2}$), η is the viscosity of permeate ($N\ s\ m^{-2}$), and R_t is the total resistance (m^{-1}).

Resistance in series models also demonstrated the components contributing to membrane total resistance (R_t) as follows:

$$R_t = R_m + R_{re} + R_{irre} \quad (2)$$

where R_t is total resistance; R_m is intrinsic membrane resistance which can be estimated by measuring the water flux of de-ionized (DI) water; the reversible resistance R_{re} can be removed through membrane cleaning, and it is calculated by subtract R_f (value [can you say “resistance” as in you measure the resistance to get a value] before membrane cleaning) by R_c (value after membrane cleaning); irreversible fouling resistance R_{irre} cannot be recovered through a cleaning process, and it can be calculated by subtract R_c value (after membrane cleaning) by R_m .

Complete membrane cleaning was conducted by following the procedure below (Lim et al. 2003):

- (1) Water rinse - soak and wash each hollow fiber module tap water.
- (2) Alkali cleaning - soak modules in 0.05% sodium hypochlorite solution for 12 hours.
- (3) Acidic cleaning - wash modules using tap water, then soak modules in 1 M HNO₃ for 12 hours.

Following the acid wash, another tap water cleaning was applied in order to complete the cleaning process. To evaluate the efficiency of the cleaning process for membrane fouling control, permeance recovery (Rickman et al. 2012) was determined according to the following equation:

$$\text{Permeance Recovery} = \frac{(R_f) - (R_c)}{(R_f) - (R_m)} \quad (3)$$

Where R_m is intrinsic membrane resistance; R_f is total resistance of fouled membrane (before membrane cleaning); and R_c is total resistance of cleaned membrane (after membrane cleaning).

2.5. Biomass and Chemical Analysis

The biomass concentration and influent and effluent water quality parameters, such as ammonia-N, nitrate-N, nitrite-N, orthophosphate-P, and COD concentrations were determined following the standard methods (American Public Health Association 2005). The pH of mixed liquid was monitored once a week. Phosphorus concentration in water was determined by the Ascorbic Acid Method (Lenore S. Clescerl 1999).

NO₃⁻ concentration was determined by the Ultraviolet Spectrophotometric Screening Method (Lenore S. Clescerl 1999).

2.6. Scanning electron microscopy (SEM) imaging

At the completion of algae-MBR study, SEM images were taken for characterization of surface morphology structure of both PVDF and PVDF+TiO₂ hollow fiber membranes with and without

membrane cleaning. All images were taken using Hitachi S-4700 Field Emission Scanning Electron Microscope.

To study the compositions of these aggregates, energy dispersive X-ray spectroscopic (EDS) imaging was conducted at specific points on aggregates.

CHAPTER THREE

RESULTS AND DISCUSSION

3.1. High-density algae cultivation

The two identical MBRs were seeded with *Chlorella Vulgaris* at the initial algal biomass concentration of about 800 mg/L (in COD units). The biomass concentration gradually increased to 1500 mg/L after about 30 days of operation (Figure 13). With more careful biomass wastage control to reach a target SRT of 25 days, the biomass concentration continued to increase. Starting day 40, the algae biomass concentrations were maintained at 2300 ± 66 mg/L and 2328 ± 75 mg/L for the MBRs #1 and #2, respectively. With the target SRT of 25 days, it appeared that steady state conditions were reached after around 3 SRTs of operation which is consistent with previous results (Cicek et al. 2001).

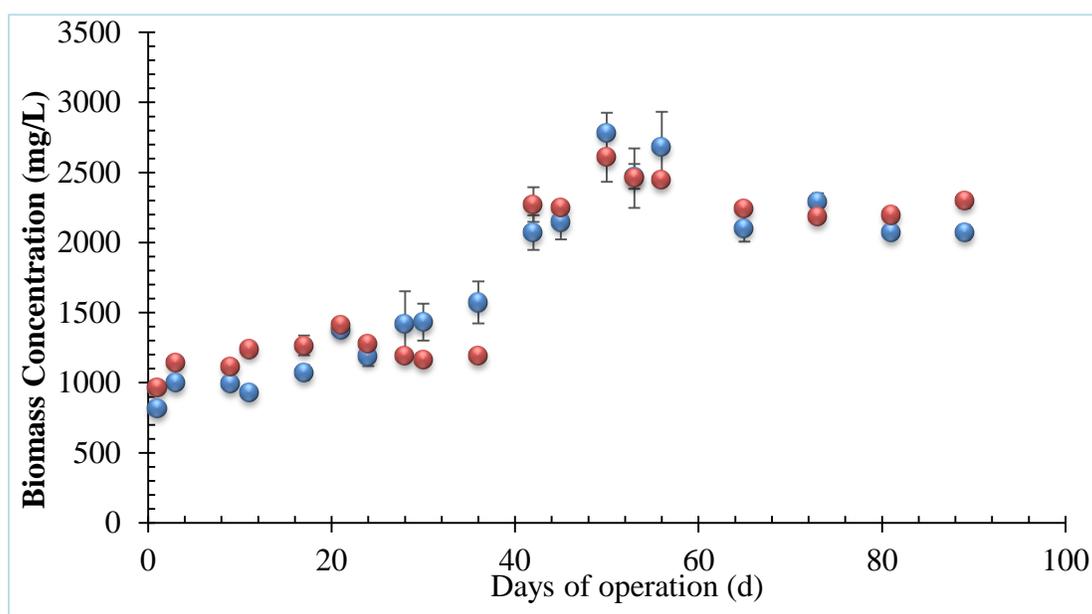


Figure 9 Biomass concentration monitoring for high-density algae cultivation in two identical bioreactors: MBR#1 (●), and MBR#2 (●).

3.2. Nitrogen and phosphorus removal by algae

The influent NO_3^- -N concentrations were controlled and varied from 4 to 11 mg/L.

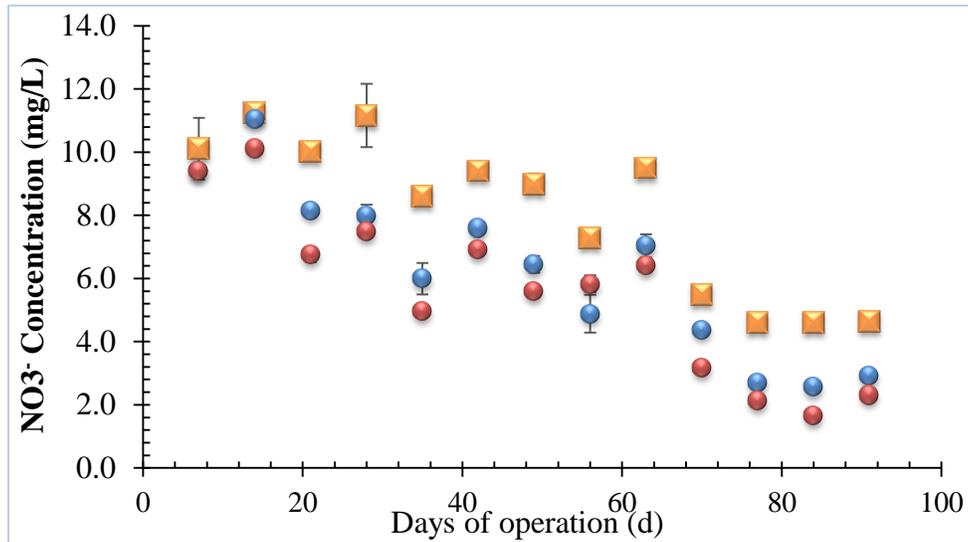


Figure 10. Influent (■) and effluent NO_3^- -N concentrations of the high-density algae cultivation systems: MBR#1 (●), and MBR#2 (●).

In general, the nitrogen removal efficiency by the algae was low, with the average efficiencies of 26 and 35% for MBR #1 and #2, respectively. Because of long SRT operation and since nitrogen removal was mainly through cell assimilation/wastage, it is not surprising the N removal was low. In contrast, the high-density algae MBR system resulted in higher P removal efficiencies, with the average efficiencies of 74 and 81 % for MBR #1 and #2, respectively. Influent phosphorus concentration ranging from 4 to 9 mg/L (Figure 15).

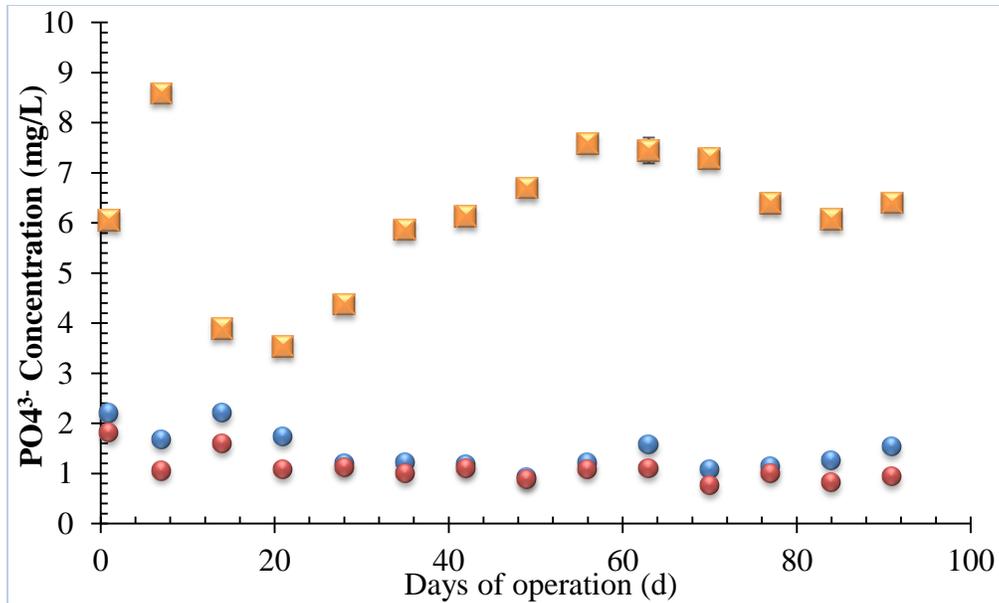


Figure 11. Influent (■) and effluent phosphorus concentrations of the high-density algae cultivation systems: MBR#1 (●), and MBR#2 (●).

3.3. Invasion of filamentous species during algae MBR operation

Open cultivation systems can be easily subjected to contamination by other species (Wu et al. 1981, Markou et al. 2011). Since the high-density algal MBR system was an open system, invasion of other microbial phototrophs could not be avoided. Light microscopy was employed to study the size and morphology of microbial phototrophs in the MBRs. While pure *Chlorella Vulgaris* is a spherical, unicellular algae species with cell size around 5 μm (Figure 11), it appeared that the system also contained filamentous species which had an average width around 5 μm, and length over 100 μm. However, unlike in activated sludge MBR systems where aggressive membrane fouling was related with filamentous bacteria growth (Meng et al. 2006, Kim et al. 2007) growth of this filamentous phototrophic species facilitated biomass aggregation and formed floc-like structure trapping *Chlorella Vulgaris* cells.

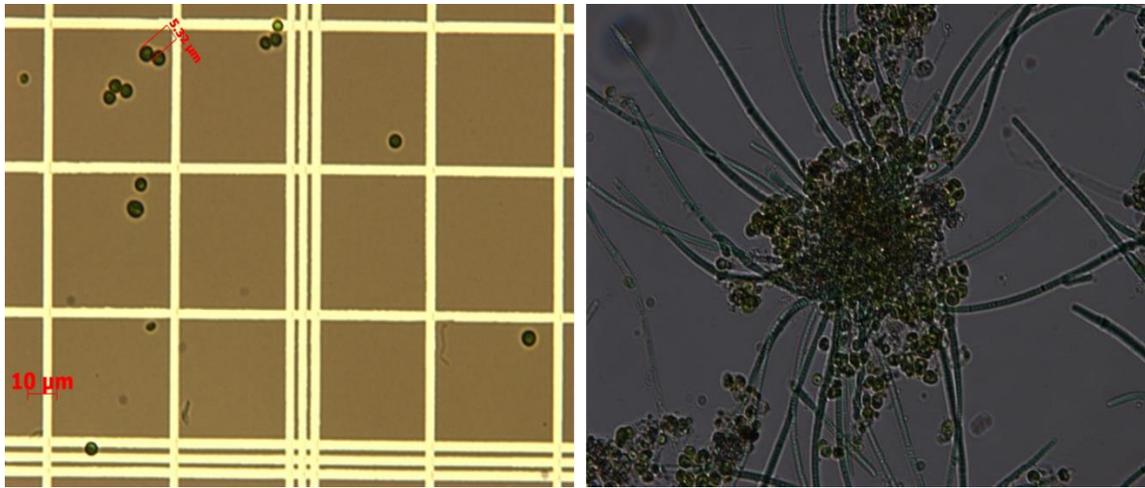


FIGURE 12. Microscopic Images of *Chlorella Vulgaris* before contamination (Left) and after contamination (right).

Formation of biomass floc could reduce the tendency for algae cells to deposit onto the membrane surface. Hence, invasion of filamentous species had no detectable negative effects on high-density algae cultivation.

On the contrary, the introduction of filamentous species enhanced biomass settling in the high-density algae MBR system. Figure 10 shows complete sedimentation of well-mixed biomass occurred within 2 min. Compared to a typical alga settling velocity ranges from 0.1 cm/h to 2.6 cm/h (S.K. Choi 2006), the settling velocity of the algal biomass in the MBRs was estimated to be 363 cm/h.

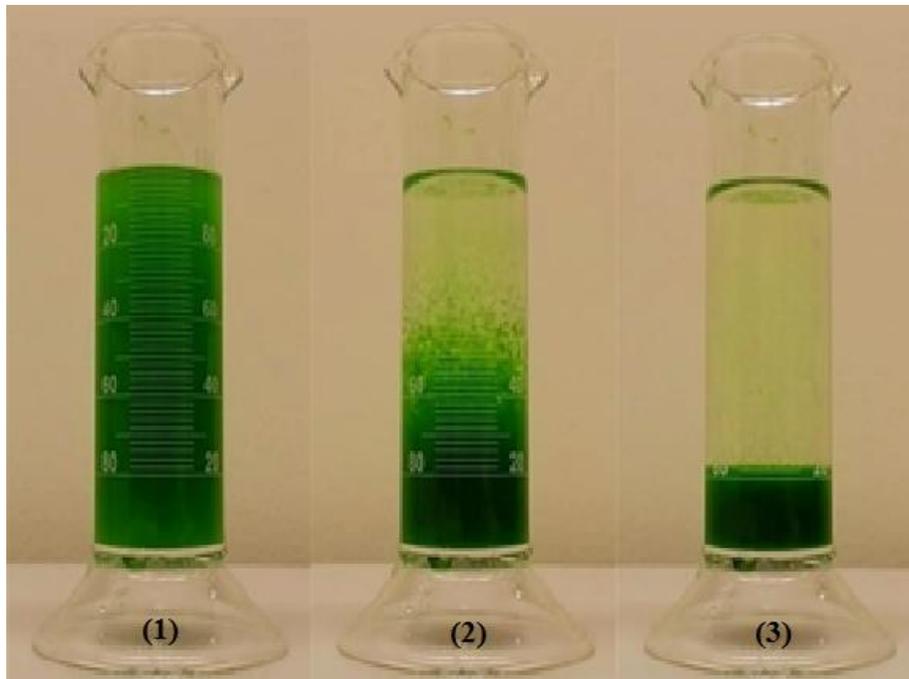


Figure 13. Settling of contaminated algae mix, (1) algae suspension right after string, (2) at 1 min settling, (3) at 1 min 40 s settling.

To monitor the change in algal floc size, algal biomass samples were taken and tested by ZEN3600 Zetasizer NanoZS each month during the research period. Figure 12 shows that the algal floc size increased by a factor of two (4357 nm to 9758 nm) from May to June, and then kept increasing by factors of 1.4 and 1.6 for June and July, respectively. The increase in floc size could explain the excellent settling property of algae biomass, as similar phenomena was reported in the growth of *Phormidium bohneri* (filamentous cyanobacteria) (Talbot et al. 1993).

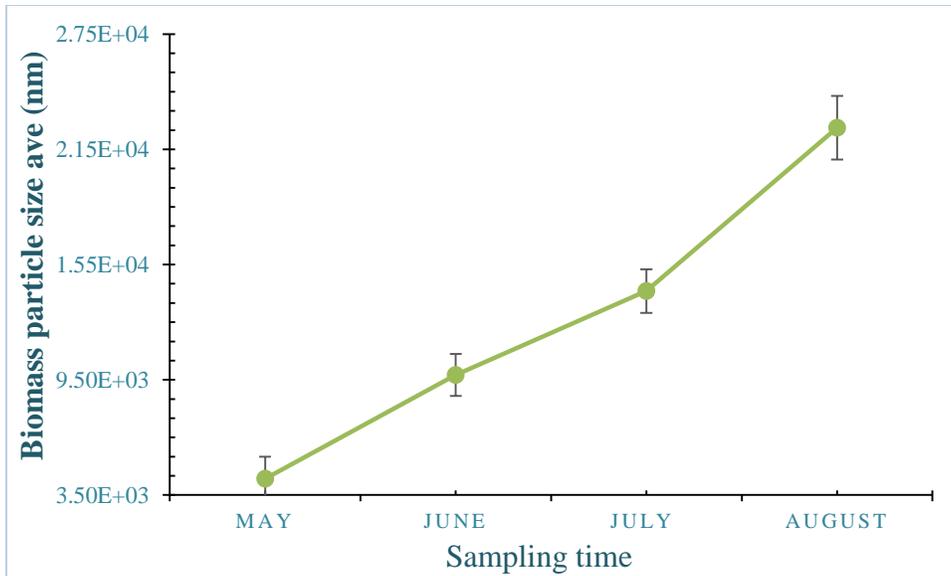


Figure 14. Change in algae floc size during the study period.

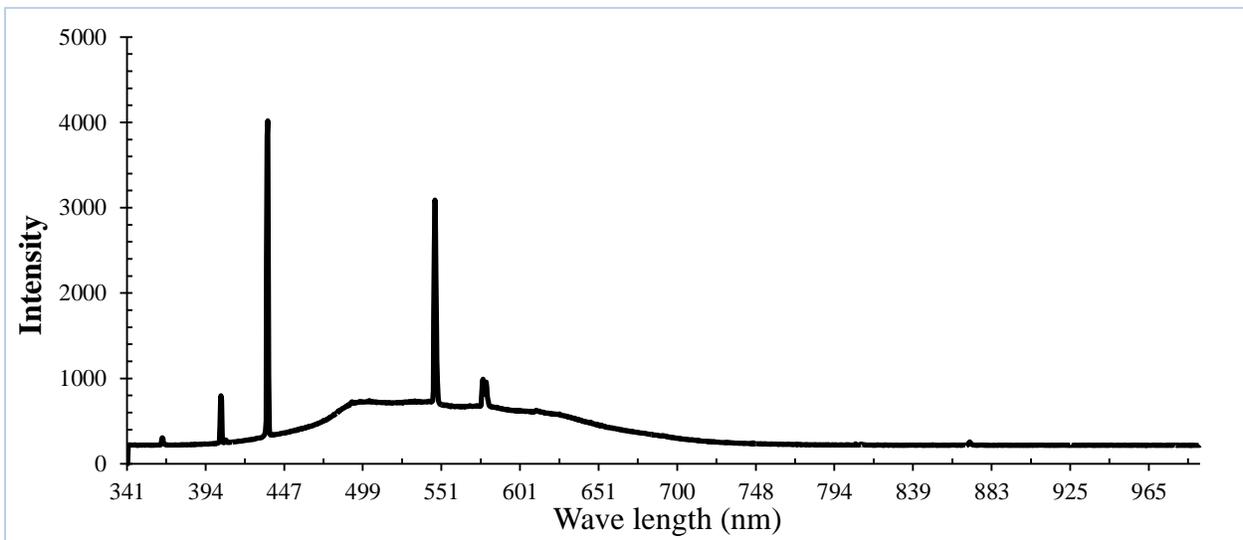


Figure 15 Fluorescence light source spectrum for algae cultivation tested by Ocean Optics PC2000 PC plug-in Spectrometer.

3.4. Membrane fouling monitoring and resistance change before and after cleaning

Figure 15 shows that PVDF hollow fiber membranes (Orange curve) had constantly higher total membrane resistance than PVDF hollow fiber membranes impregnated with TiO₂ (Blue curve). And the total resistance difference between PVDF and PVDF+TiO₂ membranes varied between 65% and 42%.

The total resistance of both PVDF and PVDF+TiO₂ membranes experienced a rapid increase during the early stage (day 1 to day 20) of operation, which was consistent with previous reported results (Babel et al. 2010, Cosenza et al. 2013, Zhang et al. 2013). The membrane resistance started to drop from day 20 and remained relatively stable thereafter. The decrease of membrane resistance could be attributed to the formation of algae biomass floc as a result of the invasion of filamentous species.

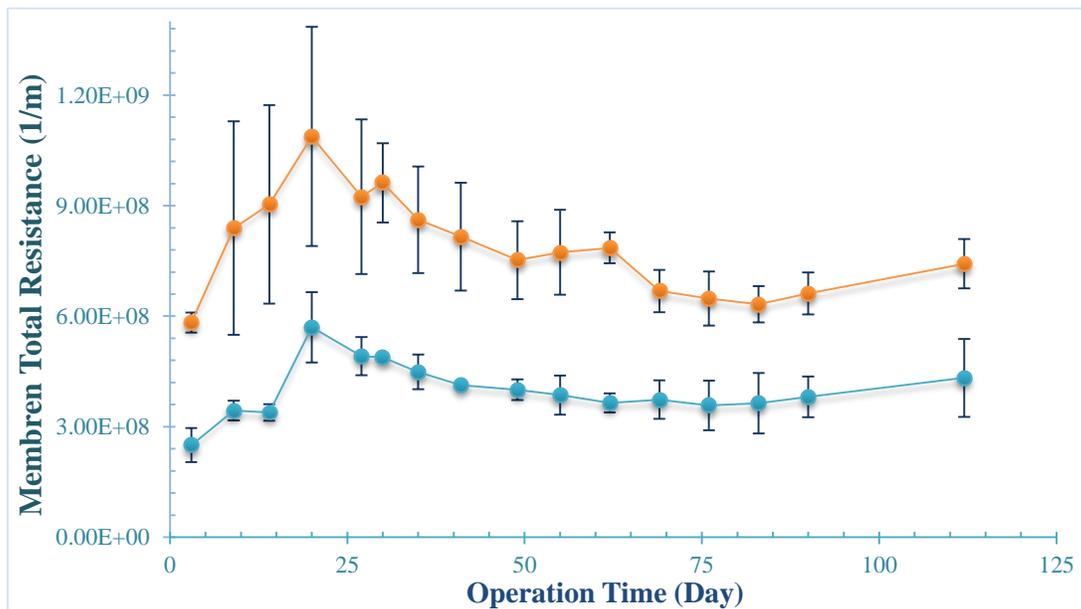


Figure 16. The change in total membrane resistance during the study period between the two types of membranes, PVDF (●) and PVDF+TiO₂ membranes (●).

After 112 days of operation, one of PVDF and PVDF+TiO₂ hollow fiber membranes were taken out of the MBRs for cleaning. The total membrane resistances (TMR) were monitored before and after this cleaning process (Table 10).

Table 10. Recovery of membrane total resistance after membrane cleaning.

Module	R_m (1/m)	MTR Before cleaning R_f (1/m)	MTR After Cleaning R_c (1/m)	Recovered Resistance (1/m)	Recovery Rate
PVDF 1	5.6 E+08	7.9 E+08	6.6 E+08	1.3 E+08	17%
PVDF+TiO ₂ 1	2.8 E+08	5.1 E+08	4.3 E+08	0.8 E+08	14%

As we can see from Table 10, the complete cleaning process applied on both membrane modules recovered 1.3 E+08 (1/m) TMR for the pure PVDF membrane, which was 17% of the TMR before cleaning; and 0.8 E+08 (1/m) TMR for the PVDF+TiO₂ membrane, which was 14% of the TMR before cleaning.

Only less than 20% of membrane total resistance was recovered for both PVDF and PVDF+TiO₂ membranes after cleaning. This was because both types of membranes were not severely fouled even after 110 days of operation, indicating that the manufactured ultrafiltration membranes (with a average pore size of 20 nm) were reliable for long-term operation.

Table 11. Reversible and irreversible resistance calculation after cleaning.

Module	R_m (1/m)	R_{rev} (1/m)	R_{irrev} (1/m)
PVDF 1	5.6 E+08	1.3 E+08	9 E+07
PVDF+TiO ₂ 1	2.8 E+08	7 E+07	1.5 E+08

Reversible membrane resistance (R_{rev}) and irreversible membrane resistance (R_{irrev}) for both PVDF and PVDF+TiO₂ were calculated after the complete cleaning process. As we can see from Table 12, R_{rev} for PVDF 1 module was 1.3 E+08 (1/m) and R_{irrev} was 9 E+07 (1/m), and for PVDF+TiO₂

1, R_{rev} was $7 \text{ E}+07$ (1/m) and R_{irrev} was $1.5 \text{ E}+08$ (1/m) which indicated that fouling on PVDF membrane was more recoverable through applied cleaning process than PVDF+TiO₂ membrane.

As shown in Table 12, permeance recovery rates for PVDF and PVDF+TiO₂ modules were 56% and 35%, respectively.

Table 12. Permeance recovery calculation after cleaning.

Module	R_m (1/m)	R_f (1/m)	R_c (1/m)	Permeance Recovery
PVDF 1	$5.6 \text{ E}+08$	$7.9 \text{ E}+08$	$6.6 \text{ E}+08$	56%
PVDF+TiO ₂ 1	$2.8 \text{ E}+08$	$5.1 \text{ E}+08$	$4.3 \text{ E}+08$	35%

3.5. Hollow Fiber Membrane Characterization by SEM and EDS Analysis.

SEM images were taken to study the morphological structure of both PVDF and PVDF+TiO₂ hollow fiber membranes. Figure 16 demonstrates that both clean PVDF (Figure 16 a, c) and clean PVDF+TiO₂ (Figure 16 b, d) appeared to have very smooth and uniform membrane surface, and that there is no significant difference in the surface morphological structure between two types of membranes.

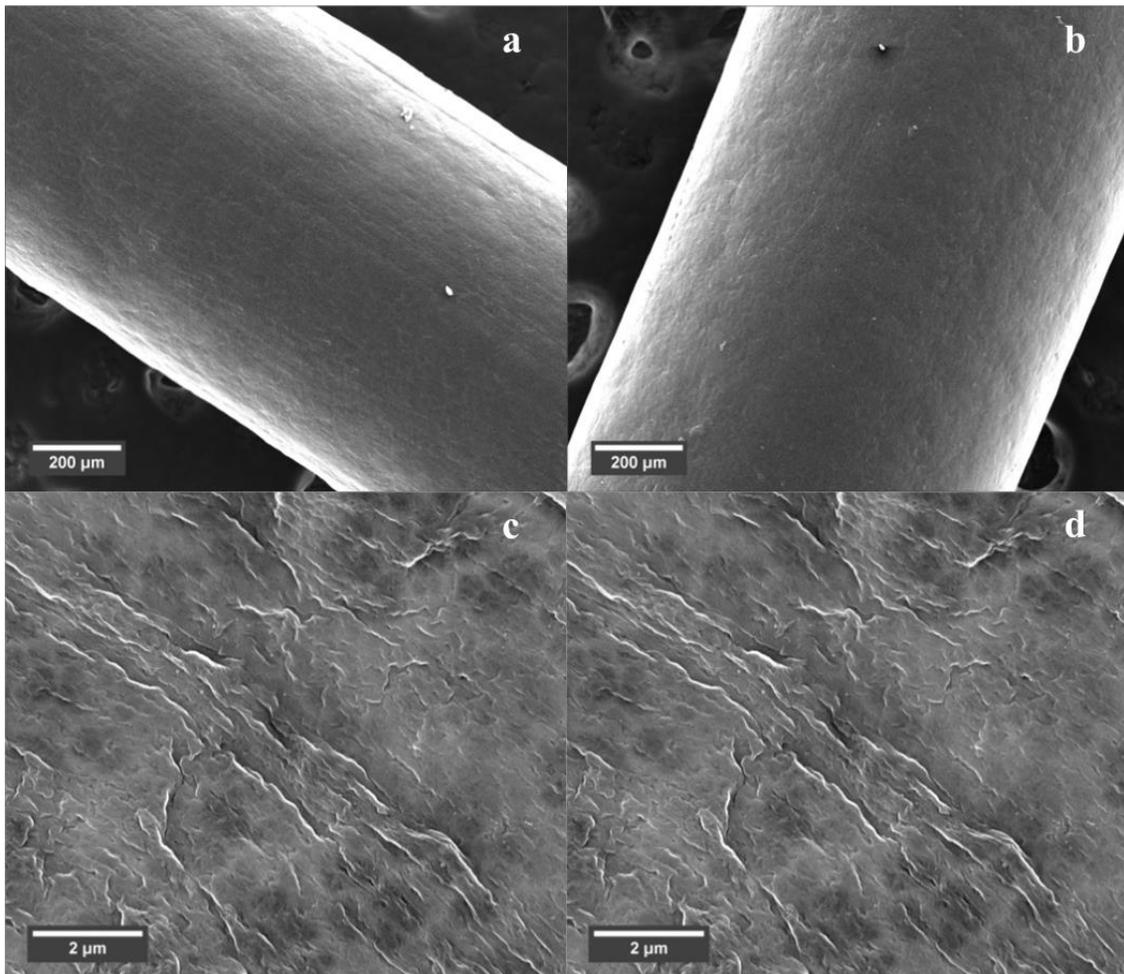


Figure 17. SEM images of the surfaces of (a), (c) clean PVDF hollow fiber membranes; (b), (d) clean PVDF+TiO₂ membranes.

Figure 17 shows the SEM images taken for both PVDF (a, c) and PVDF+TiO₂ (b, d) hollow fiber membranes after 110 days of operation in the algae MBRs. The images clearly show that bio-debris consisted of both filamentous species cells and *chlorella vulgaris* cells attached on the membrane surfaces.

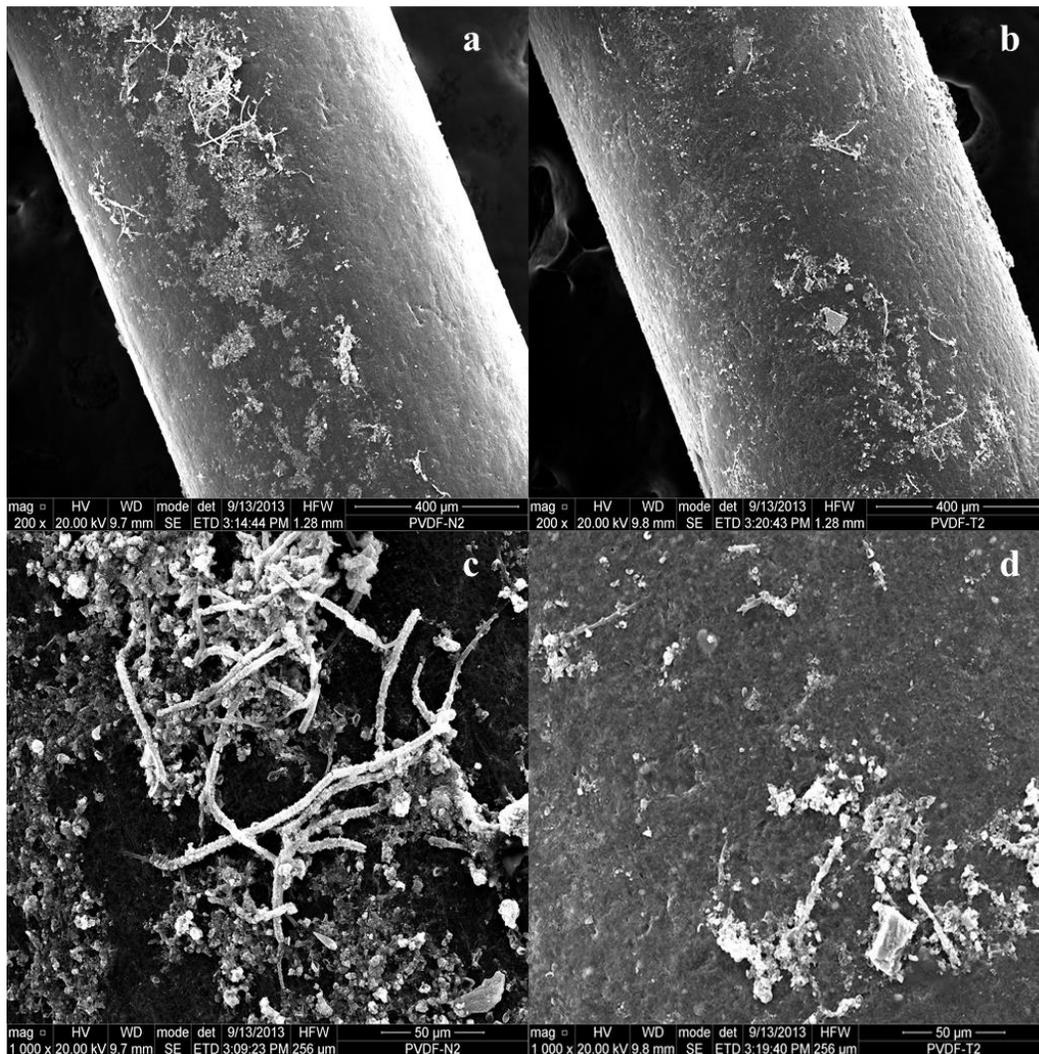


Figure 18. SEM images of the surfaces of (a), (c) fouled PVDF hollow fiber membranes; (b), (d) fouled PVDF+ TiO₂ membranes after 112 days of operation.

SEM images were also taken from modules after complete cleaning. As Figure 18 (a, b) shows, the surfaces of both membranes became rough after long-term operation and cleaning processes. This became more obvious under higher resolution (mag 75000) as shown in Figure 18 (c, d). Aggregates on membrane surface were highlighted in Figure 18 (c, d).

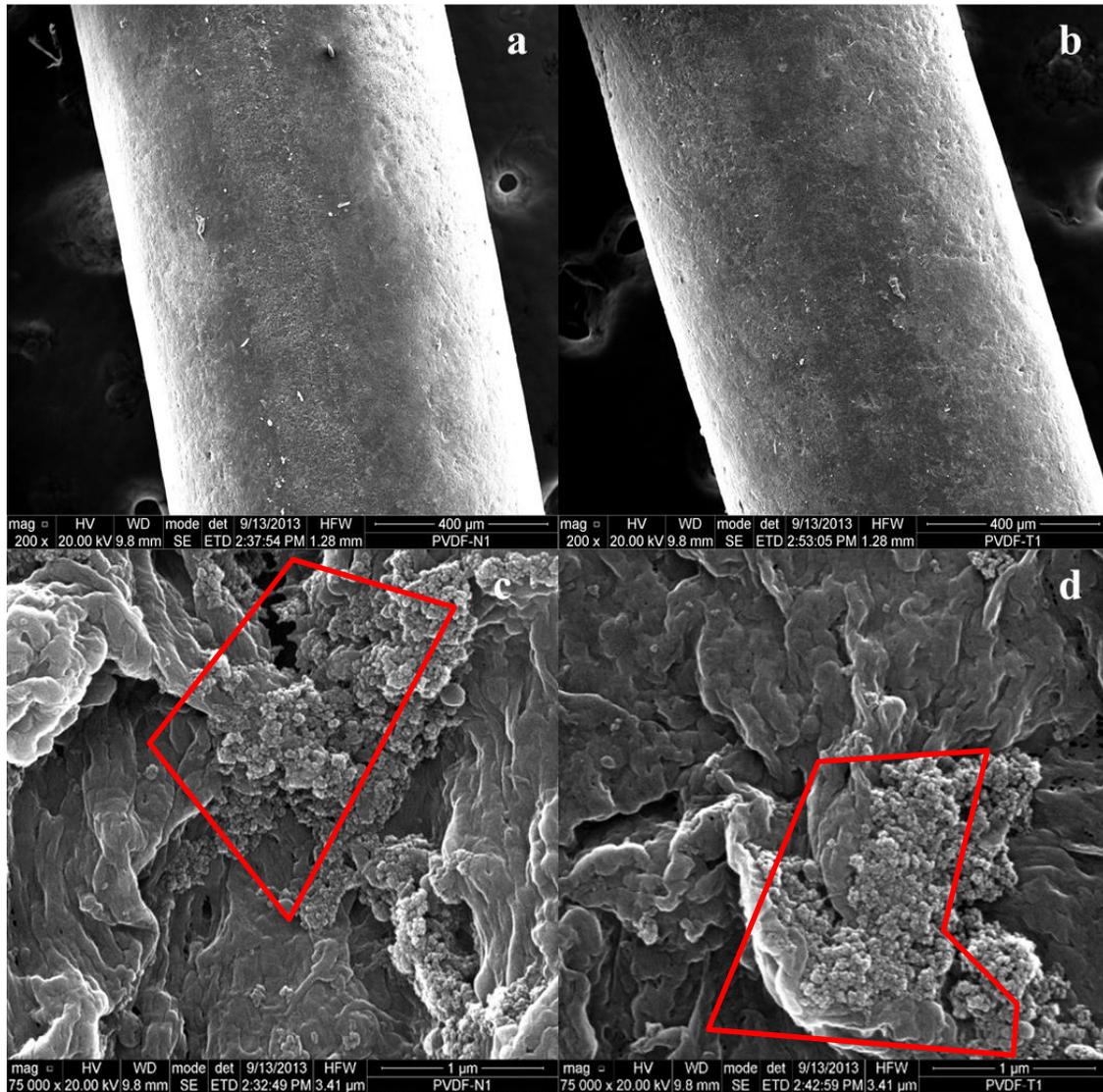


Figure 19. SEM images of the surfaces of (a), (c) cleaned PVDF hollow fiber membranes; (b), (d) cleaned PVDF+TiO₂ membranes after complete cleaning.

EDS Analysis of the membranes (Figure 19) showed the existence of a variety of elements that could be responsible for the formation of these aggregates including phosphorus, calcium, and iron, which indicates that the nature of these aggregates on membrane surface could be chemical precipitations that were not removed even through complete cleaning process. This result is consistent with previous findings. For example, You (You et al. 2006) also reported that inorganic fouling was not easily recovered even after chemical cleaning. Shirazi (Shirazi et al. 2010) found that a number of cations and anions usually present in MBR systems, such as Ca^{2+} , Mg^{2+} , Al^{3+} , Fe^{3+} , CO_3^{2-} , PO_4^{3-} and OH^- , and high concentrations of these inorganic salts are mainly responsible for inorganic fouling.

CHAPTER FOUR

DISCUSSION

Studies on microalgae for wastewater treatment have been numerous? in recent years. However, a major disadvantage of algal wastewater treatment is the difficulty of biomass separation and harvesting (Huntley 1989). Membrane separation can be an ideal solution because it offers perfect solid-liquid separation, requires less space, and it is becoming more economically competitive (Uduman et al. 2010). High-density algae MBR systems were successfully demonstrated in this research for synthetic wastewater polishing, nutrients removal and algae biomass production.

The invasion of filamentous species during operation did not bring any negative impacts on nutrient removal and algal growth. In fact, the presence of filamentous species assisted the self-aggregation of biomass resulting in improved biomass settling properties. Hashimoto (Hashimoto et al. 1989) also found a high nutrient removal rate and easy harvestability of *Oscillatoria* when it was cultivated on activated sludge effluent. This finding shows the potential of culturing mixed phototrophic species including filamentous species to achieve excellent nutrient removal and good settling property simultaneously.

Membrane modification resulted in better antifouling property (Liu et al. 2011). In this research, we chose TiO₂ nanoparticles because they have photo-catalytic property, through which organic foulants on membrane surface could be degraded and removed. Furthermore, the hydrophilicity of PVDF membrane can be increased by entrapping TiO₂ particles inside due to the higher affinity of metal oxide to water (Bae et al. 2005). As a result, the PVDF membrane embedded with TiO₂

nanoparticles resulted in a significant decrease (42-65%) of membrane total resistance, which could greatly reduce operating cost in large-scale operations.

CHAPTER FIVE

CONCLUSION

PVDF and PVDF+TiO₂ (5%) hollow fiber membrane modules were developed and evaluated for high-density algae cultivation. Both PVDF and PVDF+TiO₂ modules experienced rapid fouling development in the first 20 days of operation. Then the fouling trend gradually decreased and remained relatively constant after day 50. The total resistance of TiO₂-embedded PVDF membrane was 42-65% lower than that of the control (without TiO₂). SEM imaging and EDS analysis indicated that a complete cleaning process could remove most biological foulants on the membrane surface (contributing to reversible resistance), but was unable to remove some chemical residues on membrane surfaces (contributing to irreversible resistance).

At the target SRT of 25 days, the high-density algae MBR systems reached a steady-state biomass concentration of about 2300 mg/L COD while removing nutrients from wastewater. The average P and N removal efficiencies were 78% and 34%, respectively. The introduction of filamentous species had no negative impact on nutrient removal and algae cultivation. On the contrary, it helped improve the settling property of biomass resulting the formation of large flocs.

FUTURE RESEARCH

Filamentous species that contaminated both high-density algae MBR systems had no negative impact on MBR system performance. On the contrary, the growth of filamentous species improved biomass settling. This phenomenon brought up a lot of questions that remain to be answered. For example, firstly, the species of this invading species, whether it was cyanobacteria or algae, was not determined, but polymerase chain reaction (PCR)-based work and sequencing in the future would help to identify the species. Secondly, even though the filamentous species and *Chlorella Vulgaris* seemed to have a symbiotic relationship with each other, the interactions between these two species was not studied in detail in this research. Questions as to “Which one was the dominant species in the end?”, “Will this symbiotic relationship last long?”, and “Can this symbolic relationship be explored for large-scale applications?” still remain to be answered.

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