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The Effect of Influent Nutrient Conditions and Biofiltration Pretreatment on Membrane Biofouling

Hyeongki Lee
University of Colorado at Boulder, hyunggi.lee@gmail.com

THE EFFECT OF INFLUENT NUTRIENT CONDITIONS AND BIOFILTRATION PRETREATMENT ON MEMBRANE BIOFOULING

by

HYEONGKI LEE

B.A., Honam University, South Korea, l998

M.S., Yonsei University, South Korea, 2000

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R. Scott Summers

Karl Linden

Mark Hernandez

Date_____

The final copy of this thesis has been examined by the signatories, and we find that both the content and the form meet acceptable presentation standards of scholarly work in the above mentioned discipline.

ABSTRACT

Lee, Hyeongki (M.S., Civil Engineering)

The Effect of Influent Nutrient Conditions and Biofiltration Pretreatment on Membrane Biofouling

Thesis directed by R. Scott Summers, Professor, Department of Civil, Environmental and Architectural Engineering, University of Colorado at Boulder

Membrane fouling, loss of flux or flow rate during a run, is still a major issue for membrane processes. Biofouling is often called the "Achilles heel" because it has been known to be responsible for about half of membrane fouling. Biofouling is thought to be caused mainly by extracellular polymeric substances (EPS), which are produced by the biomass and affected by nutrient conditions. In a few cases, biofilters have been considered as a method to reduce membrane biofouling. The efficiency of biofilters, however, can be affected by metabolic conditions and nutrient conditions. However, the relationships between membrane biofouling, the metabolic and nutrient conditions, and the use of biofiltration pretreatment, are not established. The main goals of this study were to understand the metabolic and nutrient conditions that impact membrane biofouling and evaluate biofiltration pretreatment as a means of controlling membrane biofouling.

Biomass developed under either autotrophic or heterotrophic conditions was quantified with adenosine triphosphate (ATP), and used to assess the effect of the metabolic conditions directly on the biofouling of UF membranes with a MWCO of 10,000 Daltons. In addition, biofilters developed under either autotrophic or

heterotrophic conditions were used to evaluate the effect of pretreatment on membrane biofouling. Both metabolic conditions showed similar flux decline behavior, yielding a 55% flux decline in 72 hours when pretreatment was not used. Biofiltration pretreatment improved the membrane flux by approximately 50% under both metabolic conditions, yielding a flux loss of only 27% in the same period. The impact of C:N:P nutrient ratios of feed water on membrane biofouling was also studied. Five different nutrient ratios were used for this study: balanced condition (100:10:1), N rich condition (100:25:1), N limited condition (100:0:1), P rich condition (100:10:5), and P limited condition (100:10:0). Without pretreatment, the balanced condition yielded the most flux decline. With pretreatment, the balanced condition yielded the least flux decline. In every condition, biofiltration pretreatment did not cause additional flux decline or significantly reduced flux decline.

Relationships between ATP, EPS, and flux decline were developed. Without pretreatment, ATP was strongly correlated ($R^2 = 0.76$) with flux decline because microorganisms grew on membranes. With pretreatment, EPS had a better relationship ($R^2 = 0.51$) with flux decline than ATP because biofilters removed substrates. ATP and EPS were inversely related without pretreatment ($R^2 = 0.61$).

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CHAPTER 1

INTRODUCTION

1.1 Problem Statement

Membrane processes have been increasingly applied in water treatment because of their ability to remove many contaminants with little chemical addition (Mosqueda-Jimenez and Huck, 2006). In spite of the research efforts and advances in membrane technology, the loss of flux or flow rate during a run, termed membrane fouling, is still one of the major factors that limit membrane process utilization. Membrane fouling includes deposition/sorption, precipitation of inorganic and organic compounds (scaling) and particulate/colloidal matter, and biofouling. Biofouling, among them, is often called the "Achilles heel" of the membrane process because microorganisms can multiply over time and the biofouling can dominate about half of membrane fouling (Guo et al., 2012). It has been reported that membrane biofouling is caused mainly by extracellular polymeric substances (EPS) that microorganisms excrete. The concentration of the microorganisms, quantified with adenosine triphosphate (ATP) concentration, and the composition and concentration of EPS are affected by nutrient conditions of influent water (Fonseca et al., 2007; Peldszus et al., 2011; Vrouwenvelder et al., 2010; Feng et al., 2012). In a few cases, biofiltration pretreatment has been considered as a method to reduce membrane biofouling (Solomon et al, 1993; Mosqeuda-Jimenez and Huck, 2009; Merkel et al., 1998; Septh et al., 2003; Sun et al., 2011). A biofilter's performance for controlling membrane biofouling can be affected by nutrient conditions (carbon:nitrogen:phosphorus ratios) of influent water and metabolic conditions (autotrophic or heterotrophic conditions) of biofilter media. However, little is known as to the characteristics of membrane biofouling under

metabolic and nutrient conditions, and with the use of a biofilter before the membranes.

1.2 Research Objectives

The overall objectives of this research were to understand the metabolic and nutrient conditions that impact membrane biofouling and evaluate biofiltration pretreatment as a means of controlling membrane biofouling.

To accomplish the objectives, the effect of autotrophic and heterotrophic conditions on membrane biofouling was first evaluated without and with biofilter pretreatment. Next, the effect of nutrient conditions, with different C:N:P ratios, on membrane biofouling was assessed without and with biofilter pretreatment.

1.3 Thesis Approach

This thesis is comprised of five chapters. Chapter 2 describes the background and general literature review of membranes, membrane fouling, and biological filtration. Chapter 3 includes materials and analytical methods. In this chapter, feed water, nutrient source, biomass media, biofilter, and UF membrane are described. In addition, the analytical methods and experimental plan are described. In Chapter 4, the results of preliminary experiments, to choose the best experimental conditions such as feed water type, proper organic carbon concentration in the feed water and to assess the reproducibility of experiments, are reported. Second, the impact of biomass, developed under either autotrophic or heterotrophic conditions, on membrane biofouling is reported. Third, the results using heterotrophic biomass media at different C:N:P nutrient ratios are reported as well as the regression analysis between ATP, EPS, and flux decline. Chapter 5 summarizes the most important results of this thesis.

CHAPTER 2

BACKGROUND AND LITERATURE REVIEW

2.1 Background of Membrane

2.1.1 General Description of Membrane Processes

Membrane processes have been increasingly used in the field of drinking water treatment because many contaminants can be removed without the addition of chemicals (Mosqueda-Jimenez and Huck, 2006). Figure 2-1 shows a membrane process consisting of feed stream, semipermeable membrane, retentate stream, and permeate stream. The pressure difference between the feed and permeate is used to transport the feed water through the membrane (Bruggen et al, 2003).

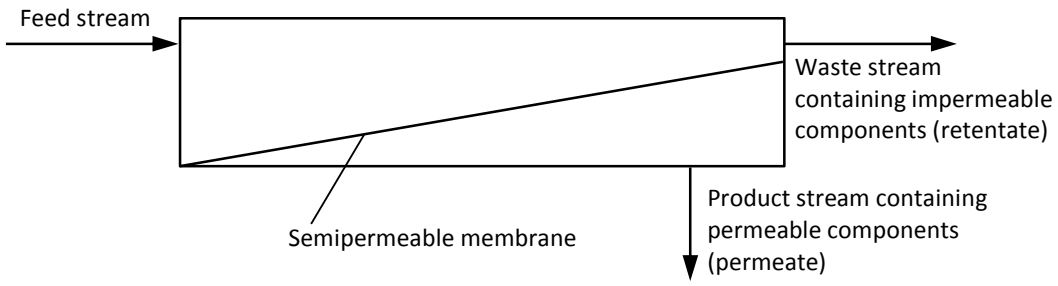


Figure 2-1 Membrane separation process (MWH, 2005)

(1) Membrane types

There are four general types of pressure-driven membranes currently used in municipal water treatment: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse-osmosis (RO) membranes. These membranes can be classified depending on pressure: MF and UF as low pressure membranes (LPM), and NF and RO as high pressure membranes. Removal capacities and characteristics of all these processes are summarized in Figure 2-2 and Table 2-1.

The size of material retained is one of the most important parameters in the membrane process. The retention rating is often called the pore size value, which is a nominal rating. Because some particles larger than the retention rating can penetrate the membrane, a molecular weight cutoff (MWCO) or nominal molecular weight limit (NMWL), which is the molecular weight of material retained by the membrane, is generally used for UF membranes.

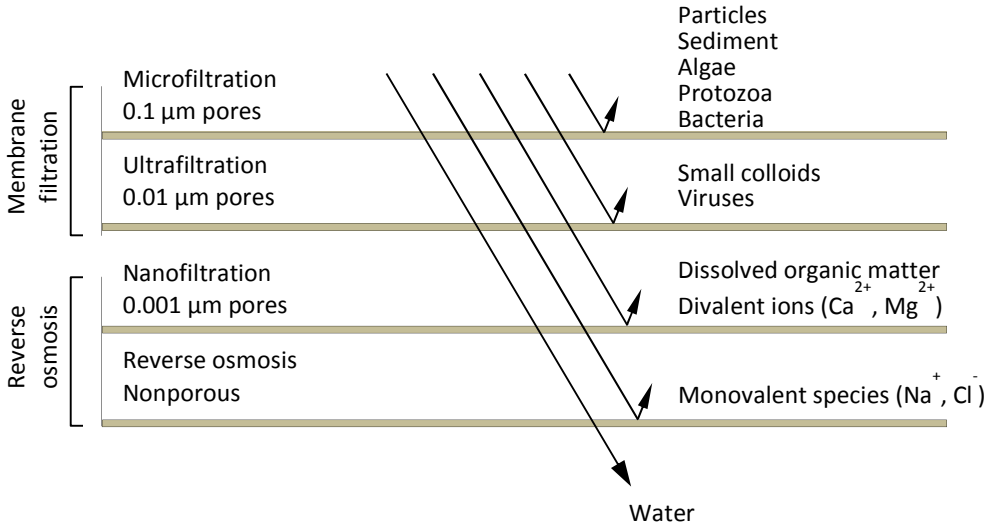


Figure 2-2 Removal capacities for each membrane category (MWH, 2005)

Table 2-1 Overview of pressure-driven membrane processes (Bruggen et al, 2003)

Category	Microfiltration	Ultrafiltration	Nanofiltration	Reverse Osmosis
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 (µm)	0.1 ~ 10	0.002 ~ 0.1	0.0005 ~ 0.002	< 0.0005
Separation mechanism	Sieving	Sieving	Sieving Charge effects	Solution-Diffusion
Applications	Clarification, pretreatment, removal of bacteria	Removal of macromolecules, bacteria, viruses	Removal of ions and relatively small organics	Ultrapure water, desalination

MF membranes have the largest pores (0.1 μm to 10 μm) of all membranes and the highest permeability at a low pressure. Compounds are removed by a sieving mechanism. MF is an efficient process to remove particles that may cause problems in further treatment steps, but viruses are not removed because of the relatively large pore size.

UF membranes have smaller pores (0.002 to 0.1 μm), so higher pressures than MF are needed to overcome the resistance caused by the membrane. A typical application for UF is to remove large dissolved molecules that constitute the largest molecules of natural organic matter (NOM) and viruses.

The pore sizes of NF membranes are smaller than UF, typically around 0.001 μm, which corresponds to dissolved compounds with a molecular weight of about 300. Ioan et al. (2000) suggested the following empirical equation for dextran:

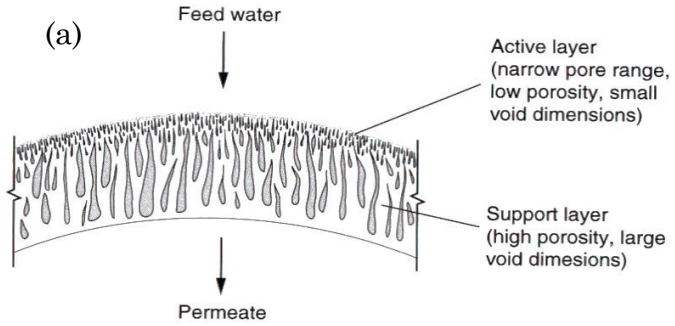
$$d_H = 0.11(MW)^{0.46} \quad (2.1)$$

Here, d_H = hydrodynamic diameter of dextran molecule (nm), MW = molecular weight (g/mole). NF is suitable for the removal of relatively small organic compounds. In addition, NF membranes have a surface charge. The surface charge is created by ionizable groups, e.g., carboxylic or sulfonic acid groups, in the presence of a feed solution. RO membranes are dense membranes and usually cannot be defined by pore sizes; therefore, the separation mechanism is not sieving, but solution-diffusion. RO membranes require high pressures because of low permeability, causing relatively high energy consumption.

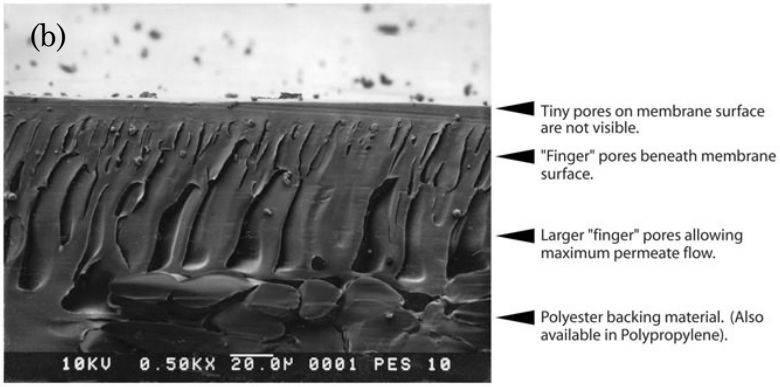
(2) Membrane structure

Most MF membranes have constant structure, porosity, and transport properties throughout their depth; in other words, they are homogeneous. Theoretically, MF membranes perform identically regardless of filtration direction.

In contrast, UF membranes have an asymmetric structure, which means that the morphology varies significantly across the depth of the membrane. Figure 2-3 shows the structure of an asymmetric UF membrane, consisting of an active layer and a support layer. The active and support layers have separate functions. The active layer functions as a filter in asymmetric membranes, but the thin active layer has no mechanical durability. To support the active layer, there is a highly porous and low hydraulically resistant layer which makes up the majority of the membrane thickness. Filtration in the "wrong" direction would cause clogging in the support layer of the membrane. Some commercial asymmetric membranes have active layers on both surfaces of the membrane to prevent the clogging (MWH, 2005).



(source: MWH, 2005)



(source : http://www.synderfiltration.com/)

Figure 2-3 Structure of an asymmetric UF membrane (a) general configuration of an asymmetric UF membrane (b) electron microscope image of PES10 membrane cross section

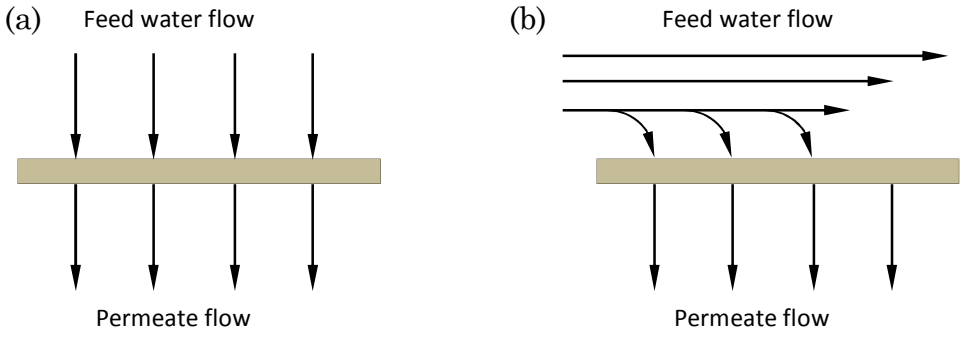
(3) Membrane materials and configuration

The most common membrane materials used in water industry are polypropylene (PP), polyvinylidene fluoride (PVDF), polysulfone (PS), polyethersulfone (PES), and cellulose acetate (CA) (MWH, 2005). Ceramic materials have recently been used in MF and UF because of superior chemical, thermal, and mechanical stability (Bruggen et al., 2003).

The typical configuration of LPM such as MF and UF is hollow fiber or tubular membrane. Both configurations allow back flushing of the membrane; therefore, the hydraulically reversible fouling of the membrane can be controlled. Packing density is higher in hollow fiber membranes than tubular membranes. The most common configuration of high pressure membrane such as NF and RO is a spiral-wound membrane having a high packing density. Unlike hollow fiber or tubular membrane, the membrane cannot be back flushed and foulant material can be removed only through chemical cleaning (MWH, 2005).

(4) Filtration modes

There are two common filtration modes: cross flow and dead-end filtration. A dead-end filtration mode is commonly used for hollow fiber and tubular membranes (e.g., MF and UF) while a cross-flow filtration mode is used for spiral wound membranes (e.g., NF and RO). Figure 2-4 shows filtration modes in membranes. In dead-end filtration mode, the feed water flows into the membrane perpendicularly, leading to the solids accumulation at the surface of the membrane. These foulants can be removed only by backwash. In cross-flow filtration mode, the feed water flows parallel to the membrane surface. Thus, this filtration mode requires higher fluxes but can be operated for longer period (MWH, 2005).



(Source: MWH, 2005)

Figure 2-4 Filtration modes in membranes: (a) dead-end filtration (b) cross-flow filtration

(5) Filtration mechanisms (Dreszer et al., 2013)

The flux J of water flowing through a membrane is expressed with the volume of effluent water V $[L]$ through a membrane with area A $[m^2]$ in time [h].

$$J = \frac{V}{A \cdot t}[L\, m^{-2}\, h^{-1}] \tag{2.2}$$

The permeability K of the membrane is defined as

$$K = \frac{J}{TMP}[L\, m^{-2}\, h^{-1}\, bar^{-1}] \tag{2.3}$$

TMP (transmembrane pressure) is the average pressure difference between the feed and permeate, and can be calculated using the following equation.

$$TMP = \frac{P_{inlet} + P_{outlet}}{2} - P_{permeate}[bar] \tag{2.4}$$

Flux and permeability vary with temperature change which affects the viscosity of water. The basic model for determining filtration resistance is expressed as the following equation using Darcy's law.

$$J = \frac{TMP}{\mu \cdot R_t}[m^{-1}] \quad (2.5)$$

where μ = dynamic viscosity of water at a given temperature, kg/m·s

R_t = total resistance of membrane filtration

Shirazi et al. (2010) reviewed a resistance-in-series model to evaluate the characteristics of membrane fouling. Total resistance of membrane filtration is as follows:

$$R_t = R_m + R_C + R_f \quad (2.6)$$

where,

R_m : intrinsic membrane resistance caused by membrane and permanent resistance.

R_C : cake resistance formed by cake layer deposited over membrane surface.

R_f : fouling resistance caused by pore plugging and/or solute adsorption onto the membrane pore and surface.

2.1.2 Ultrafiltration Membrane Applications

UF has been accepted as a promising process in drinking water treatment "because of its compactness, easy automation, and high removal rate of turbidity, organic matters (such as humic substances), *Giardia* and also viruses". UF can prevent people from waterborne diseases by removing bacteria and viruses. UF continues being applied to meet more strict drinking water regulations. In addition, as the cost of the ultrafiltration membrane is decreasing, UF technology is gradually becoming more accepted by the developing countries, compared to MF (Gao et al., 2011).

2.2 Membrane Fouling

Membrane fouling is one of the critical issues because it limits membrane utilization in drinking water production. Mosqueda-Jimenez et al. (2006) noted that "fouling is known as the deposition and/or accumulation of materials that reduce membrane permeability". Membrane fouling reduces permeate flux under a constant pressure, while the fouling requires the increase of pressure to obtain a constant flux. Therefore, fouling can cause the increase of chemical consumption and capital costs of a water treatment plant (Mosqueda-Jimenez et al., 2006). Several studies about ultrafiltration membrane fouling in municipal water treatment have been carried out by researchers and Table 2.2 shows a list of papers which have studied UF membrane fouling.

2.2.1 Fouling Classification and Formation Mechanism

Membrane fouling is physically classified as reversible fouling or irreversible fouling. The cake layer or concentration polarization of materials causes reversible fouling while chemisorption, pore plugging, and biofouling cause irreversible fouling. Flux loss cannot be recovered hydrodynamically or chemically in the irreversible fouling (Guo et al., 2012).

Figure 2-5 shows the fouling mechanisms in membrane filtration. Figure 2-5 (a) shows pore sealing, in which particles seal the pores. Figure 2-5 (b) shows pore constriction, in which particles or dissolved matter reduce cross-sectional area of the pores. Figure 2-5 (c) shows cake layer formation, in which accumulated particles completely block the membrane.

Table 2-2 List of papers that studied UF membrane fouling

Membrane type	Membrane material	MWCO (KDa)	Water source	Pressure (psi)	Pre-treatment	Membrane cell	Reference
Amicon PM10 Flat sheet	PS	10	Lake	55	MF, GAC, Coagulation, Biofiltration, Ozone	Stirred dead-end (Amicon 8400)	Solomon and Summers (1992)
Millipore PES100 Flat sheet	PES	100	Synthetic water	N/A	-	Stirred dead-cell (Millipore XFUF07601)	Juang et al. (2008)
Amicon YM10 Flat sheet	CA	10	Lake	N/A	-	Stirred dead-end (Amicon 8200)	Chiou et al. (2010)
Hollow fiber	PVDF, PES	0.02μm	Surface water	N/A	Magnetic Ion Exchange	Submerged pressurized mode	Huang et al. (2012)
GE Flat sheet	CA	20	Synthetic water	20	-	Osmonics Sepa CF	Motlagh et al. (2013)
Zenon Hollow fiber	PVDF	0.04μm	Surface water	N/A	Ozone, Biofiltration	Zenon ZW10 pilot module	Sun et al. (2011)
GE Hollow fiber	PVDF	400	Surface water	N/A	Biofiltration	Dead-end mode	Peldszus et al. (2011)
NADIR Flat sheet	PES	150	Lake	N/A	-	Unstirred dead-end (Amicon 8200)	Tian et al. (2013)
Millipore Flatsheet	PVDF	0.22μm	Synthetic water	N/A	-	Stirred dead-end (Amicon 8400)	Xiao et al. (2013)

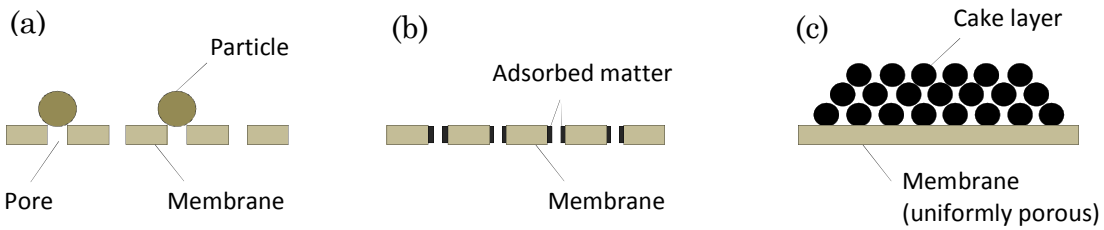


Figure 2-5 Fouling mechanisms in membrane filtration: (a) pore sealing (b) pore constriction. (c) cake layer formation (MWH, 2005)

Foulants, which cause the membrane fouling, can be classified into four categories: particulates, organic matter, inorganic compounds, and microorganisms. Particulates can be inorganic or organic particles/colloids which can cause the blocking of pores or the cake layer formation. Organic matter can be dissolved compounds and colloids, such as humic and fulvic acids which can adsorb onto the membrane. Inorganic compounds, such as iron and manganese, may precipitate onto the membrane. Microorganisms can adhere to the membranes and cause biofouling (Guo et al., 2012).

2.2.2 Biofouling

Among the different types of fouling, "biofouling is hard to control due to the ability of microorganisms present even at very small concentrations in nearly all water systems to colonize almost any surface and to survive under extreme conditions" (Motlagh et al., 2013). Since other types of fouling can be controlled by reducing foulant concentration in the feed water, Komlenic (2010) noted that "biofouling is recognized as a contributing factor to more than 45% of all membrane fouling".

(1) Biofilms

A biofilm is assembled with microbial cells and extracellular polymeric substances (EPS). In most biofilms, the EPS matrix dominates over 90% of the dry mass of biofilm and microorganisms account for less than 10%. The microorganisms

themselves produce mostly the EPS matrix which has three-dimensional structure and helps the biofilms adhere to surfaces (Flemming & Wingender, 2010).

(2) Biofilm formation

The biofouling life cycle is shown in Figure 2-6. The Center for Biofilm Engineering at Montana State University described the biofilm formation as following: First, free-floating, or *planktonic*, bacteria become attached to a surface, produce EPS, and colonize on the surface. Second, biofilm community, which has a complex and three-dimensional structure, is developed by EPS production. The biofilm communities can develop within hours. Third, detachment of "small or large clumps of cells" or "a type of seeding dispersal that releases individual cells" allows biofilms to propagate. Either scenario leads bacteria to attach to a surface downstream of the original biofilm community.

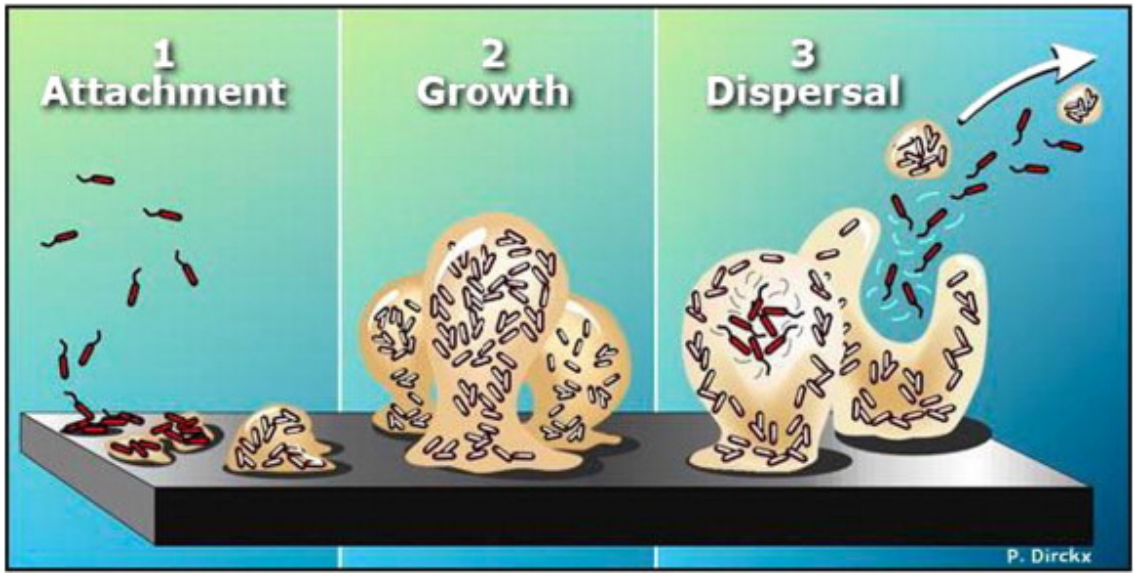


Figure 2-6 Biofilm life cycle (Center for Biofilm Engineering, Montana State University)

(3) Extracellular Polymeric Substances

Beer & Stoodley (2006) reported that "EPS may account for 50~90% of the total organic carbon (TOC) of biofilms". Figure 2-7 illustrates EPS component of a bacterium encountering a non-biological surface in water. EPS consists primarily of polysaccharides, proteins, glycoproteins, lipoproteins and other macromolecules (Beer & Stoodley, 2006). Table 2-3 shows that among these components, polysaccharides dominate 40~95% of EPS mass (Flemming & Wingender, 2001).

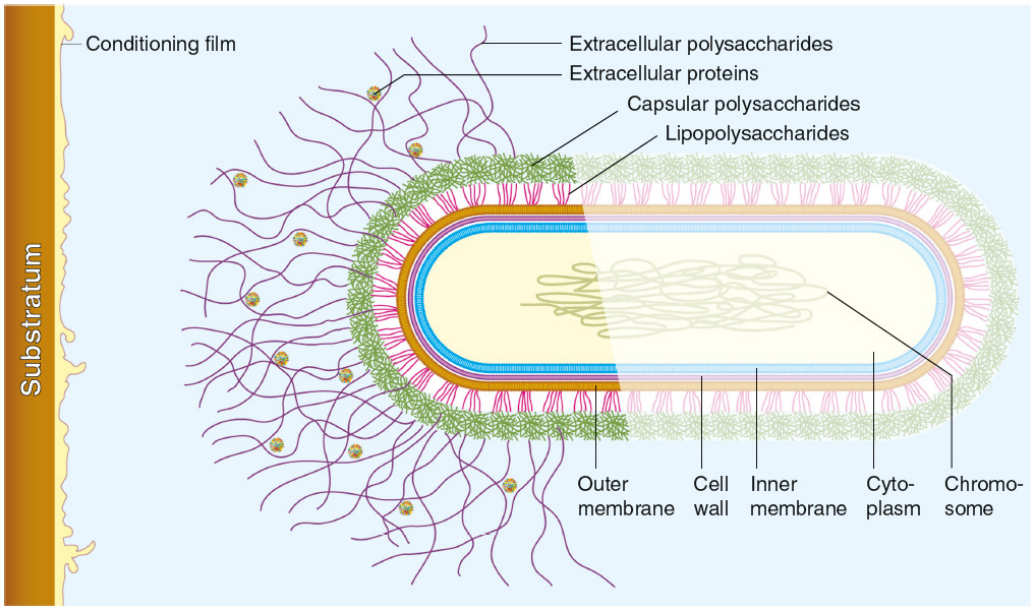


Figure 2-7 EPS component of a bacterium encountering a non-biological surface in water (Flemming, 2011)

Table 2-3 Composition of EPS and range of component concentration (Flemming & Wingender, 2001)

Component	Content in EPS
Polysaccharides	40-95%
Protein	<1-60%
Nucleic acids	<1-10%
Lipids	<1-40%

In addition, the EPS may help biofilms have the antimicrobial resistance properties to prevent antibiotics from reaching the microbial cells. Martin et al. (2011) stated that "the EPS matrix can also sequester nutrients from the environment, which represents a general microbial strategy for survival under oligotrophic conditions".

The EPS can be divided into free (or soluble) and bound EPS (Laspidou & Rittmann, 2002). Bound EPS is closely attached to cells, while free EPS is weakly attached to cells or dissolved into the solution. Generally, EPS can be separated into free EPS and bound EPS by centrifugation. The supernatants become free EPS and the pellets become bound EPS. Figure 2-8 shows the structure of the free EPS and the bound EPS. Bound EPS is composed of tightly bound EPS (TB-EPS) and loosely bound EPS (LB-EPS) (Sheng et al., 2010).

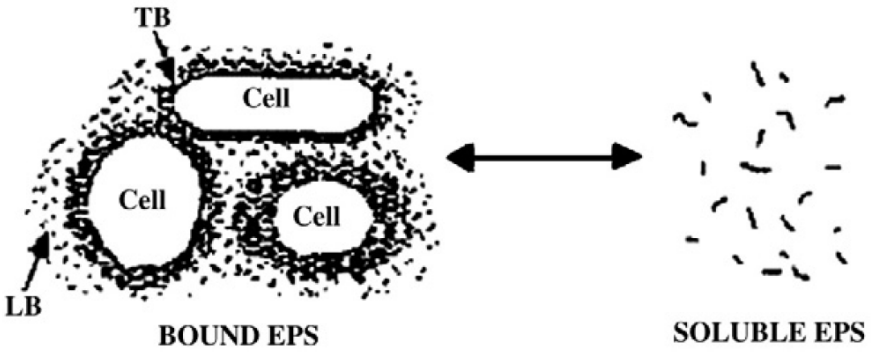


Figure 2-8 Sketch of free (or soluble) EPS and bound EPS structures (Sheng et al., 2010)

(4) Recent Research

Fonseca et al. (2007) related EPS measured as extracellular polysaccharides, soluble microbial products (SMP), and natural organic matter (NOM) to nanofiltration membrane flux decline. They found that membrane flux decline was associated with increases in surface EPS mass, and SMP might have a

biofouling potential significantly greater than some types of NOM. Principal component analysis (PCA) of fluorescence EEM was applied by Peldszus et al. (2011) to characterize reversible and irreversible low-pressure membrane foulants in drinking water treatment. They found that protein content of EPS was highly correlated with irreversible fouling of polymeric ultrafiltration membrane. Vrouwenvelder et al. (2010) used phosphate limitation to control biofouling on RO membrane. They used a 100:20:10 molar concentration ratio of C:N:P and nutrients were dosed to the influent of RO membrane. They showed that phosphate limiting conditions restricted biofouling, even in the presence of high substrate concentrations within short-term experiments.

Xie et al. (2012) characterized autotrophic and heterotrophic SMP fractions from activated sludge. They showed that the SMP produced by heterotrophs contributed 92% to the total SMP, while the SMP produced by autotrophs contributed less than 8%, and SMP produced by AOB accounted for just 5%. Feng et al. (2012) studied the role of influent COD/N ratio in controlling membrane fouling and found that higher COD/N ratio promoted the production of more EPS and higher carbohydrate proportion in EPS. SMP concentration was not positively correlated with EPS under a high content of $NH4^+$ in the supernatant, which resulted in excessive $NH4^+$, replacing polyvalent cations and extracting compositions from the EPS. Thus, high SMP and low EPS were observed in the system under a COD/N ratio of 5. The membrane fouling rate was not only determined by the total amount of SMP, but also showed dependence on the properties (e.g., compositions, MW distribution, and hydrophobicity) of SMP. Lauderdale et al. (2012) considered free EPS (SMP) and bound EPS in explaining the effects of nutrient enhancement on biofilter media. It was found that ATP concentration increased and EPS decreased under the nutrient enhancement condition which had the C:N:P ratio of 100:10:1 (molar concentration).

2.2.3 Reducing Membrane Fouling

(1) Pretreatments

Huang et al. (2009) reported that "pretreatment of the feedwater to LPMs has become more commonly used for two major reasons: enhancement of the removal of aquatic contaminants, such as micropollutants and DBP precursors; and reduction of membrane fouling". There are several commonly used pretreatments for UF: coagulation, adsorption, oxidation, ion exchange (such as MIEX (magnetic ion exchange)), and biological treatment (Gao et al., 2011).

Coagulation is the most widely used pretreatment for UF due to its low cost and relatively easy operation. However, "more research is needed to optimize and establish a particular coagulation way directly aiming at better ultrafiltration" (Gao et al., 2011).

For adsorption, powdered activated carbon (PAC) is the most popular absorbent when adsorption is used as the pretreatment for ultrafiltration. Because of some concern that PAC particles could block the membrane pores, "a new absorbent, which should be developed for membrane fouling control, e.g. carbon black, is demonstrated to be a better selection in river water ultrafiltration than PAC" (Gao et al., 2011).

For oxidation, oxidants such as ozone, permanganate, and chlorine are typically used in a water treatment plant. Gao et al. (2011) stated that "ozone was reported to be incompatible with the most commercially available polymeric UF membranes. Thus, most of studies were carried out by using the ceramic membranes".

MIEX can also be used as the pretreatment for UF. Huang et al. (2012) studied the effects of MIEX pretreatment on low pressure membrane filtration of natural surface water. They found that MIEX had a substantial impact on the removal of DOC, but the extent of membrane fouling reduction was not related to

MIEX dose, therefore other pretreatments are required to enhance fouling reduction. However, because of the lack of data about the large-scale of MIEX, more studies are needed to better understand the effect of MIEX on UF fouling.

Lastly, biological processes are more often used in wastewater treatment compared to drinking water treatment because of the low substrate concentration in drinking water sources. The use of biofilters to reduce membrane fouling has been limited to a few studies because the biological mechanism is difficult and complicated to understand. Solomon et al. (1993) showed that biotreatment performance was better than other pretreatments. They used five pretreatments to reduce UF membrane fouling: microfiltration (0.22μm), granular activated carbon (GAC) filtration, alum coagulation, biofiltration, and ozonation/biofiltration. It was concluded that the order of pretreatment performance was ozonation/biofiltration > biofiltration > coagulation > GAC filtration ≈ microfiltration. Mosqeuda-Jimenez and Huck (2009) used biofiltration as the pretreatment on the fouling of NF membranes and found that biofiltration pretreatment reduced the flux decline to one-third or less and microbial counts were 0.7-log lower in pretreated membranes. Merkel et al. (1998) showed that riverbank filtration reduced NF fouling. Septh et al. (2003) showed biofiltration to have some impact in reducing NF fouling. Sun et al. (2011) conducted experiments with ozone/biofiltration to characterize UF membrane biofouling at different operating conditions (flux) in drinking water treatment.

(2) Operational conditions

In addition to pretreatment, several operation conditions can help reduce membrane fouling: running modes, rinsing (backwashing or forward flushing), chemical cleaning, and air scouring (Gao et al., 2011).

One of the most practical options is to change the running modes, but the proper running modes currently used are mostly based on operating experience.

Rinsing, such as backwashing, can remove the aggregation attached to the membrane surface. Chemical agents such as acid solution, alkali solution, and biocide solution are used for chemical cleaning. A proper chemical reagent is chosen based on the properties of water source. In general, it is known that acid solution controls inorganic fouling, alkali solution controls organic fouling, and biocide solution removes biofouling. The foulants accumulated on the membrane surface can also be removed by air scouring. The combination of the air scouring with rinsing is often used intermittently or continuously (Gao et al., 2011).

2.3 Biological Filtration

2.3.1 Background

Biological filtration can be used to remove compounds which may be ineffectively removed by conventional water treatments, such as biodegradable organic compounds, ammonia, nitrate, and iron. Microorganisms decrease available substrates for microbial growth, reduce tastes and odors, and decrease the formation of disinfection by-products by oxidizing organic matter and ammonia (Bouwer and Crowe, 1988). Biological filtration has commonly been applied in Europe. In The Netherlands and Germany, biological treatment is often applied through bank filtration, ground passage, slow sand filtration, or rapid filtration following ozonation. In France, biological processes are usually performed in second stage granular activated carbon (GAC) contactors (Bouwer and Crowe, 1998; Kuehn and Mueller, 2000; Sontheimer, 1980). Meanwhile, other countries have not seriously considered introducing the biological filtration for water treatment until recently. However, as target contaminants are expanding and drinking water regulation becomes more stringent, the biological treatment is gradually considered as an emerging treatment in other countries as well.

2.3.2 Biological Process Fundamentals

(1) Classification of microorganisms

As shown in Figure 2-9, microorganisms can be classified into two types according to how they get carbon: autotrophs or heterotrophs. Autotrophs use carbon dioxide (CO_2) or other inorganic carbon sources while heterotrophs obtain carbon from organic sources. Autotrophs and heterotrophs are further subdivided into photo- and chemo- depending on the energy source which is either from light or from the oxidation of inorganic chemicals (Table 2-4).

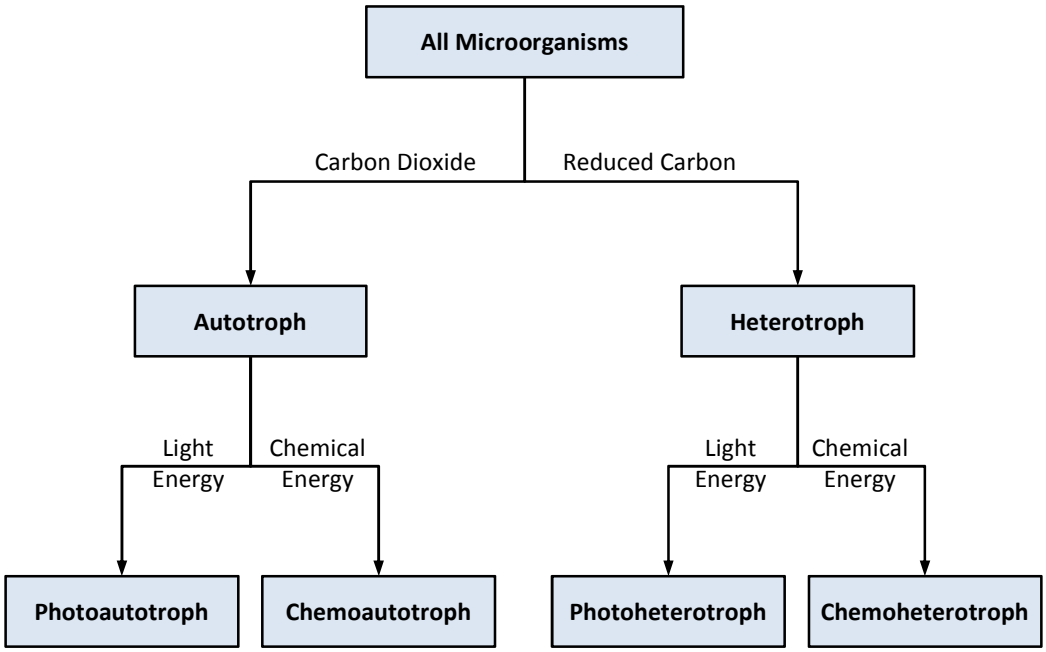


Figure 2-9 Classification of organisms

Table 2-4 Major nutritional types of organisms (Todar, 2012)

Nutritional type	Energy source	Carbon source
Photoautotrophs	Light	CO_2
Photoheterotrophs	Light	Organic compounds
Chemoautotrophs	Inorganic compounds	CO_2
Chemoheterotrophs	Organic compounds	Organic compounds

(2) Microbial metabolism

Heterotrophic bacteria use biodegradable organic matter as an electron donor and as a carbon source (Bouwer and Crowe, 1988). Brown (2007) stated that "bacteria gain energy and reproduce by mediating the transfer of electrons from reduced compounds (i.e., compounds that readily donate electrons) to oxidized compounds (i.e., compounds that readily accept electrons). Once electrons are donated by a reduced compound, they travel back and forth across a cell's mitochondrial membrane in a series of internal oxidation reduction reactions. Ultimately, the electrons are donated to the terminal electron-accepting compound" (Figure 2-10). These processes lead to an electrochemical gradient across the cell membrane. Bacteria use the electrochemical gradient to generate adenosine triphosphate (ATP).

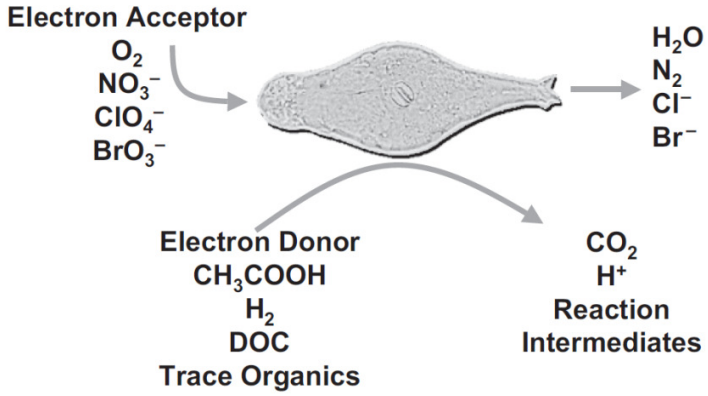
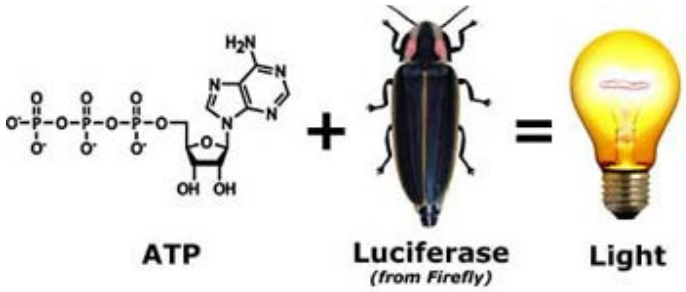


Figure 2-10 Microbially mediated oxidation-reduction reactions (Brown, 2007)

The energy released from the oxidation-reduction reactions is carried for a short time by ATP, which is found in all living organisms such as animal, plant, bacteria, and yeast. The ATP is correlated to cell counts, making it possible to measure biomass concentration by measuring the ATP (Karl, 1980). The ATP is

quantified by measuring the light coming from its reaction with Luciferase (Figure 2-11). The amount of light is directly proportional to the concentration of microorganisms (LuminUltra Technologies Ltd., 2010).



(source: SELECTECH, http://www.selectech.co.za)

Figure 2-11 The reaction of ATP with Luciferase

Enzymes play an important role for microbial metabolism because bacteria use enzymes for biodegradation. Enzymes are a special category of proteins found in all living organisms. Enzymes act as catalysts which speed up reactions by decreasing the energy required for reactions. Equation 2.7 shows the reaction between enzymes (E) and substrates (S) to form the ES. Then, as shown in Equation 2.8, the complex ES breaks down into the free enzyme (E) and product (P). The enzymes are conserved and can then react with new substrate.

$$E + S \leftrightarrow ES \tag{2.7}$$

$$ES \leftrightarrow E + P \tag{2.8}$$

(3) Microbial growth

The growth of microbial cells, depicted in Figure 2-12, is usually divided into lag, exponential, stationary, and death phase (Black, 1996). The lag phase is

generally thought to be a period for cells to adjust to a new environment by undergoing intracellular changes; thus, cell growth doesn't happen. Black (1996) stated that "some species adapt to new medium in an hour or two; others take several days. Organisms from old cultures, adapted to limited nutrients and large accumulations of wastes, take longer to adapt to a new medium than those transferred from relatively fresh, nutrient-rich media. Organisms transferred to a minimal nutrient medium take longer to adapt than do those transferred to a rich medium". Once organisms adapt to a new environment, they grow exponentially. This period is called exponential or log phase. When cell growth starts to decrease, organisms are in the stationary phase. In this phase, new cells are produced at the same rate as old cells die. After the stationary phase, organisms reach the death phase due to the lack of nutrient.

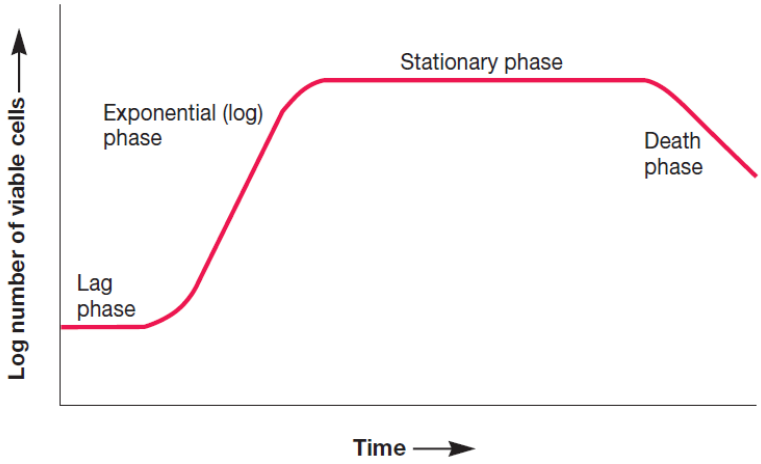


Figure 2-12 Microbial growth curve in a closed system (Black, 1996)

(4) Nutrient conditions

Nutrients are also an important factor in the microbial production and secretion of EPS (Lauderdale et al., 2012). Table 2-5 shows major elements composed of bacteria cells. Redfield (1934) first described the ratio of nutrient

stoichiometry of marine biomass from all ocean regions. He found that the most common molar C:N:P ratio was 106:16:1. EPA (1994) reported that the typical C:N:P ratio necessary for biodegradation was in the range of 100:10:1 to 100:1:0.5. Heterotrophic bacteria are commonly considered to require carbon, nitrogen, and phosphorus in a molar ratio of approximately 100:10:1, which is called a balanced nutrient condition (Flemming, 2011; Kirisits et al., 2013; LeChevallier et al., 1991). Flemming and Wingender (2001) noted that "under an unbalanced nutrient condition, when nitrogen and phosphorus are growth limiting, bacteria try to store carbon outside of the bacteria cell which causes biofilm to generate and EPS to increase".

Table 2-5 Major elements in bacterial cells (Todar, 2012)

Element	% of dry weight	Source	Function
Carbon	50	organic compounds or CO_2	Main constituent of cellular material
Oxygen	20	H_2O, organics, CO_2, and O_2	Constituent of cell material and cell water
Nitrogen	14	NH_3, NO_3, organic compounds, N_2	Constituent of amino acids, nucleic acids nucleotides, and coenzymes
Hydrogen	8	H_2O, organic compounds, H_2	Main constituent of organic compounds and cell water
Phosphorus	3	inorganic phosphates (PO_4)	Constituent of nucleic acids, nucleotides, phospholipids, LPS, teichoic acids
Sulfur	1	SO_4, H_2S, organic sulfur compounds	Constituent of cysteine, methionine, glutathione, several coenzymes
Potassium	1	Potassium salts	Main cellular inorganic cation and cofactor for certain enzymes
Magnesium	0.5	Magnesium salts	Inorganic cellular cation, cofactor for certain enzymatic reactions
Calcium	0.5	Calcium salts	Inorganic cellular cation, cofactor for certain enzymes and a component of endospores
Iron	0.2	Iron salts	Component of cytochromes and a cofactor for some enzymatic reactions

CHAPTER 3

MATERIALS AND METHODS

3.1 Materials

3.1.1 Feed water and Nutrient Source

Initially, several types of water, such as natural water and dechlorinated tap water (DTW), were compared to decide which water is most appropriate for the experiment. Preliminary experiments (Section 4.1) showed that the DTW should be used for the experiments because the DTW yielded adequate flux decline to distinguish difference. The tap water of the City of Boulder, CO, was dechlorinated to create the feed water for the experiments. The tap water ran through a column of granular activated carbon (GAC) at an empty bed contact time of 10 min and then through a series of two filters with a 25 μm and 0.45 μm pore openings to minimize particulate matter and microbial growth in the feed water. The DTW was confirmed to have no free chlorine. The water quality for the DTW is presented in Table 3-1. The feed water was kept covered in a 225 liter blue polyethylene barrel to decrease light exposure and prevent contamination.

Table 3-1 The characteristics of dechlorinated tap water

TOC	TN	TP
BDL (<0.07 mgC/L)	0.009 mgN/L	< 0.0012 mgP/L

The nutrient concentration in the DTW was low (Table 3-1), thus to support growth in the experimental system, carbon, nitrogen, and phosphorus were added to the DTW. Sodium acetate trihydrate ($CH_3COONa \cdot 3H_2O$) was used for carbon, ammonium chloride (NH_4Cl) for nitrogen, and phosphoric acid (H_3PO_4) for

phosphorus. Sodium acetate trihydrate was used to yield a concentration of 1 mgC/L. Nitrogen and phosphorus were added proportionally to yield the appropriate nutrient ratio.

3.1.2 Biomass Media

Two types of bio-acclimated media were taken from different water treatment plants. Sand media was taken from filters at the Richard Miller Plant at Great Cincinnati Water Works (GCWW). The GCWW plant treats Ohio River water impacted by agricultural run-off and municipal and industrial treated wastewater discharges that include ammonia. Anthracite media was taken from the filters at the City of Longmont's Flanders Water Treatment Plant. This plant receives water from the St. Vrain Creek and Colorado-Big Thompson Project sources, which are not impacted by wastewater discharges. At both plants the raw water is treated by alum coagulation, flocculation and sedimentation, and the filter is backwashed with unchlorinated water.

The bio-acclimated media were recirculated in an upflow reactor prior to use. The reactor was constructed of three-inch Schedule 40 PVC pipe with threaded caps on both ends. Stainless steel connectors were tapped into the caps to attach plastic tubing and stainless steel mesh was placed at the bottom of the filter to prevent media loss. Three liters of DTW, spiked with NOM from Big Elk Meadows, CO (BEM) at a TOC concentration of 3 mg/L, were held in an amber glass bottle and recirculated through the reactor. The BEM water flowed upwards through the reactor at a flow rate of 2 mL/min and the reservoir was changed weekly.

From preliminary experiments with ammonia addition (Section 4.1), it was observed that the sand media from GCWW behaved autotrophically and the anthracite media from Longmont WTP behaved heterotrophically, as expected based on their full-scale acclimation conditions.

3.2 Biofilter Design and Operation

3.2.1 Experimental Apparatus

Glass chromatography columns with Teflon caps (Ace Glass, Vineland, NJ) and stainless steel metal fittings (Swagelok Cleveland, OH) were used for constructing biofilters. The bio-acclimated sand media was packed in 11 mm diameter columns. The sand media had a uniformity coefficient of approximately 1.3 and an effective size of 0.45 mm. The bio-acclimated anthracite media with an effective size of 1.0 mm, was packed in 15 mm diameter glass columns. In both cases, the aspect ratio was less than 15, which should to minimize short-circuiting. The bottom of each column was first filled with two inches of 2 mm diameter glass beads encased in wire mesh to prevent media loss and clogging. The media in both cases was packed to a height of 30.7 cm. The columns were run using pumps (Masterflex Models 7553-30 and 7518-10). The columns were covered to minimize the growth of photosynthesizing microorganisms.

3.2.2 Biofilter Operation

Both columns used the same hydraulic loading rate and empty bed contact time (EBCT), 2.5 m/hr (1.0 gpm/ft^2) and 7.5 min, respectively. The sand media filter was run at a flow rate of 4 mL/min and the anthracite media filter was run at a flow rate of 7.2 mL/min.

In order for microorganisms to adjust to each new influent condition, the biofilters were acclimated for 5 days prior to an experiment. Figure 3-1 shows the normalized TOC removal for different organic carbon using the GCWW sand media at an EBCT of 7.5 min over a 5 to 8 day single pass experiment. Two kinds of water were used: DTW with BEM, and DTW with acetate. TOC of the natural water was 4.3 mg/L and the DTW had 2.0 mgC/L of acetate. Normalized TOC (C/C_0), where C is the effluent TOC concentration and C_0 is initial TOC concentration, was used to

express removal. It was found that the TOC removal reached to a plateau after 3 days in both cases, indicating that the sand media biofilter adjusted to a new environment after around 3 days for both DTW with BEM and DTW with acetate.

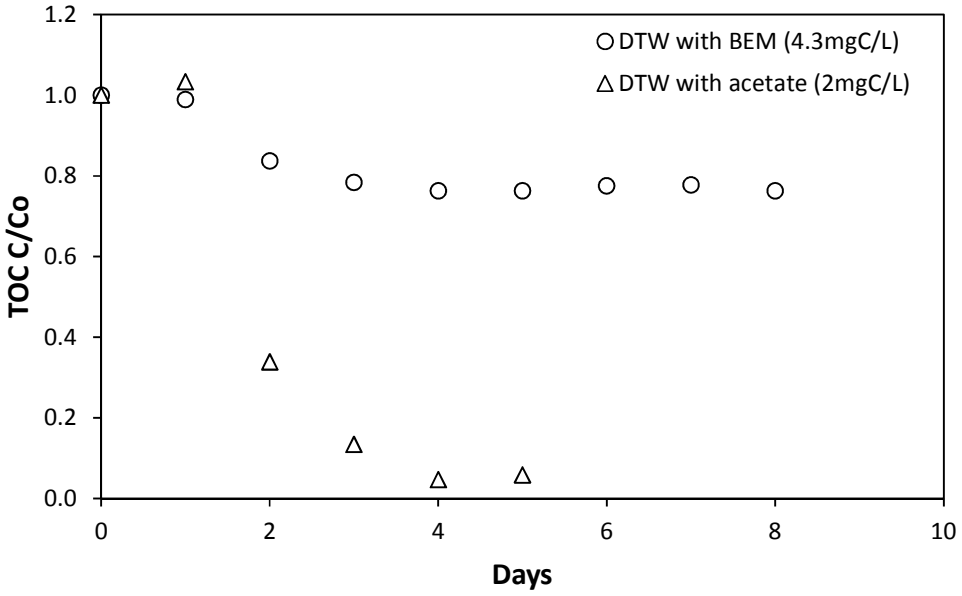


Figure 3-1 Normalized TOC removal for DTW with BEM and DTW with acetate

Different nutrient ratios were used to maintain the biofilters' autotrophic condition or heterotrophic condition. Van Niel et al. (1993) found that autotrophic bacteria outcompeted heterotrophic bacteria at a C/N ratio of 2 and heterotrophic bacteria outcompeted autotrophic bacteria at a C/N ratio of 10. For the autotrophic biomass on the sand media, the nutrients were added to the feed water at a molar C:N:P concentration ratio of 100:50:1 to select for an autotrophic condition. For the heterotrophic biomass on the anthracite media, the nutrients were added to the feed water at a molar C:N:P concentration ratio of 100:10:1 to select for a heterotrophic condition.

3.3 Ultrafiltration Membrane Operation

3.3.1 UF General Characteristics

An ultrafiltration membrane was selected for this experiment as they are commonly used membranes in the water treatment. Table 3-2 shows the general characteristics of UF membranes used in this experiment.

Table 3-2 The general characteristics of UF membrane

Type	Diameter (mm)	Surface area(cm^2)	Material	MWCO (Da)	Max. Oper. Pressure(psi)	Manufacturer
Flat sheet	76	41.8	Cellulose Acetate	10K	70	Millipore

3.3.2 UF Experimental Apparatus

Xiao et al. (2013) stated that "for fundamental investigations of membrane fouling during constant pressure MF and UF, there are three representative scenarios of batch tests that have usually been considered: dead-end filtration (DEF), crossflow filtration (CFF), and stirred dead-end filtration (SDEF)". SDEF is more practical than DEF because it can simulate both DEF and CFF through merely adding a stirrer to the DEF systems. The stirrer can simulate the cross flow condition of CFF by stirring the feed solution. (Xiao et al., 2013).

Two stirred dead-end cells with a volume of 400 mL and sized for 76 mm diameter membranes (Amicon 8400, Millipore, USA) were used in parallel for this experiment. Figure 3-2 shows the UF membrane system, composed of an N_2 gas tank, reservoir, stirred dead-end cell, and magnetic stirrer, used in the experiment.

3.3.3 UF Cell Operation

At the beginning of each test, deionized water (DI) was permeated through the membrane under standard operating conditions for 10 minutes to remove

glycerine on the membrane surface which is pretreated to prevent drying. Preliminary experiments (Section 4.1) showed that there was no flux decline in the first 20 hours with DI and little flux decline in the next 24 hours with DTW due to membrane compaction or compound accumulation. For each experiment, DTW was permeated through the membrane for 30 minutes at a pressure of 25 psi to obtain the initial flux of the membrane. Next, the UF membrane cell was operated for 72 hours with the water of interest at a 25 psi for each experiment.

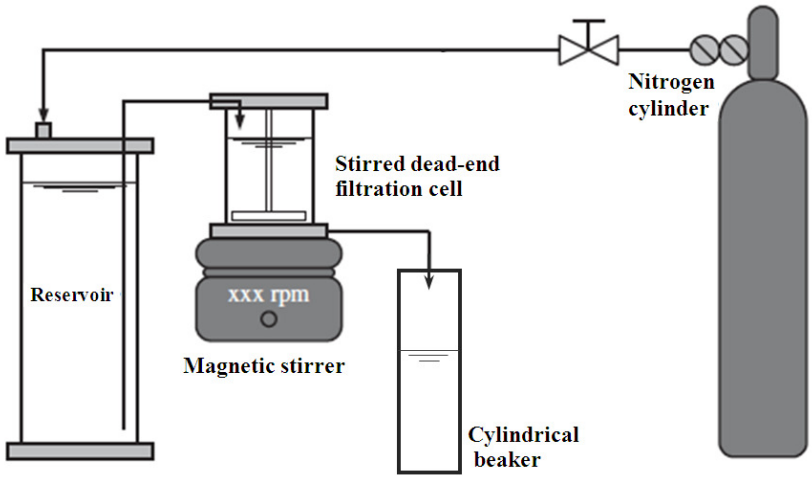


Figure 3-2 UF membrane system run in parallel (Adapted from Xiao et al., 2013)

To simulate the condition without biofiltration pretreatment, the membrane was inoculated with microorganisms. After setting the membrane with DI water, the membrane was inoculated with 20 mL of biomass solution extracted from acclimated sand media or acclimated anthracite media. Once 2 g of sand or anthracite media was extracted from biofilters, the media were put into a 30 mL glass vial mixed with 20 mL of DTW. The vial was submerged in a sonicator bath (Branson 1200, Branson Ultrasonics Corporation, USA) for 1 minute and vortexed for 5 seconds. This process was repeated 5 times. Next, the 20 mL of the biomass suspension was transferred to the membrane surface. The UF membrane system,

including tubes and reservoir, was disinfected with 7 mg/L of sodium hypochlorite solution (NaOCl) after finishing each experiment to remove microorganisms remaining in the system. No microorganisms were inoculated on membrane for the condition with biofiltration pretreatment.

The volume of the membrane effluent was measured every 8 to 15 hours using 4 liters of a cylindrical beaker to calculate the membrane flux. At the end of each run, each membrane was cut into two: one for ATP measurement, and the other for EPS measurement. Biomass was scraped from membranes with sterile spatulas and eluted into tubes containing appropriate analytical solutions. The following parameters were measured from these membranes: ATP, proteins, and polysaccharides.

3.4 Analytical Methods

3.4.1 Water Quality Analysis

Table 3-3 summarizes all water quality analyses for quantifying compounds. TOC and TN were run using a Shimadzu TOC-V_{CSN} analyzer. For TOC and TN measurement, each 25 mL sample was acidified to a pH of 2 and stored at 4℃ before being analyzed. TP was run using a Lachat QC 8500 FIA analyzer. For TP measurement, each 40 mL sample was frozen before being analyzed. Ammonia, nitrate, and nitrite were run using HACH test kits which are TNT 830, TNT 835, and TNT 839, respectively.

Table 3-3 Water quality analysis instruments and methods

Analyte	Measuring Units	Detection Limit	Equipment /procedure	Reference method
pH	N/A	N/A	Denver Instruments Model 220 pH and conductivity meter	SM 4500-H^+
TOC	mg/L	0.07	Shimadzu TOC-V_{CSN}	SM 5310 C
TN	μEQ/L	0.98	Shimadzu TOC-V_{CSN}	SM 4500-N
TP	μEQ/L	0.04	Lachat QC 8500 FIA	SM 4500-P
UVA	cm^{-1}	0.001	Hach DR-4000 UV Spectrophotometer	SM 5910 B
Alkalinity	mg/L as $CaCO_3$	2	Hach Digital Titrator Model 16900-01	SM 2320 B
Free chlorine	mg/L as Cl_2	0.02	Hach Pocket Colorimeter/Hach Method 8021	SM 4500-Cl G
NH_3	mg/L NH_3-N	0.015	Hach DR 5000 UV Spectrophotometer/ Hach Method 10205	
NO_3	mg/L NO_3-N	0.23	Hach DR 5000 UV Spectrophotometer/ Hach Method 10206	
NO_2	mg/L NO_2-N	0.015	Hach DR 5000 UV Spectrophotometer/ Hach Method 10207	

3.4.2 Adenosine TriPhosphate (ATP)

The LuminUltra Deposit and Surface Analysis (DSA) test was used for all ATP testing. A Kikkoman C-110 luminometer was used to read light output from samples. Meanwhile, different extraction methods for measuring the ATP were applied to biofilters and UF membranes.

For biofiltration samples, approximately one gram of media was taken from the top of the biofilter and drip-dried using a vacuum with a 0.45 μm filter. 5 mL of UltraLyse 7 was then added to the tube and vortexed. The sample was allowed to extract for a minimum of 5 minutes. After the extraction, 1 mL of liquid was transferred to a second test tube which contained 9 mL of UltraLute to dilute the extracted liquid. The mixture was then vortexed. 100 μL of the dilution liquid was then added to three 12 x 55 mm tubes each. Two drops of Luminase were then added, followed by the vortex of the test tubes. These test tubes were then inserted

into the luminometer and read. Results were given in relative light units (RLU's). The RLU's are converted to pg tATP/g using the ratio of the RLU's of the sample to the blanks and the mass of the sample. The detection limit varies slightly by the age of the luciferase enzyme and a LuminUltra blank solution. Results are reported in units of pg tATP/g.

For UF membrane samples, biomass was scraped from UF membrane sample using sterile spatulas and put directly into the test tube which contained 5 mL of UltraLyse7. Otherwise, the procedures for the membrane were the same as those for biofiltration samples except for the units. The units for UF samples were pg tATP/cm^2.

3.4.3 Extracellular Polymeric Substances (EPS)

Both free EPS and bound EPS were assessed with polysaccharide and protein measurements.

(1) EPS extraction and separation from media and UF membrane

Approximately 2 grams of media from biofilter were taken and added to a 15 mL centrifuge tube. 10 mL PBS (phosphate buffered saline) was added to the tube. The tube was submerged in a sonicator bath for 1 minute, and vortexed for 5 sec. This was repeated 5 times to dislodge the biofilm from the media. 8 mL of suspension of the tube was transferred to a clean 50 mL centrifuge tube. Then the 50 mL tube was centrifuged (BECKMAN Model J-21C) for 15 minutes at 10,000 rpm at 4℃ for separating EPS of the biofilm into free and bound portions. The supernatant in the tube was free EPS and the pellet was bound EPS after the centrifuge. Around 5.5 mL of the supernatant was transferred to a clean 15 mL centrifuge tube to measure free polysaccharides and free proteins. The pellet was added to another clean 50 mL centrifuge tube which contained 8 mL of buffer comprised of 10 mM Tris/HCl, 10 mM EDTA, and 2.5% NaCl. The tube was

incubated for 8 hours at room temperature, and centrifuged for 15 minutes at 10,000 rpm at 4 ℃. Around 5.5 mL of the supernatant was transferred to a clean 15 mL centrifuge tube to measure bound polysaccharides and bound proteins.

For UF membrane samples, biofilms were scraped from UF membrane sample using sterile spatulas and directly put into a clean 50 mL centrifuge tube which contained 10 mL of PBS without sonication and vortexing. Otherwise, the procedures for the membrane were exactly the same as biofiltration samples.

(2) Polysaccharide

Polysaccharides were measured using the Phenol-Sulfuric acid method (Taylor, 1995). Seven dextrose (D-glucose) standard solutions (0, 5, 10, 20, 30, 40, and 50 μg/mL) were made first. A 5% phenol solution was made and wrapped with a foil to prevent the reaction with the light. 680 μL of DI water and 500 μL of each sample were added into borosilicate culture tubes which were previously baked for 3 hours at 550℃ to make them sterile. Every standard solution was vortexed before being added to tubes. 680 μL of DI water and 500 μL of standard solutions were added into a standard tube. 680 μL of 5% phenol solution was added to every tube and vortexed immediately. Then the tubes were placed in a chemical hood for 10 minutes. 3.35 mL of concentrated sulfuric acid was carefully added to each tube using a pipette. Because the tubes were very hot and dangerous, they were left in a chemical hood for 30 minutes to cool off. After the tubes were vortexed again, 2 mL of each sample was added into three 2.5 mL UV-Vis disposable cuvettes. The absorbance for each sample was measured using a UV spectrophotometer at the wavelength of 488 nm. Absorbances were compared to a calibration curve developed with glucose standard solutions and the final units for polysaccharides were μg/g or $\mu g/cm^2$.

(3) Protein

Proteins were measured using the Bradford method (Braford, 1976). Five BSA (Bovine Serum Albumin) standard solutions (0, 1.2, 3, 6, and 10 μg/mL) were made. 800 μL of each standard solution and 800 μL of each sample were added to a test tube separately. After the dye reagent concentrate was inverted a few times to mix, 200 μL of the dye reagent was added to each tube and vortexed. The tubes were incubated at room temperature for at least 5 minutes and no more than 1 hour because absorbances increase over time. 1 mL of each sample was added into three 1.5 mL semi-micro UV-Vis disposable cuvettes. The absorbance for each sample was measured using a UV spectrophotometer at the wavelength 595 nm. Absorbances were compared to a calibration curve developed with BSA standard solutions and the final units for proteins were μg/g or μg/cm^2.

3.4.4 Sampling Frequency

The water quality membrane and filter biomass sampling plan is shown in Table 3-4.

Table 3-4 Sampling plan

Location	Parameter	Per run		
		Number of Samples	Number of Replicates	Sampling Frequency
Feed water	TOC	1	2	1
	TN	1	2	1
	TP	1	2	1
	Temperature	-	continuous	>2x/day
	pH	1	-	1
	Alkalinity	1	-	1
Biofilter Effluent (right after acclimation)	TOC	1	2	1
	TN	1	2	1
	TP	1	2	1
	pH	1	-	1
	Alkalinity	1	-	1
	ATP	1	3	1
	Proteins	1	3	1
	Polysaccharides	1	3	1
UF Membrane Surface	ATP	1	3	1
	Proteins	1	3	1
	Polysaccharides	1	3	1
	Pressure	-	continuous	>2x/day
UF Membrane Effluent	Flux	1	-	>2x/day
	TOC	1	2	1
	TN	1	2	1
	TP	1	2	1
	pH	1	-	1
	Alkalinity	1	-	1

3.5 Experimental Plan

The experimental approached was designed for effectively assessing the effect of influent conditions, e.g. metabolic and nutrient conditions, and biofiltration pretreatment on membrane biofouling. Figure 3-3 shows the general configuration of an experiment with parallel operation of the two membrane reactors.

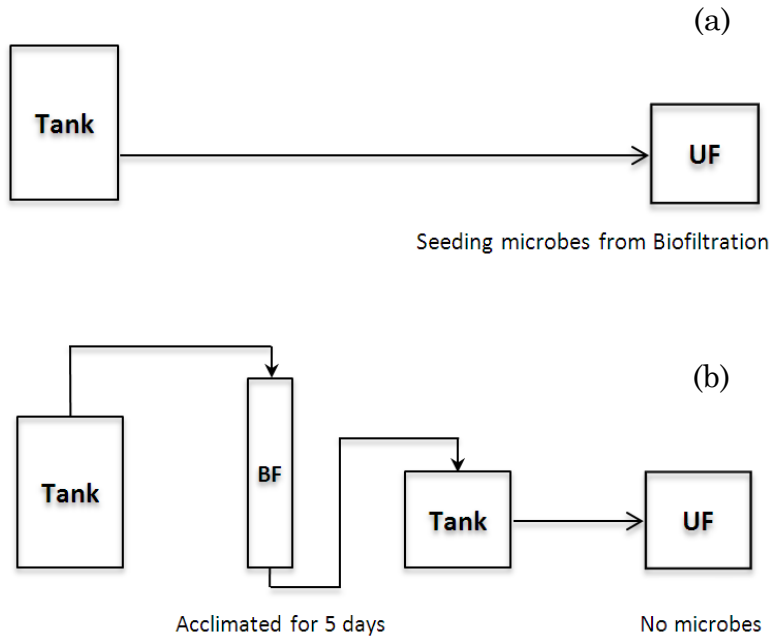


Figure 3-3 General configuration of an experiment (a) without pretreatment and (b) with biofiltration pretreatment

Table 3-5 shows experimental conditions which were comprised of three steps. First, the control was conducted to assess the flux decline caused by only DTW with no additional nutrients. In Phase I, the effect of autotrophic and heterotrophic conditions on membrane biofouling was investigated. The acclimated sand media was used for an autotrophic condition and the acclimated anthracite media was used for a heterotrophic condition. DTW spiked with 1mgC/L of acetate and with nutrients at C:N:P molar ratios of 100:50:1 and 100:10:1, respectively, for

autotrophic and heterotrophic conditions. Two experiments were conducted for each metabolic condition: without pretreatment and with biofilter pretreatment. In Phase II, the effect of different C:N:P nutrient ratios under heterotrophic conditions on membrane biofouling was evaluated. Five different C:N:P ratios were considered: balanced condition (100:10:1), N rich condition (100:25:1), N limited condition (100:0:1), P rich condition (100:10:5), and P limited condition (100:10:0). The anthracite media were used for all experiments of Phase II. 1mgC/L of acetate was added to the feed water with the different C:N:P ratios. Each case conducted two experiments: without pretreatment and with biofilter pretreatment.

Table 3-5 Overview of experimental conditions in Phase I and II

Condition	**Influent water**	**Biofilter**
Control	DTW	-
Phase I	1mgC/L of acetate C:N:P=100:50:1 C:N:P=100:10:1	Autotrophic(C:N:P=100:50:1) - without pretreatment - with pretreatment Heterotrophic(C:N:P=100:10:1) - without pretreatment - with pretreatment
Phase II	1mgC/L of acetate Balanced(100:10:1) N rich(100:25:1) N limited(100:0:1) P rich(100:10:5) P limited(100:10:0)	Heterotrophic with C:N:Ps* - Balanced(100:10:1) - N rich(100:25:1) - N limited(100:0:1) - P rich(100:10:5) - P limited(100:10:0) * each case conducts two experiments (without and with pretreatment)

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Preliminary Experimental Results

Preliminary experiments were conducted to choose the best experimental conditions such as feed water type, proper organic carbon concentration in the feed water, and the assessment of metabolic conditions and the reproducibility of the experiments. Typical initial flow rates were in the range of 5.0 mL/min to 6.8 mL/min, which resulted in fluxes of 0.113 mL/min/cm^2 to 0.147 mL/min/cm^2 after temperature adjustment to 20℃.

4.1.1 Membrane Compaction

When an ultrafiltration membrane is operated under a certain pressure, the membrane can be compacted at the beginning of the operation. Figure 4-1 shows the normalized flux decline for DI water and dechlorinated tap water (DTW) without additional nutrients at a pressure of 25 psi. The initial flow rate with DI was 5.0 mL/min, which is equivalent to a flux of 0.113 mL/min/cm^2. After switching from the DI water to the DTW, membrane flux increased approximately by 20% because of the 100 fold increase in ionic strength. Total dissolved solids (TDS) were 0.7 mg/L for DI water and 70.8 mg/L for DTW. Results show that there was no membrane compaction by both DI water in the first 20 hours and by DTW in the next 10 hours.

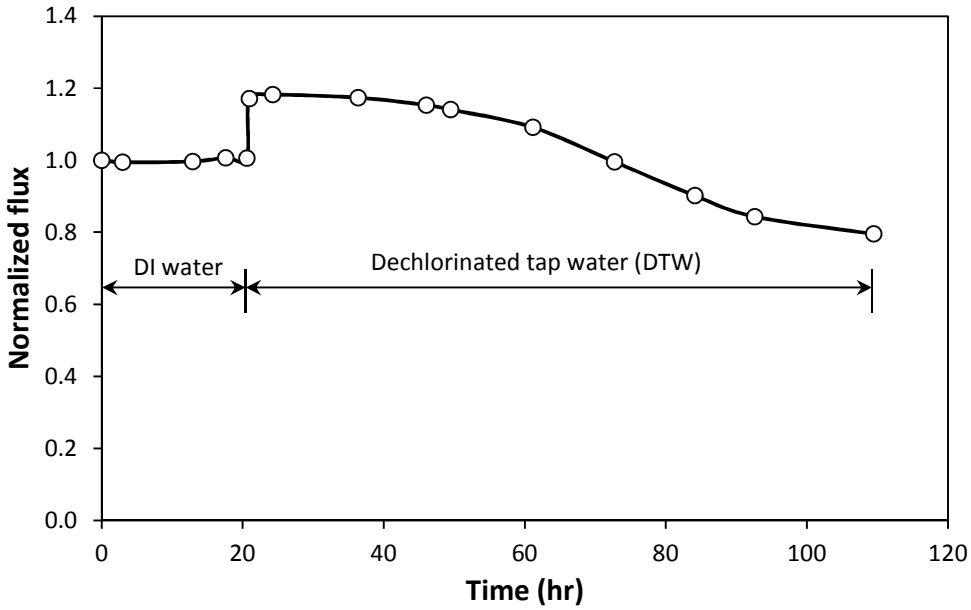


Figure 4-1 Normalized flux decline by DI water and dechlorinated tap water (DTW)

4.1.2 The Effect of Feed Water Type on Flux Decline

In order to effectively evaluate the effect of microbial conditions on membrane biofouling, the condition which causes as a substantial membrane flux decline was preferred. Two kinds of water were used to determine the feed water appropriate for this experiment: one is the BEM at a TOC of 3 mg/L, and the other was DTW spiked with 1 mgC/L acetate. Biomass from 2 g of acclimated autotrophic sand biomass was seeded on the membrane prior to each experiment.

Figure 4-2 shows the normalized flux decline caused by the BEM water and the DTW. When the BEM water was used, microorganisms were added after 72 hours; 40% of flux decline. 92 hours after the addition of microorganisms, an additional 20% flux decline occurred (Figure 4-2 (a)). Figure 4-2 (b) shows that there was little flux decline with DI after 4 days and the addition of 1 mgC/L yielded little change after one additional day. The DTW with the higher ionic strength caused membrane flux to go up, then over the next 2 days the flux changed little; 20%. After the addition of microorganisms and 1 mgC/L, the flux declined by 40% over

the next 72 hours. This flux decline was twice that with the BEM water. Therefore, it turned out that the DTW spiked with acetate is a better setup to explore the impact of pretreatment and metabolic and nutrient conditions using a 5 day run time. In addition, it was observed that microbes themselves didn't change flux decline much while microbes with substrates changed significantly. Figure 4-2 (c) shows that 20% of flux decline occurred by DTW and an additional 20% of flux decline occurred with DTW and microorganisms, which is similar to Figure 4-2 (a).

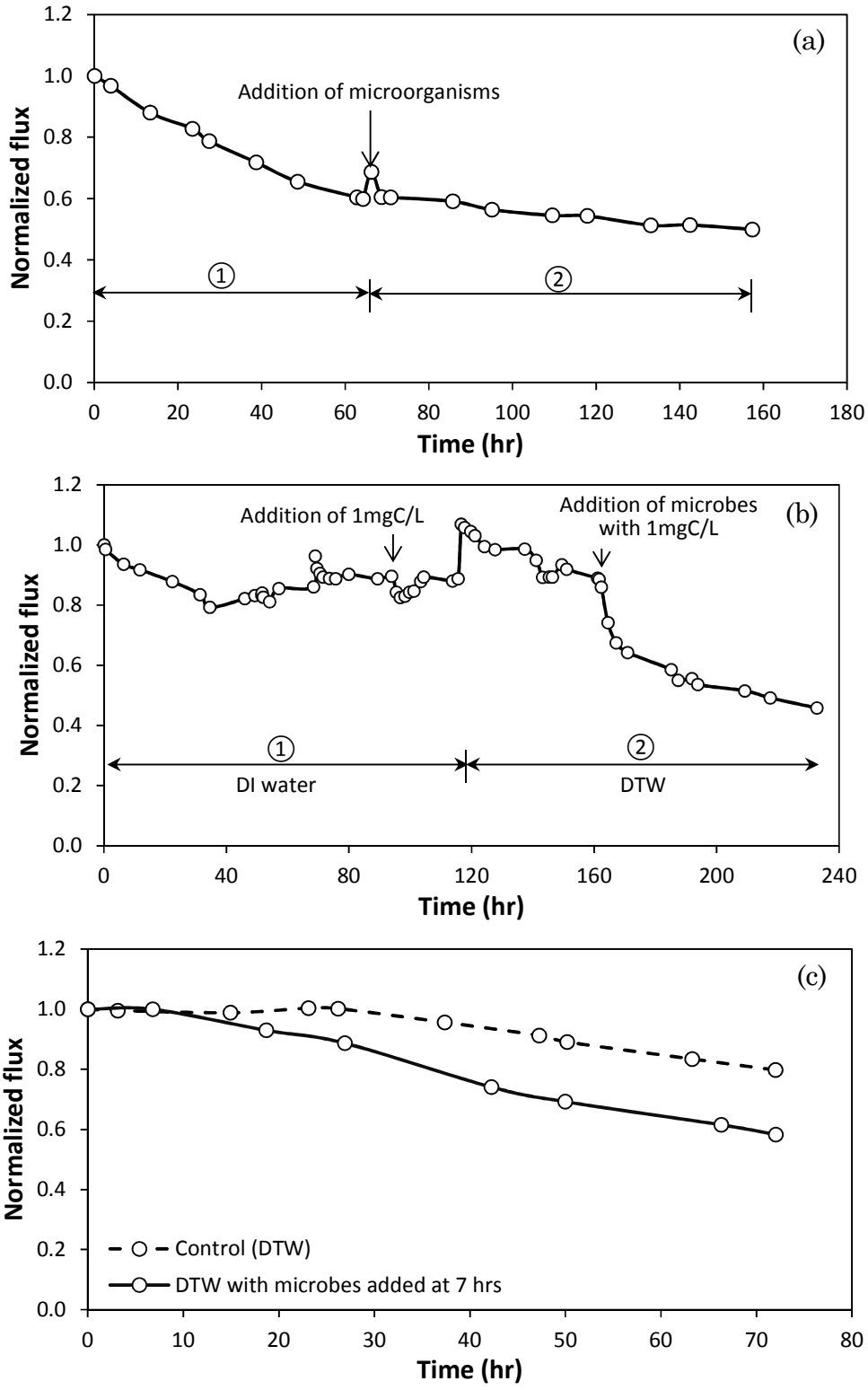


Figure 4-2 Normalized flux decline by (a) BEM water (TOC=3 mg/L) (b) DTW with 1 mgC/L nutrients (c) DTW with no nutrients

4.1.3 The Effect of Seeding Concentration on Flux Decline

To simulate the condition in which microorganisms grow on membrane surfaces without pretreatment, biomass from an acclimated biofilter was transferred to the membrane. To assess the effect of seeding concentration on flux decline, biomass from 2 g or 4 g of sand was seeded on a membrane at the beginning of each experiment. Two different organic carbon concentrations, 1 mgC/L and 10 mgC/L, were considered. Nitrogen and phosphorus were not added to 1 mgC/L, but they were added to 10 mgC/L 20 hours after the operation of the experiment with the ratio of 100:10:1 for C:N:P.

Figure 4-3 shows the normalized flux decline for different seeding concentrations with 1 mgC/L or 10 mgC/L. The control used only DTW with no nutrients. Results show that there was no difference in flux decline caused by the different biomass seeding concentrations. Therefore, biomass from 2 g of media was considered to be appropriate seeding concentration for all experiments. In addition, it was observed that organic carbon concentration also didn't affect flux decline. After adding nitrogen and phosphorus, however, flux started to decline rapidly because the balanced nutrient condition provided microorganisms with a favorite environment in which to grow.

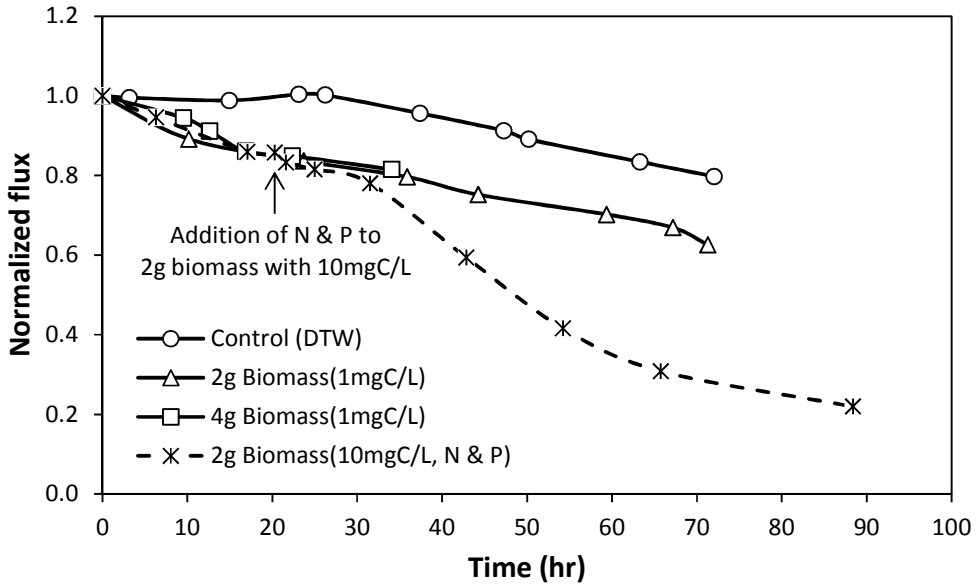


Figure 4-3 Normalized flux decline with different seeding concentrations

4.1.4 The Effect of Organic Carbon Concentration on Flux Decline

To determine the appropriate organic carbon concentration used in this experiment, several carbon concentrations, 1 mgC/L, 3 mgC/L, and 10 mgC/L, were considered under a balanced condition (molar C:N:P ratio of 100:10:1). For this experiment, biomass from 2 g of sand media was seeded on a membrane at the beginning of each experiment.

Figure 4-4 shows the normalized flux decline caused by different organic carbon concentrations. The control with DTW yielded a 20% flux decline after 72 hours. Acetate addition at 1 mgC/L yielded 40% flux decline (60% total) at 72 hours due to microorganisms. Acetate addition at both 3 mgC/L and 10 mgC/L yielded around 60% flux decline at 24 hours. These results show that acetate addition at 1 mgC/L was enough to distinguish the change of flux caused by microbial conditions.

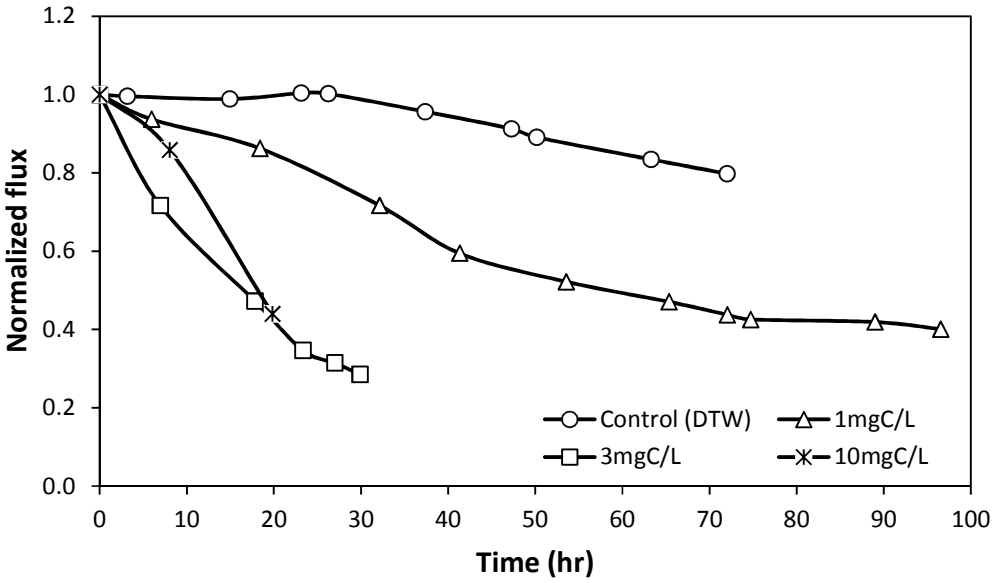


Figure 4-4 Normalized flux decline at different organic carbon concentrations under balanced condition

4.1.5 The Assessment of Metabolic Condition of Media

It was desired to have one system with an autotrophic condition and another system with a heterotrophic condition to simulate different metabolic conditions. Ammonia removal was measured to assess the status of the metabolic condition of each media because ammonia is converted to nitrite and nitrate under autotrophic condition and ammonia oxidizing bacteria (AOB) are the dominating species in an autotrophic condition. For this experiment, the BEM water at a TOC concentration of 6 mgC/L was used with nitrogen and phosphorus in proportion to 100:10:1. The water was recirculated through the columns containing either the autotrophic biomass sand media or the heterotrophic biomass anthracite media.

Figure 4-5 (a) shows that under autotrophic conditions, all the ammonia was consumed, 0.9 mg/L, within 24 hours and nitrate was formed at around 60% of the initial ammonia concentration. No nitrite was detected. The nitrate continued to decrease over the next 4 days of recirculation. With the heterotrophic biomass, all the ammonia was consumed within 48 hours, but little, about 20%, nitrite and

nitrate were formed. It is recognized that both autotrophic and heterotrophic bacteria are present in both filters. However, it is concluded that autotrophic bacteria on the sand media are more active than that on the anthracite media. Operationally, it is considered in this thesis that when nitrogen rich nutrient conditions are used, then the sand media is under a more active autotrophic condition.

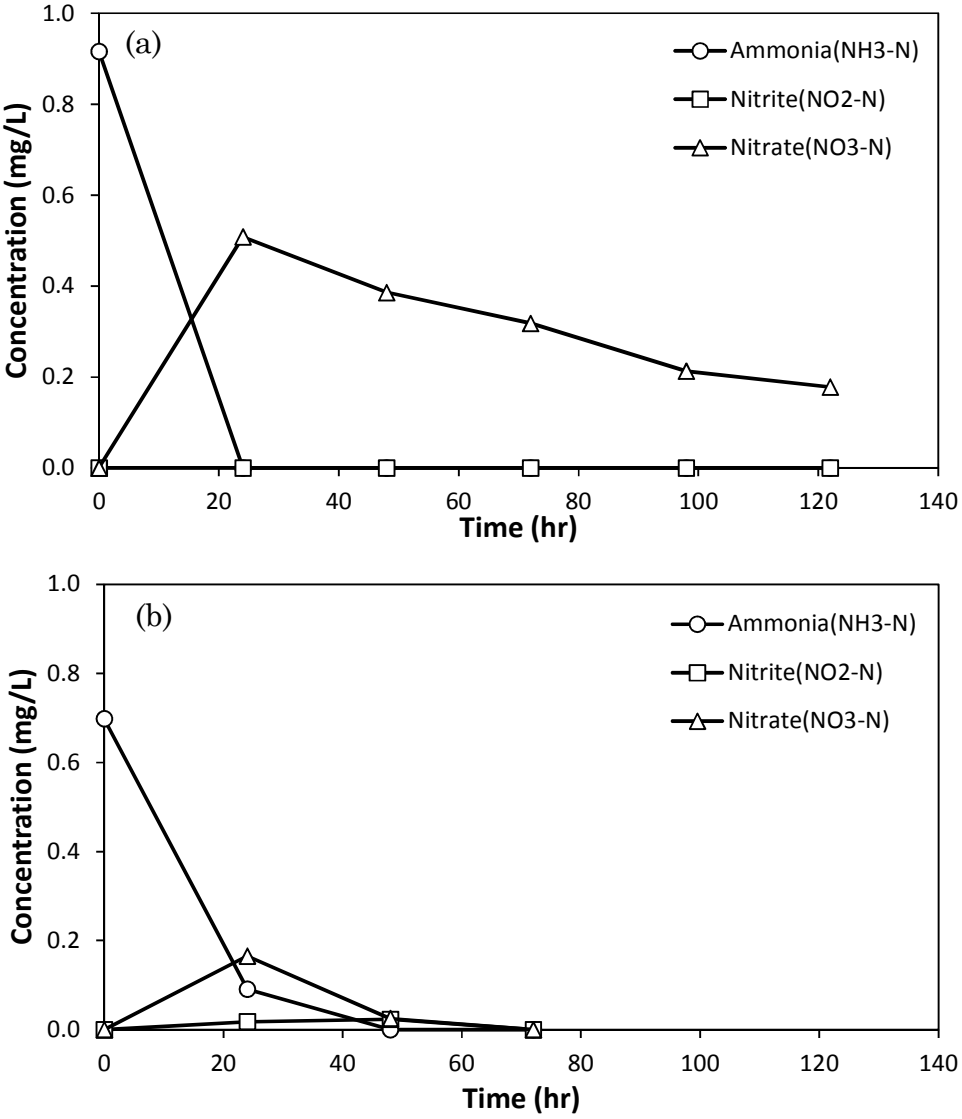


Figure 4-5 Ammonia removal under different metabolic conditions: (a) sand media - autotrophic, and (b) anthracite media - heterotrophic

4.1.6 Standard Error of Duplicate Experiments

The reproducibility of duplicate experiments was assessed by calculating the standard error of flux decline and ATP. The heterotrophic balanced condition was used in duplicate under the same environment without and with biofilter pretreatment. The initial fluxes for these four runs were 0.138 mL/min/cm^2 to 0.146 mL/min/cm^2. As shown in Figure 4-6, little difference in normalized flux decline for duplicate experiments without and with pretreatment could be measured over the 72 hour test. It is shown in Figure 4-7 that both experiments yielded similar flux decline and ATP concentration at 72 hours, with the exception of ATP concentration without pretreatment. The calculated standard error of the mean for flux decline and ATP concentration at 72 hours is shown in Table 4-1. The standard error of the mean was calculated using the following equation where s is sample standard deviation and n is the number of the samples.

$$SEM\ (Standard\ error\ of\ the\ mean) = \frac{S}{\sqrt{n}} \tag{4.1}$$

The sample standard deviation was calculated using following equation where $\boldsymbol{x_i}$, …, $\boldsymbol{x_N}$ is the sample data set, $\bar{\boldsymbol{x}}$ is the mean value of the sample data set, and N is the size of the sample data set.

$$\boldsymbol{s} = \sqrt{\frac{\mathbf{1}}{\boldsymbol{N-1}}\sum_{\boldsymbol{i=1}}^{\boldsymbol{N}}(\boldsymbol{x_i} - \bar{\boldsymbol{x}})^{\mathbf{2}}} \tag{4.2}$$

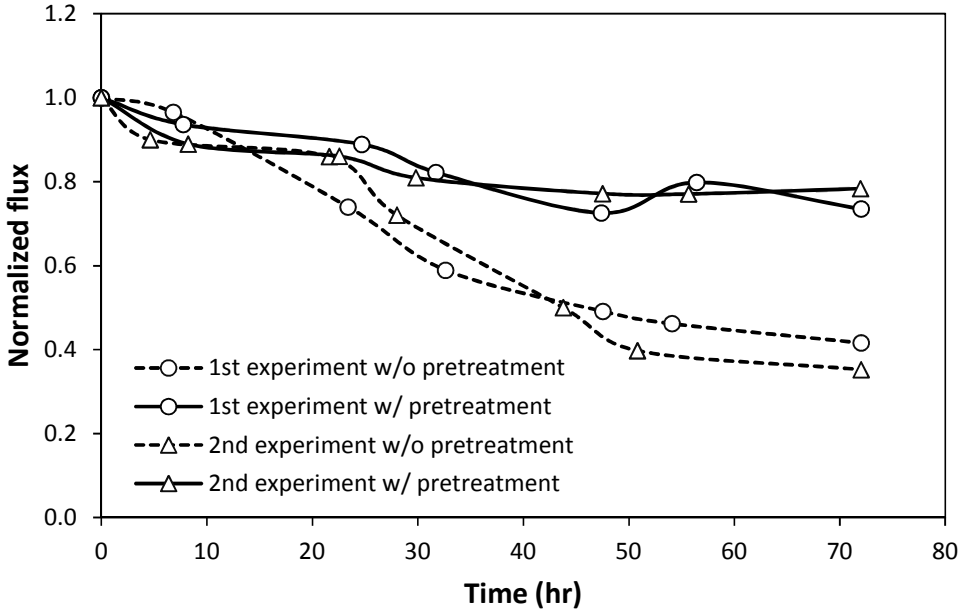
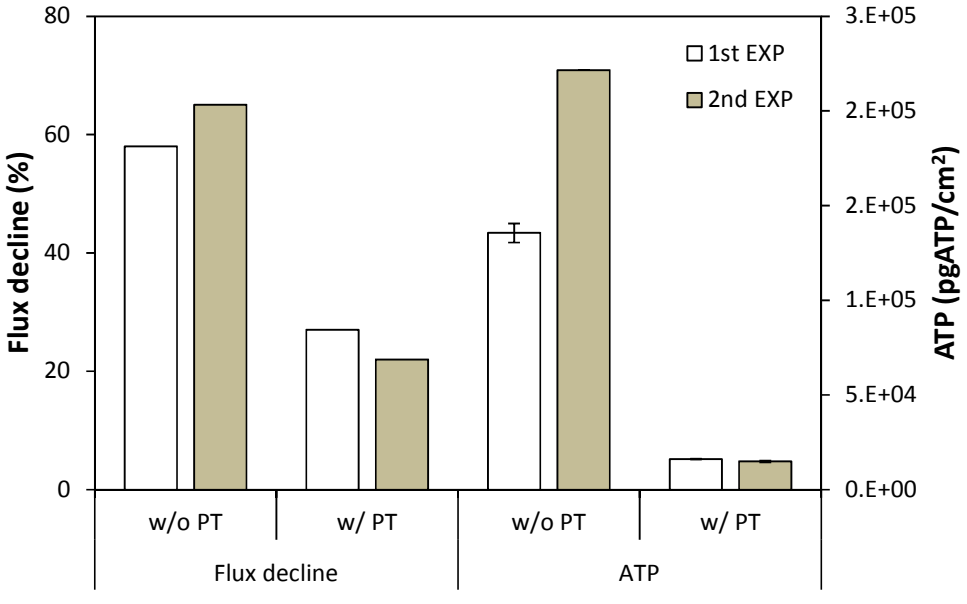


Figure 4-6 Normalized flux decline for duplicate experiments without and with biofilter pretreatment



**PT : pretreatment*

Figure 4-7 Flux decline and ATP for duplicate experiments at 72 hours (error bars represent standard error of triplicate measurements)

Table 4-1 Standard error of duplicate experiments at 72 hours

Condition	Flux decline (%)			ATP (pgATP/cm^2)		
	1st Exp.	2nd Exp.	Standard error	1st Exp.	2nd Exp.	Standard error
Without pretreatment	58	65	3.5	135,000±5,020	221,400±0	42,900
With pretreatment	27	22	2.5	16,000±170	14,900±410	550

4.2 The Effect of Metabolic Conditions on Membrane Biofouling

4.2.1 The Impact of Metabolic Conditions on ATP and EPS

The ATP concentration in this study is used to represent the viable biomass and the sum of the concentration of polysaccharides and proteins, both free and bound, the EPS (total) concentration.

(1) On the biofilter

DTW spiked with acetate at 1 mgC/L was used for this experiment. Nitrogen and phosphorus were added at the C:N:P molar ratio of 100:50:1 to select for an autotrophic condition and 100:10:1 for a heterotrophic condition. The initial ATP concentration from each media before the operation of the biofilters was different. The ATP of autotrophic biomass (sand media), 540,000 pgATP/g, was 6.5 times greater than that of heterotrophic biomass (anthracite media), 83,000 pgATP/g. The ATP and EPS (total) concentrations from the biofilters after 5 days of acclimation are shown in Figure 4-8. After acclimation, ATP and EPS (total) concentrations were 1.5 and 2.5 times larger, respectively, for the autotrophic condition compared to that for the heterotrophic condition. The high EPS concentration under the autotrophic condition was likely caused by the unbalanced nutrient ratio, while the heterotrophic condition was under a balanced nutrient ratio. The unbalanced nutrient ratio in the autotrophic condition caused high excretion of EPS from microbes, while the balanced nutrient ratio in the

heterotrophic condition helped microbes grow (Flemming and Wingender, 2001). The ATP and EPS component concentrations at 72 hours for both metabolic conditions are shown in Table 4-2.

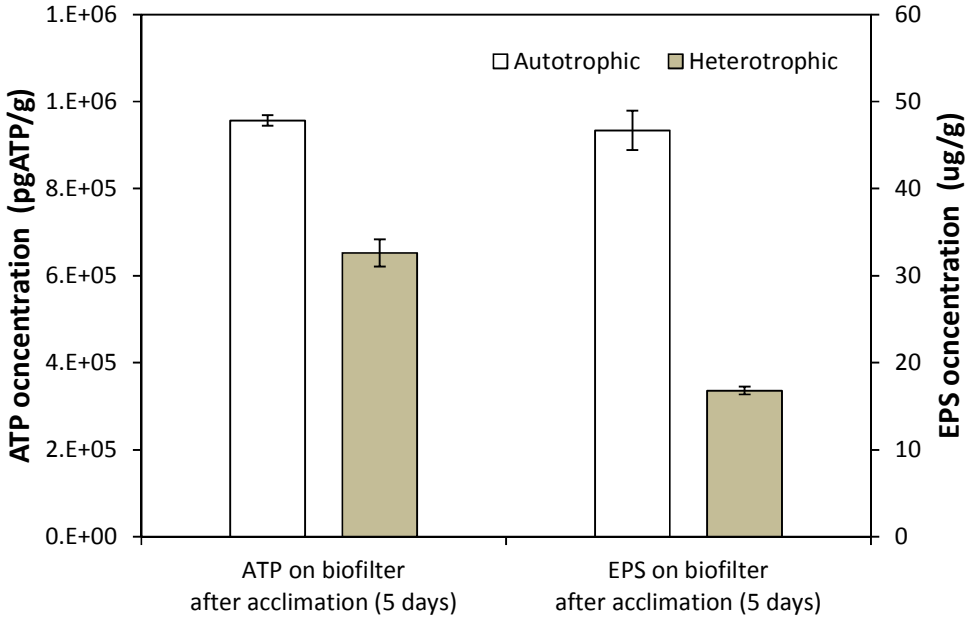


Figure 4-8 ATP and EPS (total) concentrations from filter biomass under both metabolic conditions after 5 days (error bars represent standard error of triplicate measurements)

Table 4-2 ATP and EPS concentrations from filter biomass under both metabolic conditions at 72 hours

On biofilter media			Autotrophic condition	Heterotrophic condition
ATP (pgATP/g)			956,400±12,000	652,000±31,600
EPS (μg/g)	Free	Polysaccharide	14.05±0.31	5.19±0.26
		Protein	8.17±0.41	1.84±0.03
		Sum	22.23±0.65	7.03±0.28
	Bound	Polysaccharide	24.46±1.62	9.40±0.24
		Protein	BDL	0.35±0.03
		Sum	24.46±1.62	9.75±0.24
	Total	Polysaccharide	38.52±1.91	14.59±0.44
		Protein	8.17±0.41	2.20±0.03
		Sum	46.69±2.26	16.79±0.45

(2) On the membrane

ATP and EPS concentrations from membrane biomass under metabolic conditions without and with pretreatment are shown in Figure 4-9. Biomass from 2 g of the appropriate media was seeded only on the membrane without pretreatment. Seeding ATP concentrations were different in the autotrophic and heterotrophic conditions because of the difference in ATP concentrations of each acclimated biofilter.

Without pretreatment, the trend of results was similar to that of the biofilter except for ATP. Seeding ATP concentration was 1.5 times higher in the autotrophic condition but there was no ATP difference between the autotrophic and heterotrophic conditions on the membranes without pretreatment because of the high growth rate of heterotrophs. EPS was higher in the autotrophic condition than in the heterotrophic condition both on the biofilter and on the membrane without pretreatment. ATP increased up to 4 times more than seeding ATP concentration, and EPS was 50% larger in the autotrophic condition than that in the heterotrophic condition even though ATP in both conditions was similar. This is probably because the autotrophic condition was under an unbalanced nutrient condition, leading to more EPS production than the heterotrophic condition.

With pretreatment, ATP concentration on the membrane was half of the seeding ATP concentration and about 10% of that on the membrane without pretreatment. This can be attributed to the near complete substrate removal on the biofilter, as indicated in Figure 3-1, and microorganisms were attached to the biofilter. Both metabolic conditions produced a large amount of EPS, despite of the small amount of ATP on the membrane, as the EPS was likely carried over from the biofilter. The EPS concentration in the autotrophic condition decreased by 50% compared to that on the membrane without pretreatment, but the EPS concentration in the heterotrophic condition changed very little.

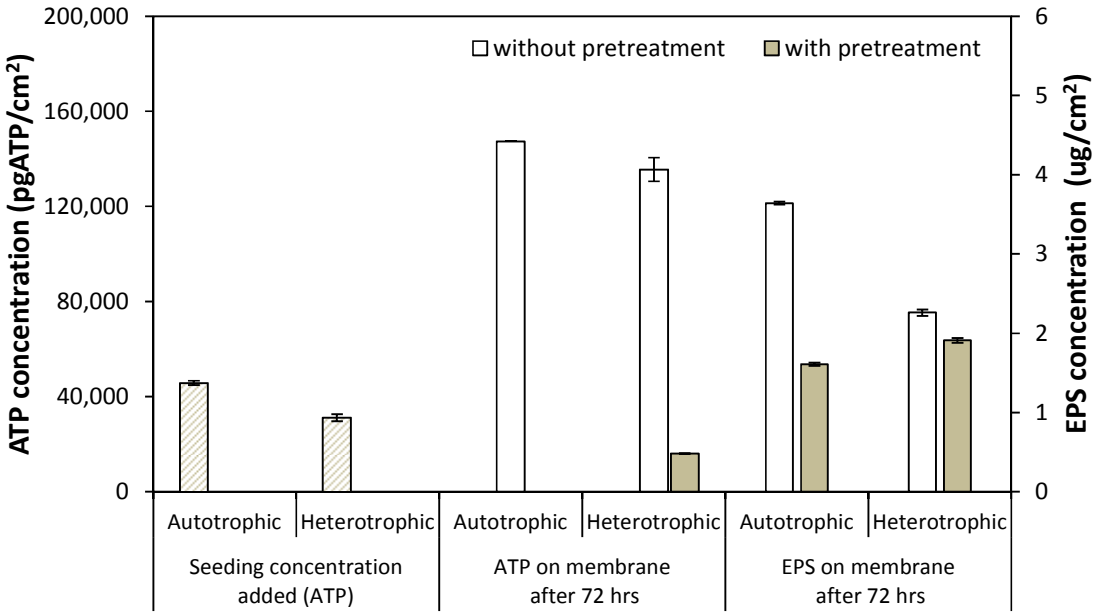


Figure 4-9 ATP and EPS concentrations on membrane for both metabolic conditions without and with biofilter pretreatment (error bars represent standard error of triplicate measurements)

The free EPS and bound EPS concentrations on the membrane for metabolic conditions without and with biofilter pretreatment are shown in Figure 4-10. Without pretreatment, there was a big difference in the free EPS and bound EPS concentrations between metabolic conditions. With pretreatment, there was no difference in free EPS and bound EPS concentrations between metabolic conditions. However, bound EPS concentration decreased, compared to that on the membrane without pretreatment, which indicates that free EPS dominated most of the carry-over of EPS from the biofilter.

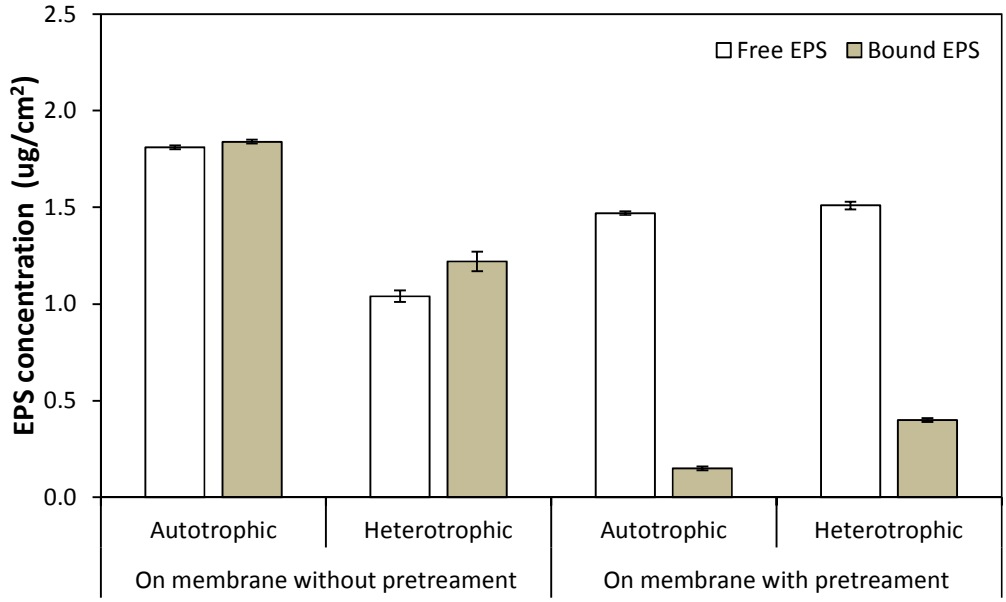


Figure 4-10 Free and bound EPS concentrations on the membrane for metabolic conditions without and with pretreatment (error bars represent standard error of triplicate measurements)

Table 4-3 summarizes ATP, free EPS, and bound EPS on the membrane for metabolic conditions without and with biofilter pretreatment. Free EPS was almost equal to bound EPS on the membrane without pretreatment in both conditions, which is similar to the results of the biofilter. Meanwhile, free EPS dominated approximately 80~90% of total EPS on the membrane with pretreatment in both conditions because of the carry-over from the biofilter. On the membrane without pretreatment, polysaccharides had similar fraction to those on the biofilter; they dominated 90% of total EPS in the autotrophic condition and 70% of total EPS in the heterotrophic condition. On the membrane with pretreatment, polysaccharides dominated approximately 80% of total EPS. The biofouling growth on the membrane in the autotrophic condition without and with biofilter pretreatment is visible in Figure 4-11 photographs.

Table 4-3 ATP and EPS concentrations on the membrane for both metabolic conditions at 72 hours

On membrane			Autotrophic condition		Heterotrophic condition	
			w/o pre-treatment	w/ pre-treatment	w/o pre-treatment	w/ pre-treatment
ATP (pgATP/cm^2)			147,300 ±0	N/A	135,500 ±5,000	16,000 ±170
EPS (μg/cm^2)	Free	Polysaccharide	1.52±0.01	1.16±0.01	0.85±0.03	1.24±0.02
		Protein	0.29±0.01	0.30±0.01	0.20±0.00	0.27±0.01
		Sum	1.81±0.01	1.47±0.01	1.04±0.03	1.51±0.02
	Bound	Polysaccharide	1.80±0.02	0.12±0.01	0.69±0.05	0.34±0.01
		Protein	0.03±0.01	0.03±0.02	0.53±0.01	0.06±0.02
		Sum	1.84±0.01	0.15±0.01	1.22±0.05	0.40±0.01
	Total	Polysaccharide	3.32±0.02	1.28±0.02	1.54±0.03	1.58±0.02
		Protein	0.32±0.00	0.33±0.03	0.72±0.01	0.33±0.03
		Sum	3.64±0.02	1.61±0.02	2.26±0.04	1.91±0.03

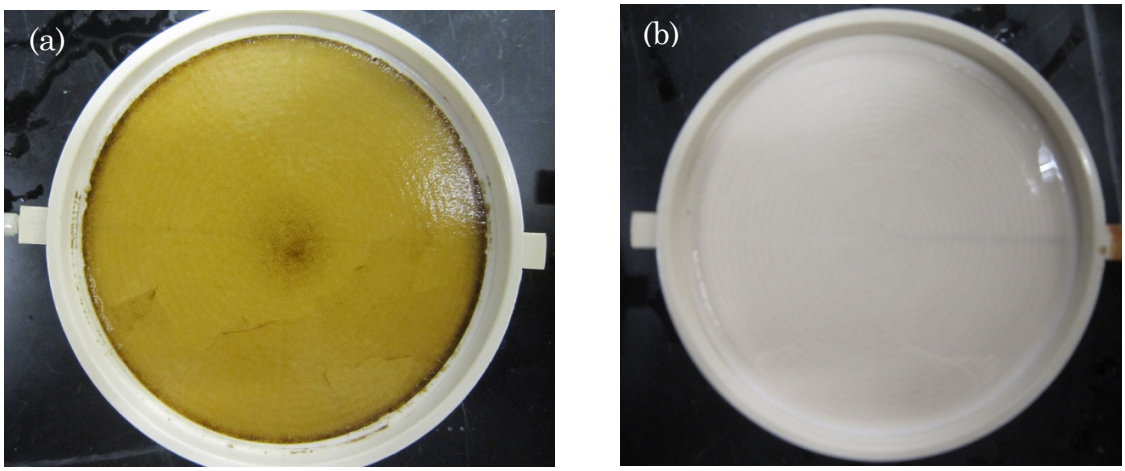


Figure 4-11 Biofouling growth on UF membrane after treatment for autotrophic condition (a) without pretreatment and (b) with pretreatment

4.2.2 The Impact of Metabolic Conditions on Flux Decline

The normalized flux decline under both metabolic conditions without and with biofilter pretreatment is shown in Figure 4-12. The control run, DTW with no nutrient addition, yielded a flux decline of about 20% after 72 hours. To select for the autotrophic condition, a molar ratio of 100:50:1 was used and for the heterotrophic condition, a molar ratio of 100:10:1 was applied. Results show that there was no difference in flux decline between the autotrophic and heterotrophic conditions, given that the flux differences between the runs varied with run time and the standard error was 3.5% (Table 4-1). Without pretreatment, there was approximately 55% flux decline at 72 hours under both metabolic conditions. For most of the run with pretreatment, there was more flux decline compared to the control, but over the last 36 hours, the rate of flux decline was very low such that at 72 hours the flux decline under both conditions was close to that of the control. Table 4-4 shows that biofiltration pretreatment substantially improved the flux by 25% for the autotrophic condition and 32% for the heterotrophic condition. TOC, TN, and TP removal data are summarized in Appendix B. The influent water TOC concentration was too low to be meaningful, likely due to instrument malfunction. TN was conservative for both conditions because ammonia was converted to nitrite and nitrate. TP decreased by about 40% without pretreatment and by about 85% with pretreatment at the UF effluent for both conditions.

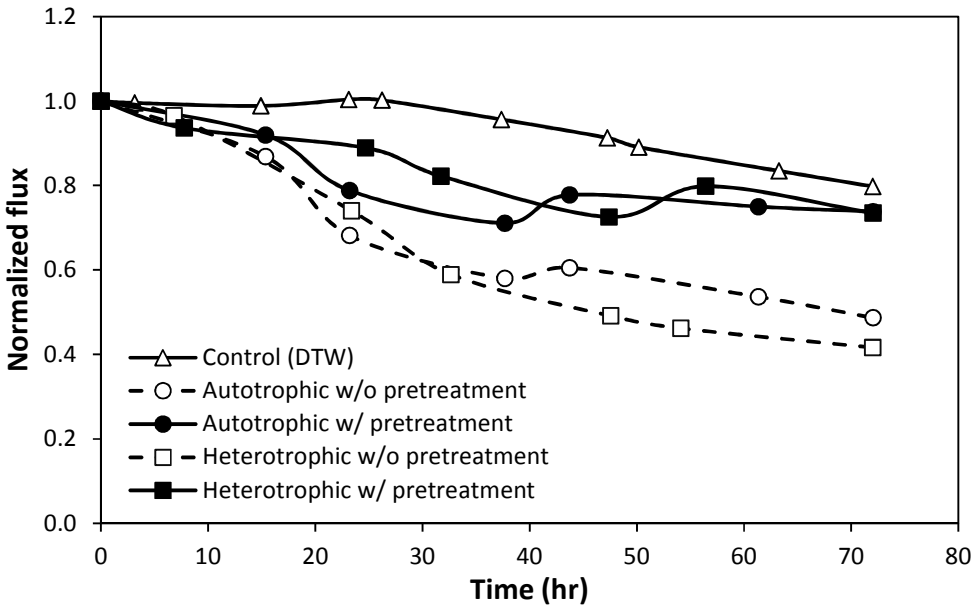


Figure 4-12 Normalized flux decline under both metabolic conditions without and with biofilter pretreatment

Table 4-4 Flux decline for metabolic conditions without and with pretreatment at 72 hours (including 20% flux decline by the control)

Condition	Autotrophic condition		Heterotrophic condition	
	w/o pre-treatment	w/ pre-treatment	w/o pre-treatment	w/ pre-treatment
Flux decline (%)	51	26	58	27

4.2.3 Summary

On the biofilter or on the membrane without pretreatment, the nutrient ratio of each condition affected the production of ATP and EPS. The heterotrophic condition with a balanced nutrient ratio produced more ATP and less EPS than the autotrophic condition. On the membrane with pretreatment, ATP decreased to one-tenth of that without pretreatment but EPS in both conditions had similar amounts because of the carry-over from the biofilter. Most of the carry-over EPS from the biofilter was free EPS because free EPS dominated approximately 90% of the EPS on the membrane with pretreatment.

The autotrophic and heterotrophic conditions showed the same flux decline behavior without and with biofilter pretreatment. On the membrane with pretreatment, it was observed that the flux decline was reduced to around half of that without pretreatment for both conditions because the biofilter captured microorganisms and removed most of the substrate.

4.3 The Effect of Nutrient Conditions on Membrane Biofouling

4.3.1 Impact of Nutrient Conditions on ATP and EPS

DTW under heterotrophic condition at 5 different C:N:P ratios was used to assess the impact of nutrient conditions on flux decline; balanced condition (100:10:1), N rich condition (100:25:1), N limited condition (100:0:1), P rich condition (100:10:5), and P limited condition (100:10:0). The anthracite media from Longmont WTP, bioacclimated under heterotrophic condition, was used for these experiments.

(1) On the biofilter

The ATP and EPS concentrations on the biofilter media for five different nutrient conditions are shown in Figure 4-13. There was considerable difference in the ATP concentration between the balanced condition and all four unbalanced conditions. ATP concentration was the highest in the balanced condition because balanced nutrients provided microbes with a favorable environment in which to grow, while the ATP concentration was the lowest in the N limited condition. EPS concentration was the lowest in the balanced condition because microbes excreted less EPS in the balanced condition while EPS concentration was the highest in the N limited condition, which is opposite to ATP results.

ATP, free EPS, and bound EPS concentrations on the biofilter for all five different conditions at 72 hours are summarized in Table 4-5.

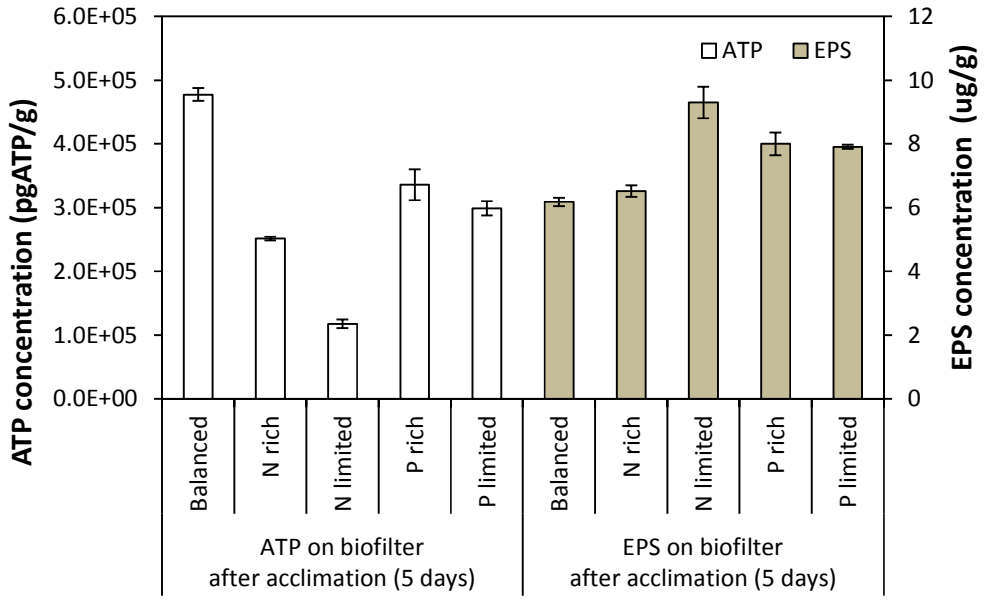


Figure 4-13 ATP and EPS (total) concentrations on the heterotrophic biofilter media for five different nutrient conditions (error bars represent standard error of triplicate measurements)

Table 4-5 ATP and EPS concentrations on the heterotrophic biofilter media for five different nutrient conditions at 72 hours

On biofilter			Balanced	N rich	N limited	P rich	P limited
ATP (pgATP/g)			478,000 ±10,200	251,400 ±2,900	118,000 ±6,500	336,000 ±24,400	299,000 ±11,300
EPS (µg/g)	Free	Polysaccharide	2.11±0.14	2.84±0.13	4.10±0.28	2.83±0.04	3.21±0.05
		Protein	1.52±0.04	0.92±0.07	1.57±0.29	1.10±0.11	1.19±0.11
		Sum	3.63±0.10	3.76±0.15	5.67±0.56	3.93±0.14	4.40±0.06
	Bound	Polysaccharide	2.20±0.26	2.64±0.03	3.61±0.11	3.60±0.01	3.39±0.04
		Protein	0.35±0.05	0.12±0.04	0.02±0.01	0.46±0.32	0.11±0.11
		Sum	2.55±0.24	2.76±0.03	3.63±0.12	4.06±0.32	3.51±0.07
	Total	Polysaccharide	4.30±0.14	5.49±0.14	7.71±0.26	6.44±0.05	6.61±0.03
		Protein	1.87±0.06	1.04±0.11	1.59±0.28	1.56±0.33	1.30±0.08
		Sum	6.18±0.13	6.52±0.18	9.30±0.49	8.00±0.36	7.91±0.06

(2) On the membrane

The ATP and EPS concentrations on the membrane under five different nutrient conditions without and with biofilter pretreatment are shown in Figure 4-14. Acclimated heterotrophic biomass from 2 g of anthracite media was seeded on the membrane without pretreatment. Seeding ATP concentrations were different because of the difference in the ATP concentrations in the five acclimated biofilters (Table 4-5).

Without pretreatment, the trend of ATP and EPS concentrations for all conditions was exactly the same as that of the biofilter. The balanced condition showed the highest ATP concentration while the N limited condition had the lowest concentrations, again indicating that the biomass increased the most under balanced conditions. There were large differences in ATP concentrations between the balanced condition and all four unbalanced conditions. EPS concentration was the highest in the N limited condition and the lowest in the balanced condition.

With biofilter pretreatment, ATP concentrations decreased significantly, compared to that without pretreatment. There was little difference in ATP concentration between nutrient conditions, except for the N limited condition, which was the highest of the unbalanced conditions, but had the lowest ATP concentration on the pretreatment biofilter. While the TOC values were compromised, it is likely that some substrate was not consumed in the pretreatment biofilter and carried over to the membrane in the N limited condition. For the other unbalanced conditions, which had two to three fold higher ATP concentrations in the biofilter (Table 4-5), more of the substrate was likely consumed in the biofilter. It is also likely that the temperature increase from 17.5℃ to 27℃ during experiment caused microorganisms to have a higher growth rate in the N limited condition.

EPS on the membranes with pretreatment was at lower, about 60~90%, compared to that on the membrane without pretreatment. Part of the EPS on the

membrane could be produced by the microorganisms on the membrane and part could be carried over from the biofilter. EPS was the lowest in the balanced condition and the highest in the P limited condition and N limited conditions. This is because ATP and EPS concentrations on the biofilter were the highest and the lowest, respectively, in the balanced condition, which means that less EPS was carried over from the biofilter in the balanced condition than in all the unbalanced conditions.

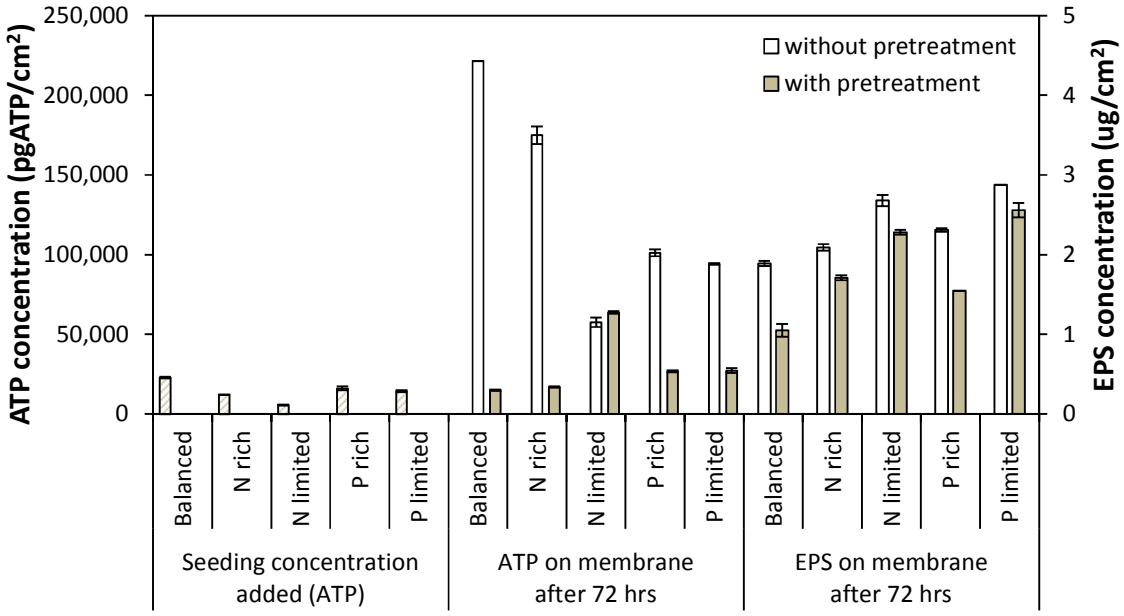


Figure 4-14 ATP and EPS concentrations on membrane for five different nutrient conditions without and with biofilter pretreatment (error bars represent standard error of triplicate measurements)

The ATP, free EPS, and bound EPS concentrations on the membrane without pretreatment for five different nutrient conditions at 72 hours are shown in Table 4-6. Free EPS dominated approximately 70% of total EPS, which is 20% greater than the fraction of free EPS in the biofilter. Polysaccharides dominated approximately 75% of total EPS in the balanced condition and 90% of total EPS in

all unbalanced conditions, which is similar to the results of the biofilter. In addition, this trend was observed in free polysaccharide and bound polysaccharides. Free polysaccharides dominated 70% of free EPS in the balanced condition and approximately 85% of free EPS in all unbalanced conditions. Bound polysaccharides dominated 85% of bound EPS in the balanced condition and approximately 95% of bound EPS in all unbalanced conditions.

The ATP, free EPS, and bound EPS concentrations on the membrane with pretreatment for five different nutrient conditions at 72 hours are shown in Table 4-7. Free EPS dominated approximately 80% of total EPS, which is similar to the result without pretreatment. The fraction of polysaccharides was the same as that without pretreatment, which indicates that the fraction of polysaccharides decreased relative to the protein fraction in the balanced condition. The fraction of free polysaccharides and bound polysaccharides was the same as the results without pretreatment.

Table 4-6 ATP and EPS concentrations on the membrane without pretreatment under five different nutrient conditions at 72 hours

On membrane without pretreatment			**Balanced**	**N rich**	**N limited**	**P rich**	**P limited**
ATP (pgATP/cm^2)			221,400 ±0	175,000 ±5,500	57,500 ±3,000	101,000 ±2,150	94,200 ±570
EPS (μg/cm^2)	Free	Polysaccharide	0.77±0.02	1.32±0.02	1.65±0.03	1.58±0.02	1.89±0.04
		Protein	0.36±0.00	0.31±0.01	0.31±0.05	0.21±0.01	0.31±0.02
		Sum	1.13±0.02	1.63±0.02	1.96±0.07	1.79±0.01	2.19±0.02
	Bound	Polysaccharide	0.65±0.01	0.45±0.02	0.70±0.01	0.50±0.01	0.65±0.02
		Protein	0.11±0.01	0.02±0.01	0.01±0.01	0.03±0.00	0.04±0.00
		Sum	0.76±0.02	0.46±0.02	0.71±0.01	0.53±0.01	0.69±0.02
	Total	Polysaccharide	1.43±0.02	1.77±0.03	2.36±0.03	2.08±0.03	2.53±0.02
		Protein	0.46±0.01	0.33±0.01	0.32±0.04	0.23±0.01	0.35±0.02
		Sum	1.89±0.03	2.09±0.04	2.68±0.07	2.31±0.02	2.88±0.00

Table 4-7 ATP and EPS concentrations on the membrane with heterotrophic biofilter pretreatment under five different nutrient conditions at 72 hours

On membrane with pretreatment			Balanced	N rich	N limited	P rich	P limited
ATP (pgATP/cm^2)			14,900 ±410	16,800 ±420	63,700 ±800	26,700 ±540	27,300 ±1,500
EPS (μg/cm^2)	Free	Polysaccharide	0.57±0.06	1.21±0.02	1.75±0.03	1.10±0.01	1.85±0.05
		Protein	0.20±0.01	0.25±0.01	0.22±0.00	0.16±0.00	0.31±0.06
		Sum	0.78±0.06	1.46±0.03	1.98±0.03	1.26±0.01	2.16±0.11
	Bound	Polysaccharide	0.20±0.03	0.25±0.01	0.29±0.00	0.27±0.01	0.33±0.00
		Protein	0.08±0.00	0	0.01±0.00	0.03±0.00	0.07±0.04
		Sum	0.28±0.02	0.25±0.01	0.30±0.00	0.30±0.01	0.40±0.04
	Total	Polysaccharide	0.77±0.07	1.46±0.03	2.05±0.03	1.37±0.01	2.18±0.05
		Protein	0.28±0.01	0.25±0.01	0.23±0.01	0.18±0.00	0.38±0.04
		Sum	1.05±0.08	1.71±0.03	2.28±0.03	1.55±0.00	2.56±0.09

4.3.2 The Effect of C/N and C/P Ratio on ATP and EPS

Feng et al. (2012) found that the ratio of carbon and nitrogen could impact EPS production. The ATP and EPS concentrations on the membrane at several C/N ratios; C/N=4 from the N rich condition (100:25:1), C/N=10 from the balanced condition (100:10:1), and C/N=∞ from the N limited condition (100:0:1), are shown in Figure 4-15. The concentration units are different for ATP and EPS on the filter, g^{-1}, and on the membrane, cm^{-2}.

On the biofilter, the ATP was the highest at C/N=10 and the lowest at C/N=∞. As C/N was less or greater than 10, the ATP decreased. The trend of EPS was opposite to that of ATP. EPS was the lowest at C/N=10 and the highest at C/N=∞. On the membrane without pretreatment, ATP and EPS had the same trend as the biofilter. Meanwhile, on the membrane with pretreatment, ATP was the lowest at C/N=10 and the highest at C/N=∞. As C/N was less or greater than 10,

ATP increased. EPS had the same trend as that without pretreatment. Figure 4-16 shows ATP and EPS on the membrane at several C/P ratios; C/P=20 from the P rich condition (100:10:5), C/P=10 from the balanced condition (100:10:1), and C/P=∞ from the P limited condition (100:10:0). It was observed that the ratios of C/P had exactly the same results as C/N. Therefore, it is concluded that ATP, at C/N=10 or C/P=100 which is the balanced condition, was the highest on the biofilter and on the membrane without pretreatment, and the lowest on the membrane with biofilter pretreatment. EPS was the lowest in all three cases at that C/N or C/P ratio.

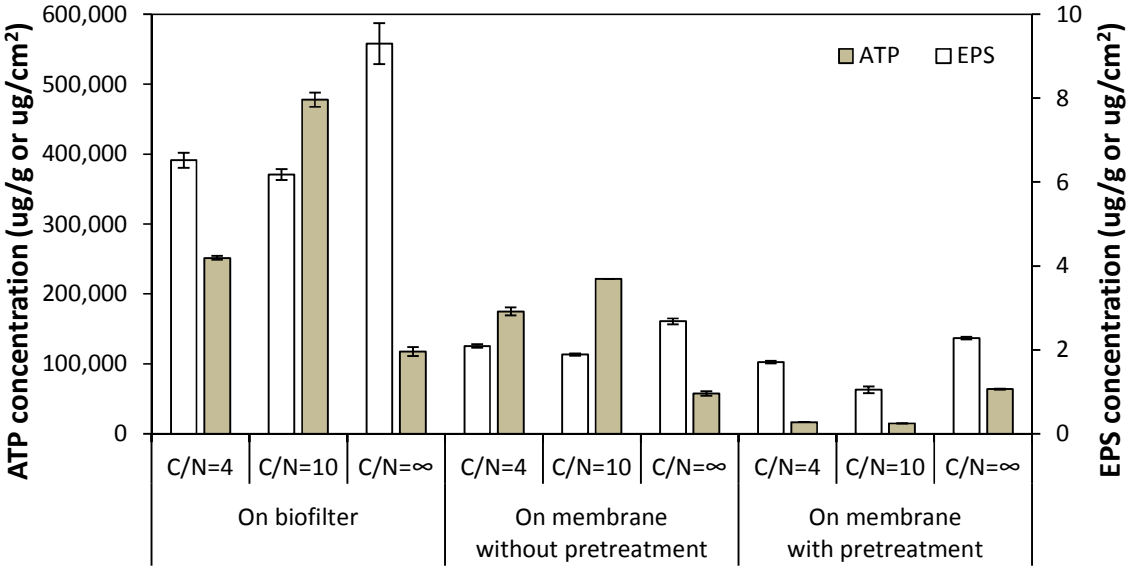


Figure 4-15 ATP and EPS concentrations on the biofilter and on the membrane without and with biofilter pretreatment at different C/N ratios (error bars represent standard error of triplicate measurements)

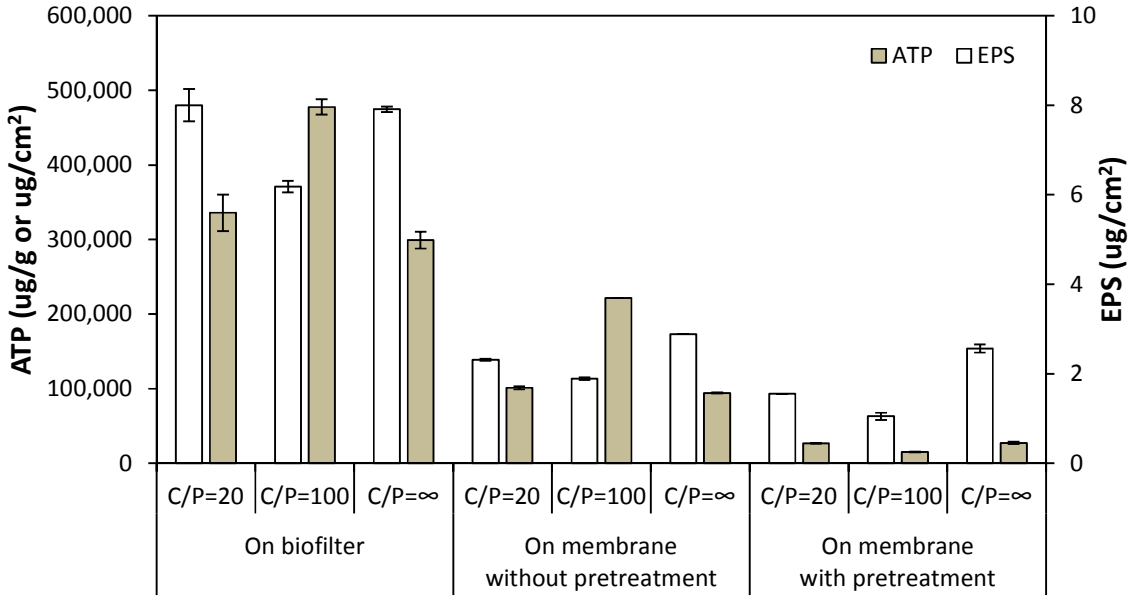


Figure 4-16 ATP and EPS concentrations on the biofilter and on the membrane without and with biofilter pretreatment at different C/P ratios (error bars represent standard error of triplicate measurements)

4.3.3 Impact of Nutrient Conditions on Flux Decline

The normalized flux decline for five different nutrient conditions without and with biofilter pretreatment is shown in Figure 4-17. The control used only DTW without nutrient addition. It was observed that biofiltration pretreatment yielded lower flux loss under the balanced condition and the N rich condition. Especially, the balanced condition showed the best performance with pretreatment; 43% of flux was increased. There was little improvement of flux in the P rich and the P limited conditions with pretreatment. Meanwhile, there was no flux improvement in the N limited condition even with pretreatment, which is probably due to the temperature increase (17.5℃ to 28℃) during the experiment, leading to a higher growth rate of microorganisms. These results emphasize that biofiltration pretreatment didn't always yield lower flux decline.

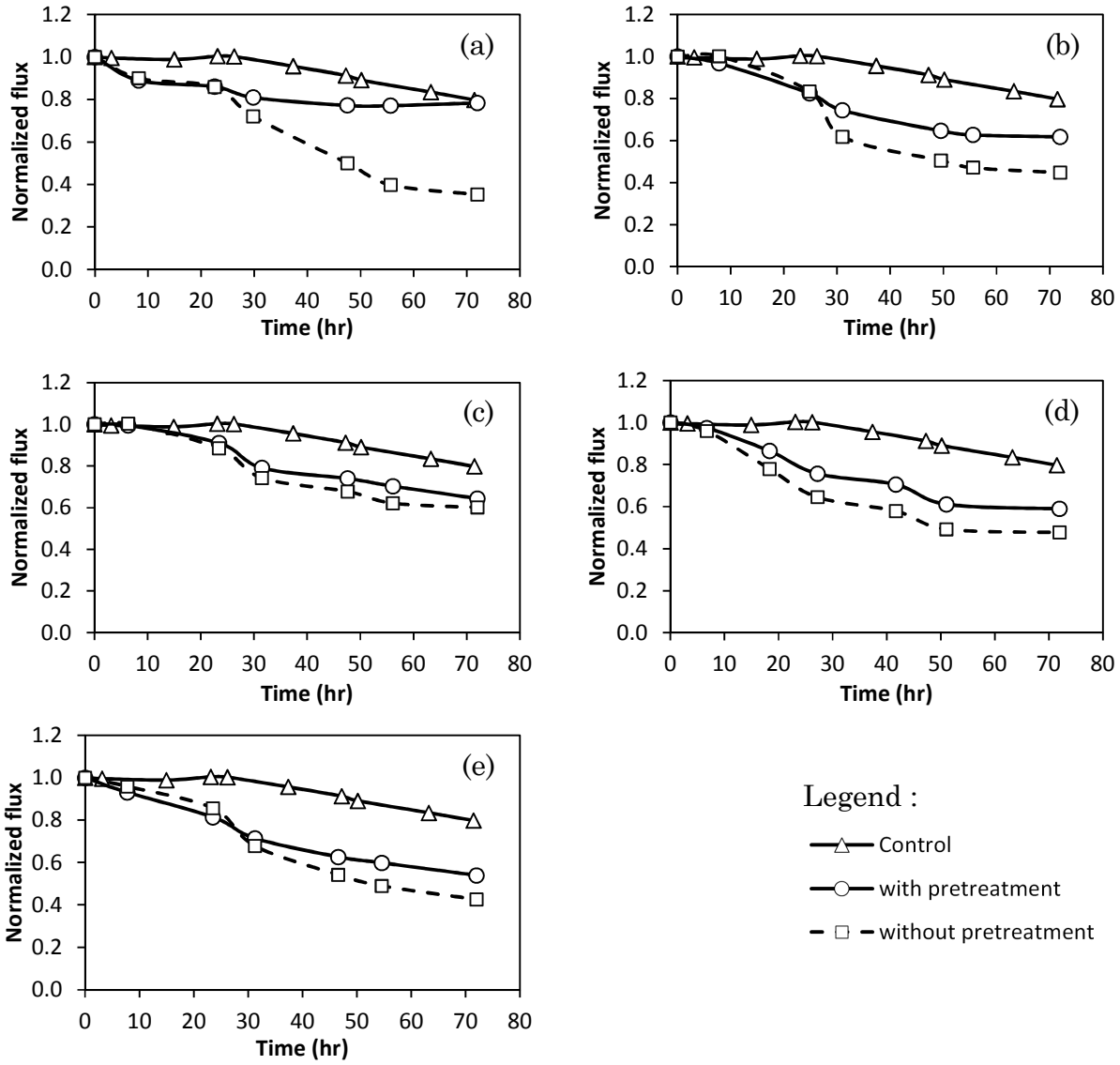


Figure 4-17 Normalized flux decline under five different nutrient conditions without and with biofilter pretreatment: (a) balanced condition (100:10:1), (b) N rich condition (100:25:1), (c) N limited condition (100:0:1), (d) P rich condition (100:10:5), (e) P limited condition (100:10:0)

Figure 4-18 shows the rearrangement of the graphs in Figure 4-17 with regards to the use of pretreatment. Without pretreatment, the flux decline in the balanced condition was the largest because ATP increased the most under the

balanced condition. The least flux decline occurred in the N limited condition. With pretreatment, the flux decline in the balanced condition was the least because most substrates were removed in the biofilter and microorganisms were captured in the biofilter, while the flux decline in the P limited condition was the largest. Table 4-8 summarizes flux decline for five different nutrient conditions without and with biofilter pretreatment at 72 hours. It was also observed that the flux decline behavior of the N rich condition was close to that of the autotrophic condition.

TOC, TN, and TP removal data are summarized in Appendix B. TOC concentration data were lower than expected after acetate addition. Instrument malfunction is suspected. TN was relatively conservative for all conditions because ammonia was converted to nitrite and nitrate. It was observed from TP removal graphs that some of phosphorus was consumed in all conditions.

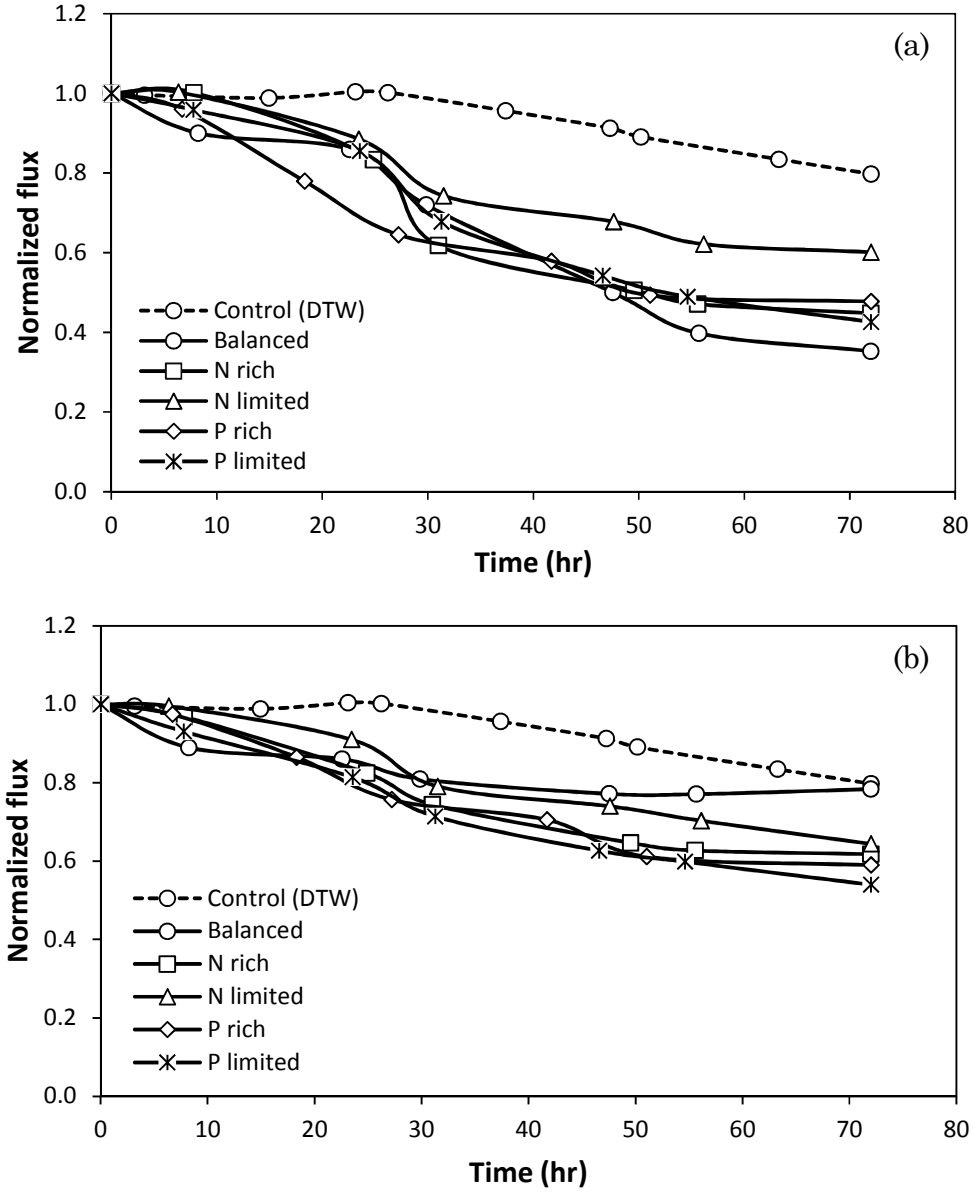


Figure 4-18 Comparison of normalized flux decline under five different nutrient conditions a) without pretreatment and b) with biofilter pretreatment

Table 4-8 Flux decline under five different nutrient conditions without and with biofilter pretreatment at 72 hours (including 20% flux decline by the control)

Condition	Flux decline (%)				
	Balanced	N rich	N limited	P rich	P limited
Without Pretreatment	65	55	40	52	57
With pretreatment	22	38	36	41	46

4.3.4 Summary

On the biofilter media or on the membrane without pretreatment, ATP concentrations were the highest in the balanced condition, while EPS concentrations were the lowest in the balanced condition. On the membrane with biofilter pretreatment, ATP concentrations in most conditions was very little and similar to each other, compared to that without pretreatment, because of the biofilter's ability to capture microorganisms and remove most substrates. The EPS carry-over from the biofilter caused membranes to have a large amount of EPS even when pretreatment was used. The amount of EPS on the biofilter also impacted the amount of EPS on the membrane with pretreatment; thus, EPS on the membrane was the least in the balanced condition because EPS on the biofilter was the least in that condition.

With regards to EPS fraction, free EPS was almost equal to bound EPS. Polysaccharides dominated 70~90% of total EPS where the fraction of polysaccharides decreased relative to the protein fraction in the balanced condition.

C/N and C/P ratios showed the same results. At C/N=10 or C/P=100 which is the balanced condition, ATP was the highest on the biofilter and on the membrane without pretreatment while it was the lowest on the membrane with pretreatment. On the other hand, EPS was the lowest at that ratio in all conditions.

On the membrane without pretreatment, all unbalanced conditions were better than the balanced condition for reducing flux decline. In the meantime, on membrane with pretreatment, the balanced condition was better than all unbalanced conditions. Biofiltration pretreatment showed the best performance under the balanced condition because the biofilter under the balanced condition controlled microorganisms and substrates better than under unbalanced conditions. Moreover, it was observed that the biofilter didn't cause additional flux decline in every condition considered.

4.4 Parameter Correlations

The relationship between ATP, EPS, and flux decline is developed in this section. Eleven data sets without and with pretreatment were used; 6 data sets from metabolic conditions and 5 data sets from nutrient conditions.

4.4.1 The Relationship of ATP on Membrane with Flux Decline

Figure 4-19 shows the relationship between ATP on the membrane and flux decline without and with pretreatment with regards to the autotrophic and heterotrophic conditions. Without pretreatment, ATP concentration was linearly well related to flux decline with a correlation coefficient of 0.76 for the heterotrophic conditions. When both metabolic conditions were considered, ATP concentration was correlated with flux decline with a correlation coefficient of 0.65. Under the autotrophic conditions, no reliable relationships were found, likely because there were not enough samples (n=6). With pretreatment, there was no significant relationship because most substrates were removed in the biofilter and microorganisms were retained in the biofilter (Table 4-9).

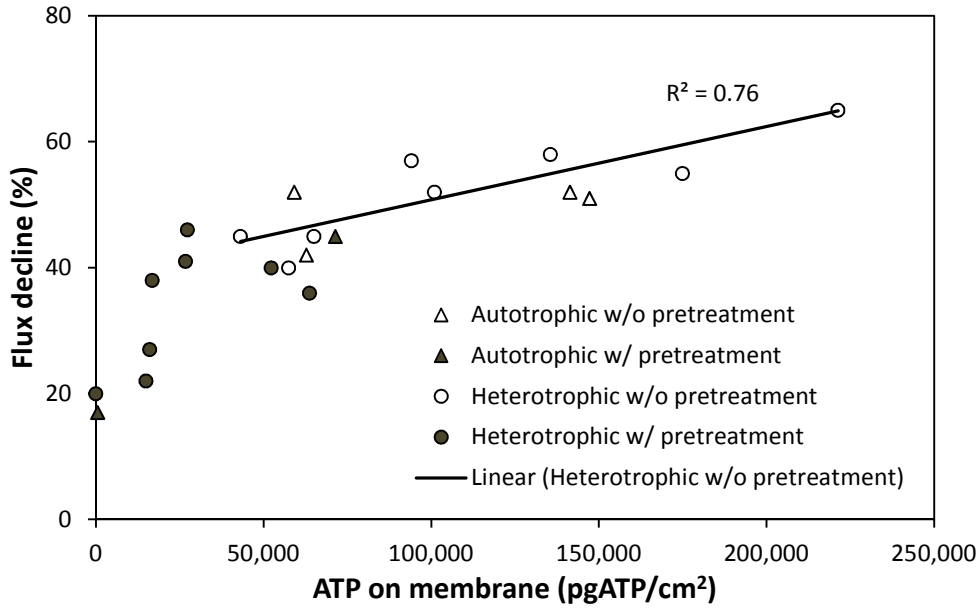


Figure 4-19 Relationship between ATP on the membrane and flux decline

Table 4-9 Correlation coefficients for the relationship between ATP and flux decline for metabolic conditions

Condition	Autotrophic condition		Heterotrophic condition		Both	
	w/o pre -treatment	w/ pre-treatment	w/o pre-treatment	w/ pre-treatment	w/o pre-treatment	w/ pre-treatment
No. of samples	4	2	8	8	12	10
R^2 (P-value)	0.25 (0.50)	Not enough samples	0.76 (0.005)	0.31 (0.15)	0.65 (0.002)	0.51 (0.02)

4.4.2 The Relationship of EPS on Membrane with Flux Decline

Since the number of samples of the autotrophic conditions was not enough, only the heterotrophic conditions were considered. On the membrane without pretreatment, there was no strong relationship between EPS and flux decline (Table 4-10). Figure 4-20 shows the relationship between EPS on the membrane and flux decline for the heterotrophic conditions when biofilter pretreatment was used. Even though EPS didn't have as strong a relationship as ATP did, free EPS showed a stronger relationship with flux decline than bound EPS.

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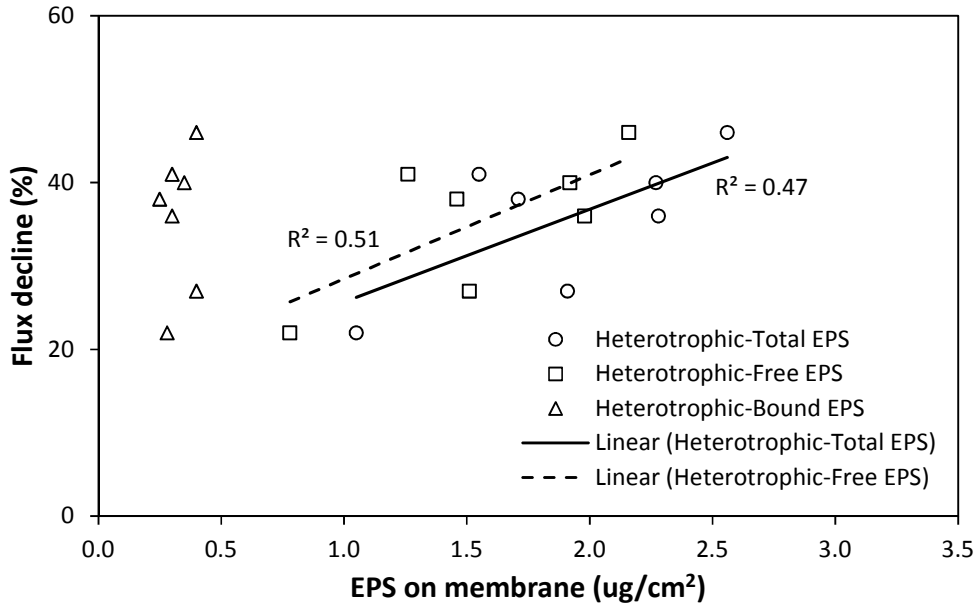

Figure 4-20 Relationship between EPS on the membrane and flux decline for heterotrophic conditions with pretreatment

Table 4-10 Correlation coefficients for the relationship between EPS and flux decline for heterotrophic conditions

Condition	Without pretreatment			With pretreatment		
	Total EPS	**Free EPS**	**Bound EPS**	**Total EPS**	**Free EPS**	**Bound EPS**
No. of samples	7	7	7	7	7	7
R^2 (P-value)	0.05 (0.62)	0.14 (0.82)	0.09 (0.55)	0.47 (0.09)	0.51 (0.07)	0.03 (0.70)

4.4.3 The Relationship of EPS Component with Flux Decline

Table 4-11 shows the correlation coefficients for the relationship between polysaccharides and proteins, and flux decline for the heterotrophic conditions. On membrane without pretreatment, there was no strong relationship for all polysaccharides and proteins. Meanwhile, on membrane with pretreatment, polysaccharides had a significant relationship with flux decline while there was no relationship with proteins. Figure 4-21 shows the relationship between polysaccharides on the membrane and flux decline for the heterotrophic conditions when pretreatment was used. Free polysaccharides among polysaccharides were more strongly correlated with flux decline than bound polysaccharides.

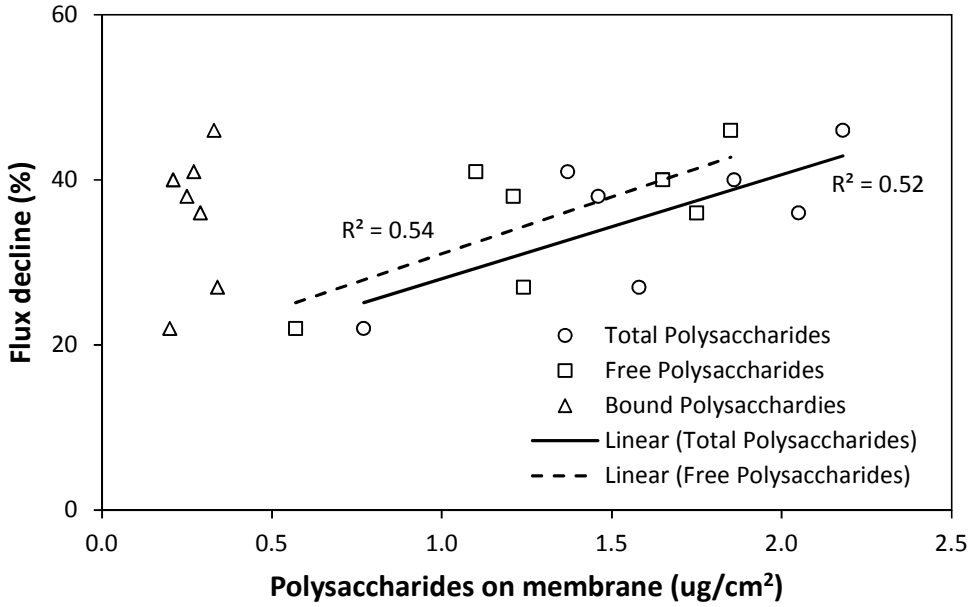

Figure 4-21 Relationship between polysaccharides on the membrane and flux decline for heterotrophic conditions with pretreatment

Table 4-11 Correlation coefficients for the relationship between polysaccharides and proteins, and flux decline for heterotrophic conditions

Condition		With pretreatment		With pretreatment	
		No. of samples	R^2	No. of samples	R^2
Polysaccharides	Free	8	0.16	7	0.54
	Bound	8	0	7	0.06
	Total	8	0.15	7	0.52
Proteins	Free	8	0.04	7	0.08
	Bound	8	0.16	7	0
	Total	8	0.26	7	0.02

4.4.4 The Relationship between ATP and EPS

The relationship between ATP and EPS was also developed. Figure 4-22 shows the relationship between them for the heterotrophic conditions on the membrane and on the biofilter. On the membrane without pretreatment, EPS was

inversely proportional to ATP with a correlation coefficient of 0.62. On the membrane with pretreatment, there was no relationship between them. On the biofilter, it was also observed that EPS was inversely proportional to ATP although correlation coefficient was not high.

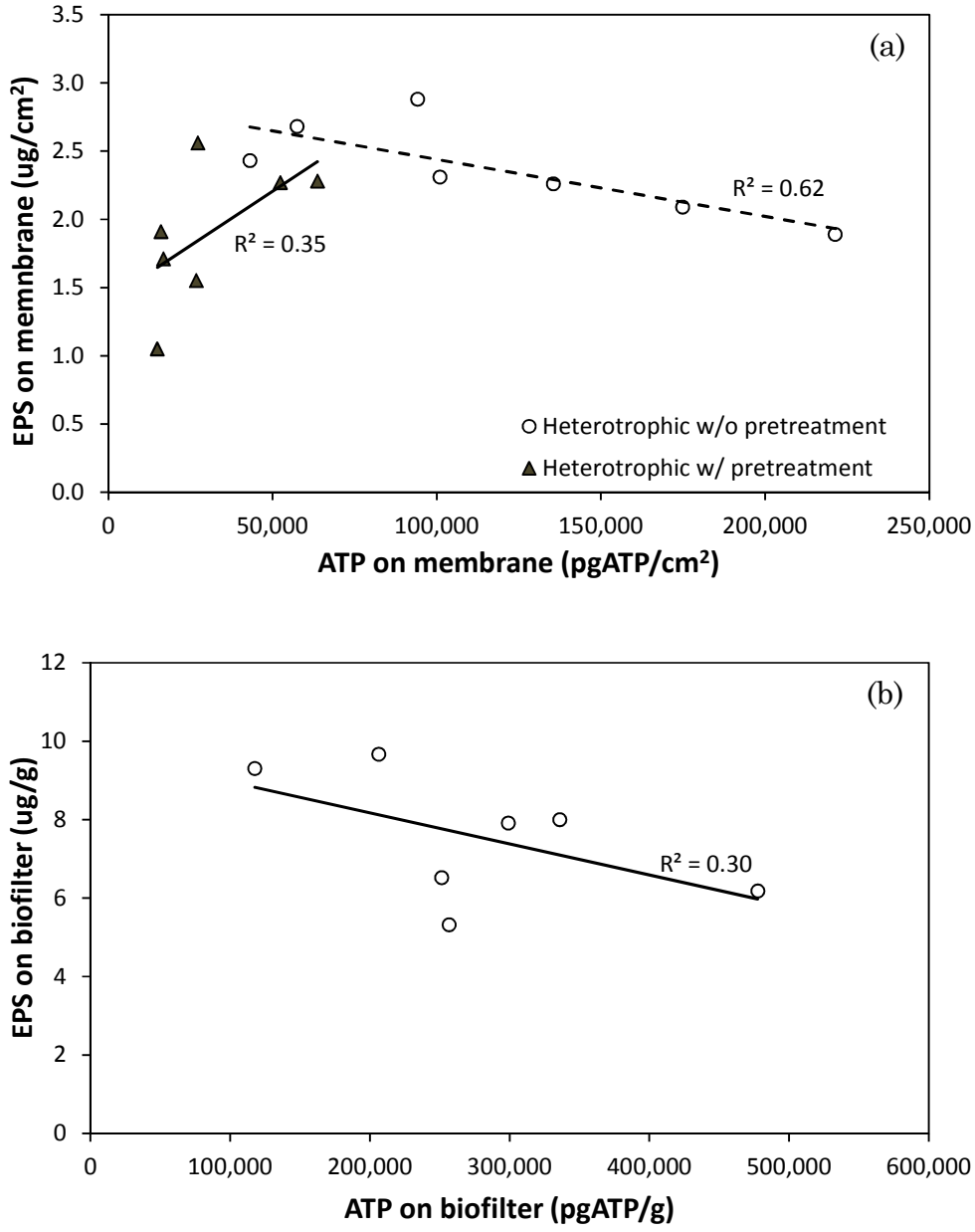

Figure 4-22 Relationship between ATP and EPS for heterotrophic conditions a) on the membrane b) on the biofilter

4.4.5 Summary

From parameter correlations between ATP, EPS, and flux decline, several relationships were developed for the heterotrophic conditions. On membrane without pretreatment, ATP and flux decline were linearly well correlated with a correlation coefficient of 0.76. On the other hand, on membrane with pretreatment, EPS showed a better relationship with flux decline than ATP; among EPS components, free polysaccharides had a significant relationship with flux decline. ATP and EPS were inversely proportional to each other on the membrane without pretreatment and on the biofilter.

CHAPTER 5

CONCLUSIONS

It has been known that biofouling can significantly affect membrane flux decline. In order to understand the effect of microbial conditions on membrane biofouling, metabolic and nutrient conditions were considered. In addition, biofiltration pretreatment was evaluated in each condition as a means of reducing flux decline.

First, the effect of metabolic conditions on membrane biofouling was evaluated. On the membrane without biofilter pretreatment, the autotrophic and heterotrophic conditions showed the same flux decline behavior although the seeding ATP concentration was 1.5 times larger in the autotrophic condition than in the heterotrophic condition. This is because heterotrophs under the balanced nutrient condition had a high growth rate and low EPS production. On the membrane with biofilter pretreatment, the biofilter significantly reduced the flux decline to around half of the flux decline without pretreatment for both conditions because the biofilter retained microorganisms and removed most of the substrates.

Second, the effect of five different nutrient conditions on membrane biofouling was assessed. On the membrane without pretreatment, the order of success in reducing flux decline was: N limited > P rich ≈ N rich ≈ P limited > balanced condition. The balanced condition yielded the highest compared to all unbalanced conditions because the balanced condition was the most favorable environment for the growth of microorganisms. On the membrane with biofilter pretreatment, the order of success in reducing flux decline was: balanced > N limited ≈ N rich ≈ P rich ≈ P limited condition. The balanced condition was better than all unbalanced conditions because the biofilter best controlled the substrate

under the balanced condition. Biofiltration pretreatment reduced the flux decline by over 40% under the balanced condition and by more or less 15% under all balanced conditions. It is remarkable that biofiltration pretreatment didn't yield additional flux decline in every condition considered. In addition, it was observed that C/N and C/P ratios impacted the production of ATP and EPS which caused membrane biofouling. At C/N=10 or C/P=100 which is the balanced condition, ATP was the highest on the biofilter and on the membrane without pretreatment while it was the lowest on the membrane with pretreatment. EPS was the lowest at the same C/N or C/P ratio in all conditions.

Lastly, regression analyses were conducted to understand relationships between ATP, EPS, and flux decline for the heterotrophic conditions. On the membrane without pretreatment, there was a strong relationship, R^2=0.76, between ATP and flux decline. On the membrane with pretreatment, EPS gave a better correlation, R^2=0.51, with flux decline than ATP. EPS was inversely proportional to ATP with a correlation coefficient of 0.62 on the membrane without pretreatment.

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Appendix A: Membrane Flux with Time

Membrane flux with time for each experiment is summarized in following tables. To adjust temperature change, all fluxes were converted to standardized fluxes at 20 ℃ using following equation (MWH, 2005).

$$J_s = J_m\ (1.03)^{(Ts-Tm)}$$

Here, T_m : measured temperature, T_s : standard temperature (20℃), J_m : flux at measured temperature, J_s : standard flux at 20℃

Cases			Temperature	Initial values			Related Figure
				Flow rate	Jm	Js	
1			22.0	5.00	0.120	0.113	Figure 4-1
2	a)		23.5	6.80	0.163	0.147	Figure 4-2
	b)		23.0	6.90	0.165	0.151	
	c)		21.5	5.70	0.136	0.130	
3	a)		21.9	5.73	0.137	0.130	Figure 4-3
	b)		23.5	6.23	0.149	0.134	
	c)		22.0	6.80	0.163	0.153	
4	a)		21.7	5.80	0.139	0.132	Figure 4-4
	b)		22.2	8.57	0.205	0.192	
	c)		22.5	7.13	0.171	0.158	
5	1st EXP	w/ PT	22.0	6.33	0.152	0.143	Figure 4-6
		w/o PT	22.0	6.10	0.146	0.138	
	2nd EXP	w/ PT	22.0	6.43	0.154	0.145	
		w/o PT	22.0	6.47	0.155	0.146	
6	Autotrophic	w/ PT	22.0	5.63	0.135	0.127	Figure 4-12
		w/o PT	22.0	5.60	0.134	0.126	
	Heterotrophic	w/ PT	22.0	6.33	0.152	0.143	
		w/o PT	22.0	6.10	0.146	0.138	
7	Balanced	w/ PT	22.0	6.43	0.154	0.145	Figure 4-17
		w/o PT	22.0	6.47	0.155	0.146	
	N rich	w/ PT	22.0	6.30	0.151	0.142	
		w/o PT	22.0	5.83	0.140	0.132	
	N limited	w/ PT	17.5	5.07	0.121	0.131	
		w/o PT	17.5	5.07	0.121	0.131	
	P rich	w/ PT	23.0	6.73	0.161	0.147	
		w/o PT	23.0	6.53	0.156	0.143	
	P limited	w/ PT	20.0	6.07	0.145	0.145	
		w/o PT	20.0	5.47	0.131	0.131	

1. Membrane flux with time by DI water and DTW (Figure 4-1)

Period	Accumulated hours	V (mL)	Flow rate (mL/min)	T (℃)	Measured		Standardized	
					Jm	J/J0	Js	J/J0
Initial Flux (Jo)	0.0	150	5.00	22.0	0.120	1.00	0.113	1.00
DI, 9/19 19:31 ~ 22:30	3.0	885	4.97	22.2	0.119	0.99	0.111	0.99
22:32 ~ 9/20 08:26	12.9	2,965	4.98	22.2	0.119	1.00	0.112	0.99
08:35 ~ 13:14	17.6	1,420	5.04	22.5	0.120	1.01	0.112	0.99
13:16 ~ 16:16	20.6	905	5.03	22.0	0.120	1.01	0.113	1.01
DCT, 16:28 ~ 16:49	20.9	123	5.86	22.0	0.140	1.17	0.132	1.17
16:49 ~ 20:08	24.3	1,182	5.91	22.0	0.141	1.18	0.133	1.18
20:27 ~ 9/21 08:31	36.4	4,255	5.87	22.2	0.140	1.17	0.132	1.17
08:37 ~ 18:22	46.0	3,350	5.77	22.0	0.138	1.15	0.130	1.15
18:28 ~ 21:53	49.5	1,175	5.70	22.5	0.136	1.14	0.127	1.12
21:58 ~ 9/22 09:37	61.1	3,820	5.46	22.5	0.131	1.09	0.121	1.08
09:43 ~ 21:17	72.7	3,460	4.98	22.6	0.119	1.00	0.110	0.98
21:23 ~ 9/23 08:46	84.1	3,080	4.51	22.9	0.108	0.90	0.099	0.88
08:52 ~ 17:22	92.6	2,155	4.22	22.9	0.101	0.84	0.093	0.82
17:28 ~ 9/24 10:19	109.5	4,020	3.98	22.9	0.095	0.80	0.087	0.77

2. Membrane flux with time by (a) BEM water (TOC=3 mg/L), (b) DTW with 1 mgC/L nutrients, (c) DTW with no nutrients (Figure 4-2)

(a) BEM water (TOC=3 mg/L)

Period	Accumulated hours	V (mL)	Flow rate (mL/min)	T (℃)	Measured		Standardized	
					Jm	J/J0	Js	J/J0
Initial Flux(Jo)	0.0	68	6.80	23.5	0.163	1.00	0.147	1.00
8/23 17:45 ~ 8/23 21:39	3.9	1,540	6.58	23.5	0.157	0.97	0.142	0.97
8/23 21:50 ~ 8/24 07:15	13.3	3,380	5.98	23.5	0.143	0.88	0.129	0.88
8/24 07:28 ~ 8/24 17:36	23.4	3,410	5.63	23.5	0.135	0.83	0.121	0.83
8/24 17:43 ~ 8/24 21:48	27.4	1,290	5.35	23.5	0.128	0.79	0.115	0.79
8/24 21:54 ~ 8/25 09:08	38.7	3,290	4.88	23.5	0.117	0.72	0.105	0.72
8/25 09:16 ~ 8/25 19:13	48.6	2,650	4.45	24.0	0.107	0.65	0.095	0.65
8/25 19:17 ~ 8/26 09:29	62.8	3,500	4.11	24.0	0.098	0.60	0.087	0.60
8/26 09:34 ~ 8/26 11:00	64.2	350	4.07	24.0	0.097	0.60	0.087	0.59
8/26 11:09 ~ 8/26 13:10	66.2	560	4.67	23.5	0.112	0.69	0.101	0.69
8/26 13:13 ~ 8/26 15:39	68.7	600	4.11	23.5	0.098	0.60	0.089	0.60
8/26 15:42 ~ 8/26 17:57	70.9	550	4.10	24.0	0.098	0.60	0.087	0.59
8/26 18:01 ~ 8/27 08:49	85.7	3,570	4.02	24.0	0.096	0.59	0.085	0.58
8/27 08:57 ~8/27 18:30	95.1	2,150	3.83	23.5	0.092	0.56	0.083	0.56
8/27 18:40 ~8/28 09:10	109.5	3,220	3.71	24.0	0.089	0.54	0.079	0.54
8/28 09:16 ~ 8/28 17:37	117.9	1,850	3.69	20.5	0.088	0.54	0.087	0.59
8/28 17:44 ~ 8/29 08:57	133.1	3,180	3.49	24.5	0.083	0.51	0.073	0.50
8/29 09:03 ~ 8/29 18:24	142.4	1,960	3.49	24.0	0.084	0.51	0.074	0.51
8/29 18:31 ~ 8/30 09:27	157.4	3,040	3.39	24.0	0.081	0.50	0.072	0.49

(b) DTW with 1 mgC/L nutrients

Period	Accumulated hours	V (mL)	Flow rate (mL/min)	T (℃)	Measured		Standardized	
					Jm	J/J0	Js	J/J0
Initial Flux(Jo)	0.0	207	6.90	23.0	0.165	1.00	0.151	1.00
DI, 9/4 10:40 ~ 9/4 11:10	0.5	204	6.80	23.0	0.163	0.99	0.149	0.99
9/4 11:12 ~ 9/4 17:07	6.4	2,280	6.46	23.0	0.155	0.94	0.141	0.94
9/4 17:13 ~ 9/4 22:32	11.7	2,020	6.33	23.0	0.151	0.92	0.139	0.92
9/4 22:38 ~ 9/5 09:13	22.3	3,850	6.06	23.0	0.145	0.88	0.133	0.88
9/5 09:19 ~ 9/5 18:25	31.4	3,140	5.76	23.0	0.138	0.83	0.126	0.83
9/5 18:32 ~ 9/5 21:43	34.6	1,050	5.47	23.0	0.131	0.79	0.120	0.79
9/5 21:50 ~ 9/6 09:15	46.0	3,890	5.67	24.0	0.136	0.82	0.121	0.80
9/6 09:22 ~ 9/6 12:37	49.3	1,120	5.74	24.0	0.137	0.83	0.122	0.81
9/6 12:45 ~ 9/6 14:54	51.5	770	5.75	24.5	0.137	0.83	0.120	0.80
Pressure off for 30mins	51.7	58	5.80	24.5	0.139	0.84	0.121	0.80
and start over	52.0	114	5.70	24.5	0.136	0.83	0.119	0.79
9/6 16:25 ~9/6 18:26	54.1	700	5.60	24.5	0.134	0.81	0.117	0.78
9/6 18:29 ~ 9/6 21:31	57.1	1,080	5.90	23.5	0.141	0.86	0.127	0.84
9/6 21:38 ~ 9/7 08:52	68.4	4,010	5.94	22.5	0.142	0.86	0.132	0.87
Run DI after disinfecting	68.9	226	6.65	22.5	0.159	0.96	0.148	0.98
pressure vessel and tube	69.5	210	6.36	22.5	0.152	0.92	0.141	0.94
	70.5	375	6.25	22.5	0.150	0.91	0.139	0.92
	71.5	370	6.17	22.5	0.148	0.89	0.137	0.91
	73.6	785	6.13	23.0	0.147	0.89	0.134	0.89
	75.6	735	6.13	23.0	0.147	0.89	0.134	0.89
	79.9	1,600	6.23	23.0	0.149	0.90	0.136	0.90
	89.3	3,460	6.12	23.0	0.147	0.89	0.134	0.89
	93.9	1,700	6.18	23.0	0.148	0.90	0.135	0.90
DI with 1mgC/L acetate 9/8 12:09 ~ 9/8 13:40	95.4	535	5.82	22.5	0.139	0.84	0.129	0.86
9/8 13:43 ~ 9/8 15:03	96.8	450	5.70	22.5	0.136	0.83	0.127	0.84
9/8 :15:04 ~ 9/8 16:32	98.2	510	5.73	22.5	0.137	0.83	0.127	0.84
9/8 16:34 ~ 9/8 18:05	99.8	535	5.82	23.0	0.139	0.84	0.127	0.84
9/8 18:08 ~ 9/8 19:30	101.2	485	5.84	23.0	0.140	0.85	0.128	0.85
9/8 19:31 ~ 9/8 21:43	103.4	800	6.06	23.0	0.145	0.88	0.133	0.88
9/8 21: 45 ~ 9/8 22:46	104.4	370	6.17	23.0	0.148	0.89	0.135	0.89
9/8 22:58 ~ 9/9 08:25	113.8	3,440	6.08	22.5	0.145	0.88	0.135	0.89
9/9 08:30 ~ 9/9 10:18	115.6	680	6.13	22.5	0.147	0.89	0.136	0.90
DTW, 9/9 10:27 ~ 9/9 11:29	116.7	450	7.38	22.5	0.176	1.07	0.164	1.09
9/9 11:32 ~ 9/9 12:35	117.7	460	7.30	22.5	0.175	1.06	0.162	1.07
9/9 12:36 ~ 9/9 14:35	119.7	865	7.21	22.5	0.172	1.04	0.160	1.06
9/9 14:37 ~ 9/9 16:02	121.1	605	7.12	21.5	0.170	1.03	0.163	1.08
9/9 16:05 ~ 9/9 19:11	124.2	1,270	6.86	20.0	0.164	0.99	0.164	1.09
9/9 19:13 ~ 9/9 22:39	127.6	1,400	6.80	22.5	0.163	0.98	0.151	1.00
9/9 22:45 ~ 9/10 08:27	137.3	3,960	6.80	22.0	0.163	0.99	0.153	1.02
9/10 08:35 ~ 9/10 12:21	141.1	1,480	6.55	21.5	0.157	0.95	0.150	0.99
9/10 12:25 ~ 9/10 14:31	143.2	770	6.16	20.0	0.147	0.89	0.147	0.98
9/10 14:33 ~ 9/10 16:46	145.4	820	6.17	22.0	0.147	0.89	0.139	0.92
9/10 16:49 ~ 9/10 17:49	146.4	370	6.17	22.0	0.148	0.89	0.139	0.92
9/10 17:52 ~ 9/10 20:55	149.5	1,180	6.45	22.5	0.154	0.93	0.143	0.95

9/10 20:57 ~ 22:31	151.0	590	6.34	22.5	0.152	0.92	0.141	0.93
9/10 22:36 ~ 9/11 08:46	161.2	3,750	6.14	22.5	0.147	0.89	0.136	0.90
9/11 08:48 ~ 09:16	161.6	165	6.11	22.5	0.146	0.89	0.136	0.90
DTW with microbes and 1mgC/L acetate 9/11 09:41 ~ 10:25	162.4	267	5.93	22.5	0.142	0.86	0.132	0.87
9/11 10:28 ~ 12:35	164.5	660	5.12	22.5	0.122	0.74	0.114	0.75
9/11 12:38 ~ 15:18	167.2	750	4.66	22.0	0.111	0.68	0.105	0.70
9/11 15:21 ~ 19:01	170.9	980	4.43	22.0	0.106	0.64	0.100	0.66
9/11 19:05 ~ 9/12 09:10	185.2	3,460	4.04	22.0	0.097	0.59	0.091	0.60
9/12 09:13 ~ 11:40	187.5	520	3.80	22.0	0.091	0.55	0.086	0.57
9/12 11:46 ~ 16:13	191.9	1,020	3.83	22.0	0.092	0.56	0.086	0.57
9/12 16:15 ~ 18:14	193.9	440	3.70	22.0	0.088	0.54	0.083	0.55
9/12 18:18 ~ 9/13 09:39	209.2	3,270	3.55	22.0	0.085	0.52	0.080	0.53
9/13 09:44 ~ 17:58	217.5	1,680	3.39	22.0	0.081	0.49	0.077	0.51
9/13 18:04 ~ 9/14 09:03	232.8	2,900	3.16	23.0	0.076	0.46	0.069	0.46

(c) DTW with no nutrients

Period	Accumulated hours	V (mL)	Flow rate (mL/min)	T (℃)	Measured		Standardized	
					Jm	J/J0	Js	J/J0
Initial Flux(Jo)	0.0	171	5.70	21.5	0.136	1.00	0.130	1.00
2/11/14 14:33 ~ 21:23	6.8	2,325	5.70	21.5	0.136	1.00	0.130	1.00
21:25 ~ 2/12 09:19	18.7	3,950	5.54	23.0	0.133	0.97	0.121	0.93
09:20 ~ 17:33	26.9	2,420	4.91	20.5	0.117	0.86	0.116	0.89
14:43 ~ 2/13 09:03	42.3	3,890	4.22	21.5	0.101	0.74	0.097	0.74
09:05 ~ 16:49	50.0	1,800	3.89	21.0	0.093	0.68	0.090	0.69
16:51 ~ 2/14 09:11	66.3	3,390	3.46	21.0	0.083	0.61	0.080	0.62
09:17 ~ 14:59	72.0	1,120	3.27	21.0	0.078	0.57	0.076	0.58

3. Membrane flux with time with different seeding concentrations (Figure 4-3)

(a) 2g biomass (1mgC/L)

Period	Accumulated hours	V (mL)	Flow rate (mL/min)	T (℃)	Measured		Standardized	
					Jm	J/J0	Js	J/J0
Initial Flux(Jo)	0.0	172	5.73	21.9	0.1372	1.00	0.130	1.00
9/27 20:22 ~ 20:52	0.5	176	5.87	21.9	0.1404	1.02	0.133	1.02
20:52 ~ 9/28 07:02	10.7	3,190	5.23	22.0	0.1251	0.91	0.118	0.91
07:09 ~ 20:40	24.2	3,980	4.91	23.5	0.1174	0.86	0.106	0.82
20:46 ~ 9/29 08:58	36.4	3,420	4.67	23.0	0.1118	0.81	0.102	0.79
09:01 ~ 17:21	44.7	2,210	4.41	20.5	0.1055	0.77	0.104	0.80
17:26 ~ 9/30 08:35	59.9	3,740	4.12	24.0	0.0985	0.72	0.088	0.68
08:37 ~ 16:28	67.7	1,840	3.92	21.0	0.0939	0.68	0.091	0.70
16:28 ~ 20:33	71.8	900	3.67	21.9	0.0879	0.64	0.083	0.64

(b) 4g biomass (1mgC/L)

Period	Accumulated hours	V (mL)	Flow rate (mL/min)	T (℃)	Measured		Standardized	
					Jm	J/J0	Js	J/J0
Initial Flux(Jo)	0.0	187	6.23	23.5	0.1491	1.00	0.134	1.00
9/30 22:23 ~ 20:53	0.5	201	6.70	23.5	0.1603	1.07	0.145	1.07
20:53 ~ 10/1 08:25	10.0	3,620	6.33	23.0	0.1514	1.02	0.139	1.03
08:29 ~ 11:33	13.1	1,130	6.11	23.0	0.1461	0.98	0.134	0.99
11:40 ~ 15:52	17.4	1,470	5.76	22.0	0.1379	0.92	0.130	0.97
15:54 ~ 21:21	22.8	1,860	5.69	22.0	0.1361	0.91	0.128	0.95
21:23 ~ 10/2 09:15	34.5	3,840	5.46	22.0	0.1307	0.88	0.123	0.92

(c) 2g biomass (10mgC/L, N&P)

Period	Accumulated hours	V (mL)	Flow rate (mL/min)	T (℃)	Measured		Standardized	
					Jm	J/J0	Js	J/J0
Initial Flux(Jo)	0.0	204	6.80	22.0	0.1627	1.00	0.153	1.00
10/3 15:26 ~ 21:44	6.3	2,425	6.43	19.3	0.1539	0.95	0.157	1.02
21:47 ~ 10/4 08:33	17.1	3,780	5.84	21.5	0.1398	0.86	0.134	0.91
08:35 ~ 11:49	20.3	1,120	5.83	21.5	0.1396	0.86	0.134	0.91
11:51 ~ 13:12	21.6	453	5.66	20.5	0.1355	0.83	0.133	0.91
Adding N&P 13:16 ~ 16:37	25.0	1,120	5.54	22.2	0.1326	0.82	0.124	0.85
16:40 ~ 23:11	31.5	2,080	5.31	22.5	0.1269	0.78	0.118	0.80
23:22 ~ 10/5 10:42	42.9	2,750	4.04	20.3	0.0966	0.59	0.096	0.65
10:47 ~ 22:09	54.2	1,930	2.83	24.2	0.0677	0.42	0.060	0.41
22:13 ~ 10/6 09:45	65.7	1,450	2.10	21.5	0.0502	0.31	0.048	0.33
09:48 ~ 10/7 08:27	88.4	2,030	1.49	23.0	0.0357	0.22	0.033	0.22

4. Membrane flux with time at different organic carbon concentrations under balanced condition (Figure 4-4)

(a) 1 mgC/L

Period	Accumulated hours	V (mL)	Flow rate (mL/min)	T (℃)	Measured		Standardized	
					Jm	J/J0	Js	J/J0
Initial Flux(Jo)	0.0	174	5.80	21.7	0.139	1.00	0.132	1.00
10/11 15:14 ~ 21:11	6.0	1,940	5.43	21.7	0.130	0.94	0.124	0.94
21:15 ~ 10/12 09:43	18.4	3,740	5.00	21.4	0.120	0.86	0.115	0.87
09:47 ~ 23:31	32.1	3,420	4.16	21.7	0.099	0.72	0.095	0.72
23:33 ~ 10/13 08:45	41.3	1,900	3.45	22.0	0.082	0.59	0.078	0.59
08:47 ~ 21:02	53.6	2,225	3.03	22.7	0.072	0.52	0.067	0.51
21:07 ~ 10/14 08:54	65.4	1,930	2.73	21.5	0.065	0.47	0.062	0.47
08:56 ~ 15:37	72.1	1,020	2.54	21.5	0.061	0.44	0.058	0.44
15:39 ~ 18:18	74.7	395	2.47	22.0	0.059	0.43	0.056	0.42
18:29 ~ 10/15 08:45	89.0	2,080	2.43	22.0	0.058	0.42	0.055	0.42
08:47 ~ 16:19	96.5	1,050	2.32	21.5	0.056	0.40	0.053	0.40

(b) 3 mgC/L

Period	Accumulated hours	V (mL)	Flow rate (mL/min)	T	Measured		Standardized	
					Jm	J/J0	Js	J/J0
Initial Flux(Jo)	0.0	257	8.57	22.2	0.205	1.00	0.192	1.00
10/8 15:05 ~ 22:00	7.0	2,560	6.14	22.0	0.147	0.72	0.138	0.72
22:05 ~ 10/9 08:58	17.8	2,640	4.04	22.0	0.097	0.47	0.091	0.47
09:01 ~ 14:31	23.3	980	2.97	22.0	0.071	0.35	0.067	0.35
14:36 ~ 18:14	27.0	590	2.69	22.0	0.064	0.31	0.061	0.32
18:18 ~ 21:11	29.9	425	2.44	22.0	0.058	0.29	0.055	0.29

(c) 10 mgC/L

Period	Accumulated hours	V (mL)	Flow rate (mL/min)	T	Measured		Standardized	
					Jm	J/J0	Js	J/J0
Initial Flux(Jo)	0.0	214	7.13	22.5	0.171	1.00	0.158	1.00
10/7 13:55 ~ 21:58	8.0	2,950	6.12	22.2	0.146	0.86	0.137	0.87
22:01 ~ 10/8 09:48	19.8	2,220	3.14	22.0	0.075	0.44	0.071	0.45

5. Membrane flux with time for duplicate experiments (Figure 4-6)

(a) 1st experiment

○ With pretreatment

Period	Accumulated hours	V (mL)	Flow rate (mL/min)	T	Measured		Standardized	
					Jm	J/J0	Js	J/J0
Initial Flux(Jo)	0.0	190	6.33	22.0	0.152	1.00	0.143	1.00
12/2 09:31 ~ 17:17	7.8	2,810	6.02	22.5	0.144	0.95	0.134	0.94
17:24 ~ 12/3 10:24	24.7	5,800	5.71	22.5	0.137	0.90	0.127	0.89
10:30 ~ 17:37	31.7	2,230	5.28	22.5	0.126	0.83	0.117	0.82
17:42 ~ 12/4 09:22	47.4	4,720	5.02	25.0	0.120	0.79	0.104	0.73
09:31 ~ 18:33	56.4	2,700	4.98	21.5	0.119	0.79	0.114	0.80
18:39 ~ 12/5 10:15	72.0	4,230	4.52	21.0	0.108	0.71	0.105	0.73

○ Without pretreatment

Period	Accumulated hours	V (mL)	Flow rate (mL/min)	T	Measured		Standardized	
					Jm	J/J0	Js	J/J0
Initial Flux(Jo)	0.0	183	6.10	22.0	0.146	1.00	0.138	1.00
10/29 10:12 ~ 17:03	6.8	2,480	6.06	23.0	0.145	0.99	0.133	0.97
17:09 ~ 10/30 09:45	23.4	4,690	4.72	23.5	0.113	0.77	0.102	0.74
09:48 ~ 19:03	32.7	1,940	3.49	21.0	0.083	0.57	0.081	0.59
19:13 ~ 10/31 10:08	47.6	2,640	2.95	21.5	0.071	0.48	0.068	0.49
10:15 ~ 16:47	54.1	1,110	2.82	22.0	0.067	0.46	0.064	0.46
16:53 ~ 11/1 10:48	72.0	2,850	2.65	23.5	0.063	0.44	0.057	0.42

(b) 2nd experiment

○ With pretreatment

Period	Accumulated hours	V (mL)	Flow rate (mL/min)	T	Measured		Standardized	
					Jm	J/J0	Js	J/J0
Initial Flux(Jo)	0.0	193	6.43	22.0	0.154	1.00	0.145	1.00
11/5 10:25 ~ 18:39	8.2	3,000	6.07	24.0	0.145	0.94	0.129	0.89
18:47 ~ 11/6 09:08	22.6	4,760	5.53	22.0	0.132	0.86	0.125	0.86
09:15 ~ 16:31	29.8	2,270	5.21	22.0	0.125	0.81	0.117	0.81
16:40 ~ 11/7 10:21	47.5	5,190	4.89	21.5	0.117	0.76	0.112	0.77
10:27 ~ 18:37	55.7	2,430	4.96	22.0	0.119	0.77	0.112	0.77
18:43 ~ 11/8 11:02	72.0	4,930	5.04	22.0	0.121	0.78	0.114	0.78

○ Without pretreatment

Period	Accumulated hours	V (mL)	Flow rate (mL/min)	T	Measured		Standardized	
					Jm	J/J0	Js	J/J0
Initial Flux(Jo)	0.0	194	6.47	22.0	0.155	1.00	0.146	1.00
11/5 10:25 ~ 18:39	8.2	3,050	6.17	24.0	0.148	0.95	0.131	0.90
18:47 ~ 11/6 09:08	22.6	4,780	5.56	22.0	0.133	0.86	0.125	0.86
09:15 ~ 16:31	29.8	2,030	4.66	22.0	0.111	0.72	0.105	0.72
16:40 ~ 11/7 10:21	47.5	3,380	3.19	21.5	0.076	0.49	0.073	0.50
10:27 ~ 18:37	55.7	1,260	2.57	22.0	0.062	0.40	0.058	0.40
18:43 ~ 11/8 11:02	72.0	2,230	2.28	22.0	0.055	0.35	0.051	0.35

6. Membrane flux with time for metabolic conditions without and with pretreatment (Figure 4-12)

(a) Autotrophic condition

○ with pretreatment

Period	Accumulated hours	V (mL)	Flow rate (mL/min)	T	Measured		Standardized	
					Jm	J/J0	Js	J/J0
Initial Flux(Jo)	0.0	169	5.63	22.0	0.135	1.00	0.127	1.00
11/23 20:20 ~ 11/24 11:44	15.4	5,220	5.66	25.0	0.135	1.01	0.117	0.92
11:47 ~ 19:37	23.2	2,280	4.85	25.0	0.116	0.86	0.100	0.79
19:50 ~ 11/25 10:20	37.7	4,030	4.64	27.0	0.111	0.82	0.090	0.71
10:23 ~ 16:25	43.7	1,590	4.38	22.0	0.105	0.78	0.099	0.78
16:33 ~ 11/26 10:10	61.3	4,600	4.35	23.0	0.104	0.77	0.095	0.75
10:16 ~ 20:58	72.0	2,670	4.16	22.0	0.099	0.74	0.094	0.74

○ without pretreatment

Period	Accumulated hours	V (mL)	Flow rate (mL/min)	T	Measured		Standardized	
					Jm	J/J0	Js	J/J0
Initial Flux(Jo)	0.0	168	5.60	22.0	0.134	1.00	0.126	1.00
11/23 20:20 ~ 11/24 11:44	15.4	4,900	5.31	25.0	0.127	0.95	0.110	0.87
11:47 ~ 19:37	23.2	1,960	4.17	25.0	0.100	0.74	0.086	0.68
19:50 ~ 11/25 10:20	37.7	3,270	3.77	27.0	0.090	0.67	0.073	0.58
10:23 ~ 16:25	43.7	1,230	3.39	22.0	0.081	0.61	0.076	0.61

16:33 ~ 11/26 10:10	61.3	3,270	3.09	23.0	0.074	0.55	0.068	0.54
10:16 ~ 20:58	72.0	1,750	2.73	22.0	0.065	0.49	0.061	0.49

(b) Heterotrophic condition

○ With pretreatment

Period	Accumulated hours	V (mL)	Flow rate (mL/min)	T	Measured		Standardized	
					Jm	J/J0	Js	J/J0
Initial Flux(Jo)	0.0	190	6.33	22.0	0.152	1.00	0.143	1.00
12/2 09:31 ~ 17:17	7.8	2,810	6.02	22.5	0.144	0.95	0.134	0.94
17:24 ~ 12/3 10:24	24.7	5,800	5.71	22.5	0.137	0.90	0.127	0.89
10:30 ~ 17:37	31.7	2,230	5.28	22.5	0.126	0.83	0.117	0.82
17:42 ~ 12/4 09:22	47.4	4,720	5.02	25.0	0.120	0.79	0.104	0.73
09:31 ~ 18:33	56.4	2,700	4.98	21.5	0.119	0.79	0.114	0.80
18:39 ~ 12/5 10:15	72.0	4,230	4.52	21.0	0.108	0.71	0.105	0.73

○ Without pretreatment

Period	Accumulated hours	V (mL)	Flow rate (mL/min)	T	Measured		Standardized	
					Jm	J/J0	Js	J/J0
Initial Flux(Jo)	0.0	183	6.10	22.0	0.146	1.00	0.138	1.00
10/29 10:12 ~ 17:03	6.8	2,480	6.06	23.0	0.145	0.99	0.133	0.97
17:09 ~ 10/30 09:45	23.4	4,690	4.72	23.5	0.113	0.77	0.102	0.74
09:48 ~ 19:03	32.7	1,940	3.49	21.0	0.083	0.57	0.081	0.59
19:13 ~ 10/31 10:08	47.6	2,640	2.95	21.5	0.071	0.48	0.068	0.49
10:15 ~ 16:47	54.1	1,110	2.82	22.0	0.067	0.46	0.064	0.46
16:53 ~ 11/1 10:48	72.0	2,850	2.65	23.5	0.063	0.44	0.057	0.42

7. Membrane flux with time for 5 different nutrient conditions without and with pretreatment (Figure 4-17)

(a) Balanced condition

○ With pretreatment

Period	Accumulated hours	V (mL)	Flow rate (mL/min)	T	Measured		Standardized	
					Jm	J/J0	Js	J/J0
Initial Flux(Jo)	0.0	193	6.43	22.0	0.154	1.00	0.145	1.00
11/5 10:25 ~ 18:39	8.2	3,000	6.07	24.0	0.145	0.94	0.129	0.89
18:47 ~ 11/6 09:08	22.6	4,760	5.53	22.0	0.132	0.86	0.125	0.86
09:15 ~ 16:31	29.8	2,270	5.21	22.0	0.125	0.81	0.117	0.81
16:40 ~ 11/7 10:21	47.5	5,190	4.89	21.5	0.117	0.76	0.112	0.77
10:27 ~ 18:37	55.7	2,430	4.96	22.0	0.119	0.77	0.112	0.77
18:43 ~ 11/8 11:02	72.0	4,930	5.04	22.0	0.121	0.78	0.114	0.78

○ Without pretreatment

Period	Accumulated hours	V (mL)	Flow rate (mL/min)	T	Measured		Standardized	
					Jm	J/J0	Js	J/J0
Initial Flux(Jo)	0.0	194	6.47	22.0	0.155	1.00	0.146	1.00
11/5 10:25 ~ 18:39	8.2	3,050	6.17	24.0	0.148	0.95	0.131	0.90
18:47 ~ 11/6 09:08	22.6	4,780	5.56	22.0	0.133	0.86	0.125	0.86
09:15 ~ 16:31	29.8	2,030	4.66	22.0	0.111	0.72	0.105	0.72
16:40 ~ 11/7 10:21	47.5	3,380	3.19	21.5	0.076	0.49	0.073	0.50
10:27 ~ 18:37	55.7	1,260	2.57	22.0	0.062	0.40	0.058	0.40
18:43 ~ 11/8 11:02	72.0	2,230	2.28	22.0	0.055	0.35	0.051	0.35

(b) N rich condition

○ With pretreatment

Period	Accumulated hours	V (mL)	Flow rate (mL/min)	T	Measured		Standardized	
					Jm	J/J0	Js	J/J0
Initial Flux(Jo)	0.0	189	6.30	22.0	0.151	1.00	0.142	1.00
11/11 09:19 ~ 17:08	7.8	2,860	6.10	22.0	0.146	0.97	0.138	0.97
17:15 ~ 11/12 10:17	24.9	5,310	5.20	22.0	0.124	0.82	0.117	0.82
10:27 ~ 16:36	31.0	1,730	4.69	22.0	0.112	0.74	0.106	0.74
16:44 ~ 11/13 11:17	49.5	4,530	4.07	22.0	0.097	0.65	0.092	0.65
11:21 ~ 17:22	55.6	1,430	3.95	22.0	0.095	0.63	0.089	0.63
17:31 ~ 11/14 09:55	72.0	3,830	3.89	22.0	0.093	0.62	0.088	0.62

○ Without pretreatment

Period	Accumulated hours	V (mL)	Flow rate (mL/min)	T	Measured		Standardized	
					Jm	J/J0	Js	J/J0
Initial Flux(Jo)	0.0	175	5.83	22.0	0.140	1.00	0.132	1.00
11/11 09:19 ~ 17:08	7.8	2,740	5.84	22.0	0.140	1.00	0.132	1.00
17:15 ~ 11/12 10:17	24.9	4,970	4.86	22.0	0.116	0.83	0.110	0.83
10:27 ~ 16:36	31.0	1,330	3.60	22.0	0.086	0.62	0.081	0.62
16:44 ~ 11/13 11:17	49.5	3,230	2.90	21.5	0.069	0.50	0.066	0.51
11:21 ~ 17:22	55.6	980	2.71	21.5	0.065	0.46	0.062	0.47
17:31 ~ 11/14 09:55	72.0	2,570	2.61	22.0	0.062	0.45	0.059	0.45

(c) N limited condition

○ With pretreatment

Period	Accumulated hours	V (mL)	Flow rate (mL/min)	T	Measured		Standardized	
					Jm	J/J0	Js	J/J0
Initial Flux(Jo)	0.0	152	5.07	17.5	0.121	1.00	0.131	1.00
12/9 09:38 ~ 16:00	6.4	1,950	5.12	18.0	0.122	1.01	0.130	1.00
16:04 ~ 12/10 09:10	23.5	4,945	4.82	19.0	0.115	0.95	0.119	0.91
09:19 ~ 17:26	31.5	2,310	4.78	23.5	0.114	0.94	0.103	0.79
17:33 ~ 12/11 09:40	47.6	4,520	4.68	25.0	0.112	0.92	0.097	0.74
09:48 ~ 18:20	56.2	2,150	4.19	23.0	0.100	0.83	0.092	0.70
18:27 ~ 12/12 10:29	72.0	3,760	3.95	24.0	0.095	0.78	0.084	0.64

○ Without pretreatment

Period	Accumulated hours	V (mL)	Flow rate (mL/min)	T	Measured		Standardized	
					Jm	J/J0	Js	J/J0
Initial Flux(Jo)	0.0	152	5.07	17.5	0.121	1.00	0.131	1.00
12/9 09:38 ~ 16:00	6.4	1,965	5.16	18.0	0.123	1.02	0.131	1.00
16:04 ~ 12/10 09:10	23.5	4,810	4.69	19.0	0.112	0.93	0.116	0.89
09:19 ~ 17:26	31.5	2,170	4.49	23.5	0.107	0.89	0.097	0.74
17:33 ~ 12/11 09:40	47.6	4,140	4.29	25.0	0.103	0.85	0.088	0.68
09:48 ~ 18:20	56.2	1,900	3.70	23.0	0.089	0.73	0.081	0.62
18:27 ~ 12/12 10:29	72.0	3,510	3.69	24.0	0.088	0.73	0.078	0.60

(d) P rich condition

○ With pretreatment

Period	Accumulated hours	V (mL)	Flow rate (mL/min)	T	Measured		Standardized	
					Jm	J/J0	Js	J/J0
Initial Flux(Jo)	0.0	202	6.73	23.0	0.161	1.00	0.147	1.00
12/12 14:23 ~ 21:06	6.7	2,605	6.46	22.5	0.155	0.96	0.144	0.97
21:09 ~ 12/13 08:47	18.3	4,175	6.00	24.0	0.144	0.89	0.128	0.86
08:51 ~ 17:47	27.2	2,720	5.09	23.0	0.122	0.76	0.112	0.76
17:58 ~ 12/14 08:28	41.7	3,895	4.48	21.0	0.107	0.66	0.104	0.71
08:32 ~ 17:52	51.1	2,205	3.94	21.5	0.094	0.58	0.090	0.61
18:00 ~ 12/15 14:57	72.0	4,775	3.80	21.5	0.091	0.56	0.087	0.59

○ Without pretreatment

Period	Accumulated hours	V (mL)	Flow rate (mL/min)	T	Measured		Standardized	
					Jm	J/J0	Js	J/J0
Initial Flux(Jo)	0.0	196	6.53	23.0	0.156	1.00	0.143	1.00
12/12 14:23 ~ 21:06	6.7	2,490	6.18	22.5	0.148	0.95	0.137	0.96
21:09 ~ 12/13 08:47	18.3	3,650	5.24	24.0	0.125	0.80	0.111	0.78
08:51 ~ 17:47	27.2	2,250	4.21	23.0	0.101	0.64	0.092	0.64
17:58 ~ 12/14 08:28	41.7	3,100	3.56	21.0	0.085	0.55	0.083	0.58
08:32 ~ 17:52	51.1	1,725	3.08	21.5	0.074	0.47	0.070	0.49
18:00 ~ 12/15 14:57	72.0	3,750	2.98	21.5	0.071	0.46	0.068	0.48

(e) P limited condition

○ With pretreatment

Period	Accumulated hours	V (mL)	Flow rate (mL/min)	T	Measured		Standardized	
					Jm	J/J0	Js	J/J0
Initial Flux(Jo)	0.0	182	6.07	20.0	0.145	1.00	0.145	1.00
12/17 09:59 ~ 17:41	7.8	2,710	5.82	21.0	0.139	0.96	0.135	0.93
17:49 ~ 12/18 09:35	23.5	4,740	5.01	20.5	0.120	0.83	0.118	0.81
09:45 ~ 17:30	31.3	2,040	4.40	20.5	0.105	0.72	0.104	0.71
17:37 ~ 12/19 08:56	46.6	3,545	3.86	20.5	0.092	0.64	0.091	0.63
09:01 ~ 17:02	54.6	1,750	3.63	20.0	0.087	0.60	0.087	0.60
17:09 ~ 12/20 10:32	72.0	3,415	3.27	20.0	0.078	0.54	0.078	0.54

○ Without pretreatment

Period	Accumulated hours	V (mL)	Flow rate (mL/min)	T	Measured		Standardized	
					Jm	J/J0	Js	J/J0
Initial Flux(Jo)	0.0	164	5.47	20.0	0.131	1.00	0.131	1.00
12/17 09:59 ~ 17:41	7.8	2,515	5.40	21.0	0.129	0.99	0.125	0.96
17:49 ~ 12/18 09:35	23.5	4,490	4.75	20.5	0.114	0.87	0.112	0.86
09:45 ~ 17:30	31.3	1,745	3.76	20.5	0.090	0.69	0.089	0.68
17:37 ~ 12/19 08:56	46.6	2,765	3.01	20.5	0.072	0.55	0.071	0.54
09:01 ~ 17:02	54.6	1,290	2.68	20.0	0.064	0.49	0.064	0.49
17:09 ~ 12/20 10:32	72.0	2,430	2.33	20.0	0.056	0.43	0.056	0.43

Appendix B: TOC (Total Organic Carbon), TN (Total Nitrogen), TP (Total Phosphorus) Data

TOC, TN, and TP were measured for each experiment in the feed water, the effluent of the biofilter, and the effluent of the UF membrane in order to assess the effect of metabolic and nutrient conditions on the removal of TOC, TN, and TP. Analytical methods and sampling frequency are mentioned in Chapter 2. TOC, TN, and TP data for N limited, P rich, and P limited conditions were not obtained due to instrument malfunction.

For TOC removal, TOC of the influent water was too low to be meaningful. This is probably because some of TOC was degraded in influent reservoirs or due to instrument malfunction. For TN removal, TN concentration changed little because TN included ammonia, nitrite, and nitrate although ammonia was converted to nitrite and nitrate. For TP removal, it was observed that bacteria consumed some of the phosphorus. For both autotrophic and heterotrophic conditions, TP decreased by about 40% without pretreatment and about 85% with pretreatment at the UF effluent. Some of phosphorus was consumed in 5 nutrient conditions, as well.

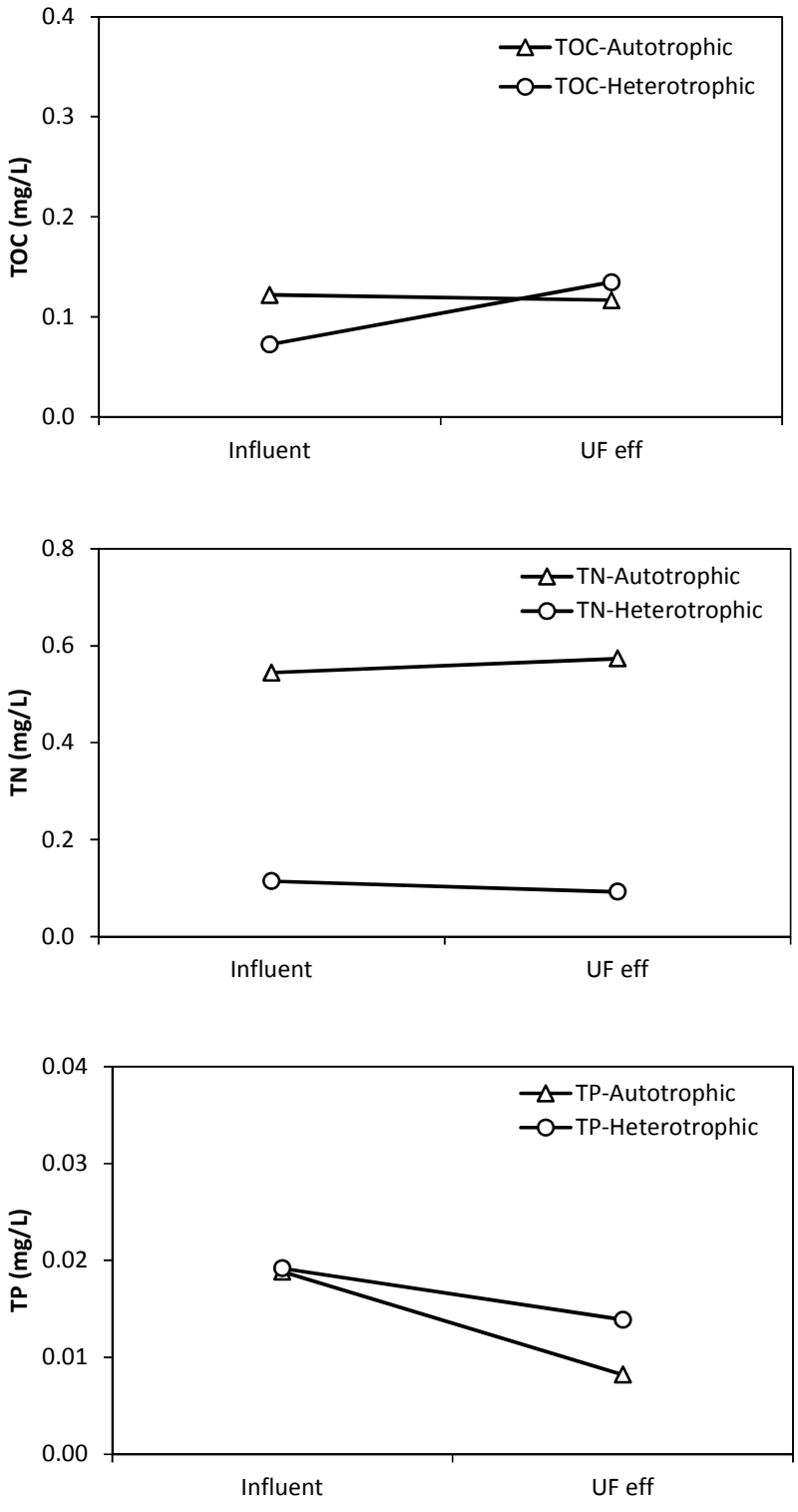

Figure B-1. TOC, TN, and TP removal for metabolic conditions without pretreatment

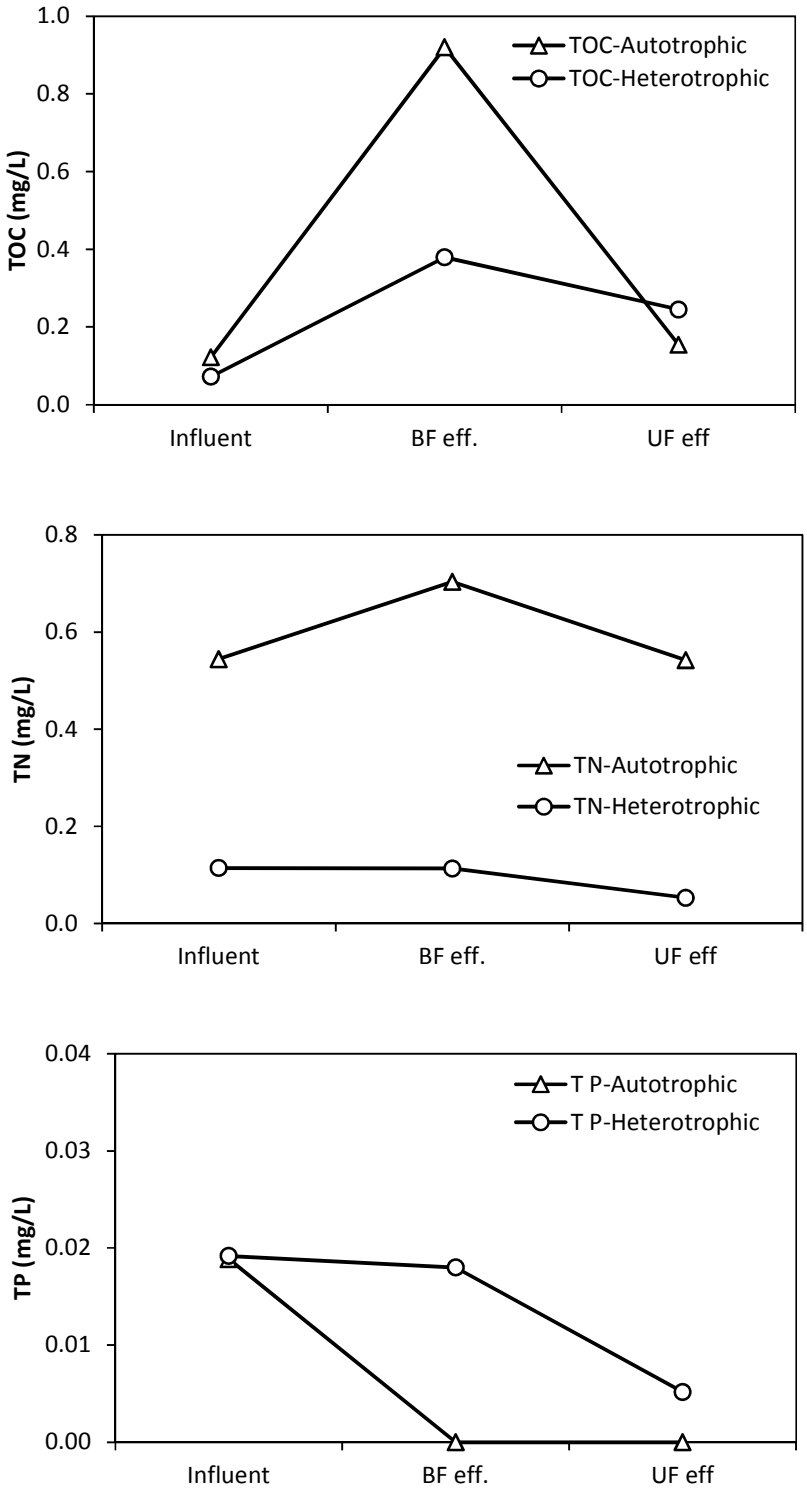

Figure B-2. TOC, TN, and TP removal for metabolic conditions with pretreatment

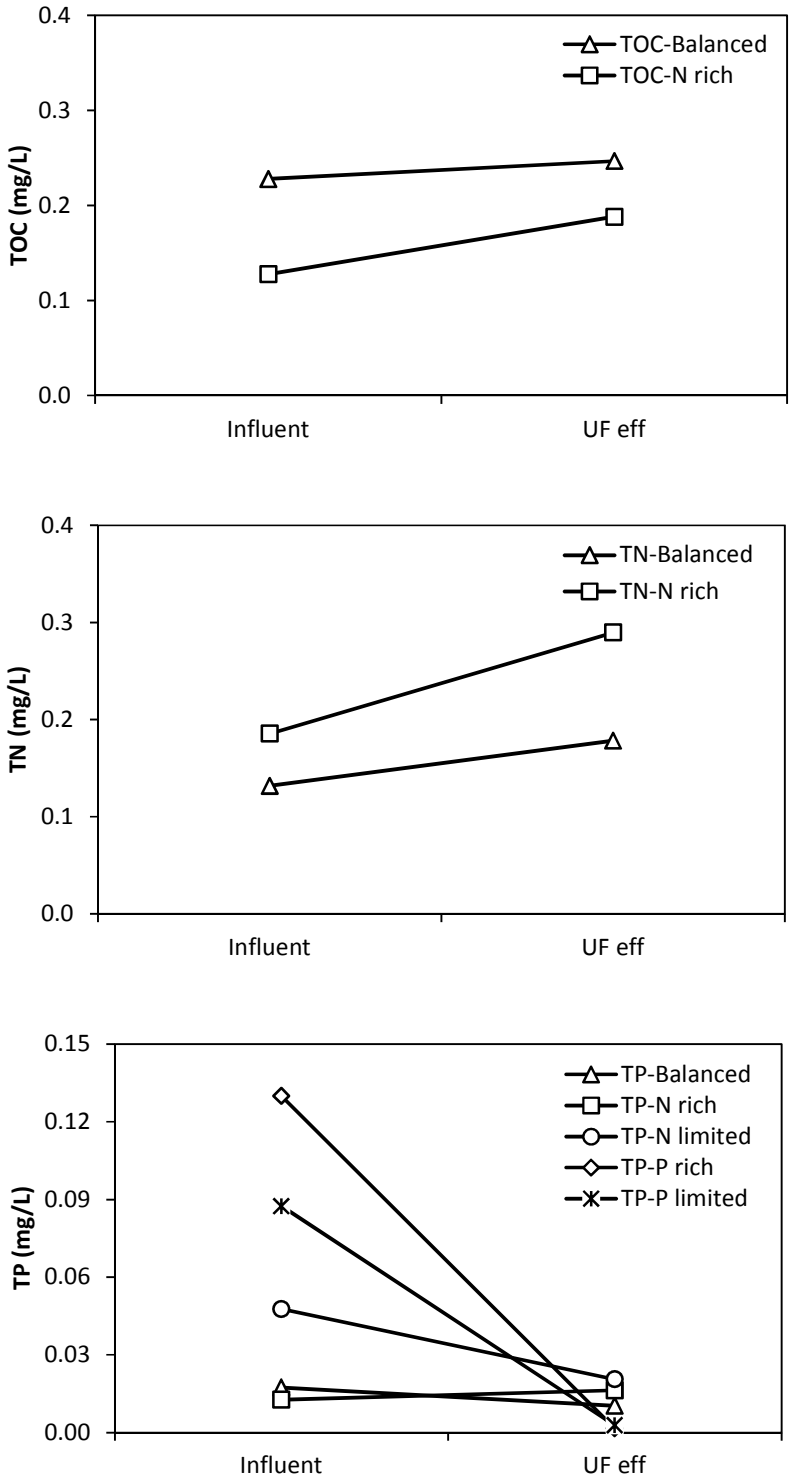

Figure B-3. TOC, TN, and TP removal for different nutrient conditions without pretreatment

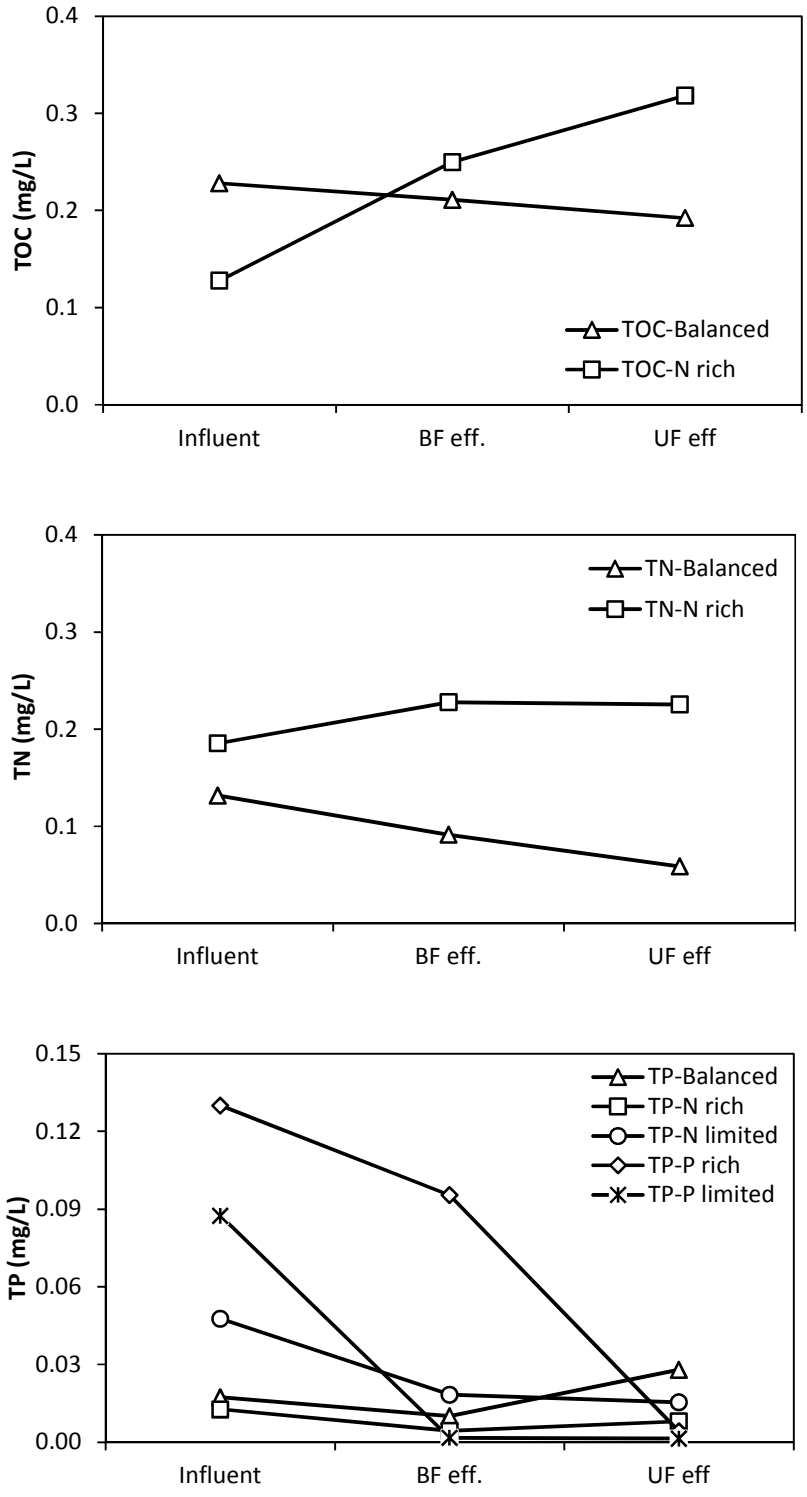

Figure B-4. TOC, TN, and TP removal for different nutrient conditions with pretreatment

Appendix C: Membrane Compaction for Old and New Membranes

Old and new membranes were used to assess the difference of membrane compaction due to DI (deionized water) between them. The old membrane is the membrane which was used several times for MWCO fractionization for about 2 months. UF membranes with a MWCO of 10,000 Daltons were operated under the pressure of 55 psi in a stirred-dead end cell (Amicon 8400, Millipore, USA). The experimental apparatus is described in Chapter 3. Figure C-1 shows the normalized flux decline for used and new UF membranes due to DI water. Flux changed little in new membranes while flux changed by about 15% in old membranes in 60 hours.

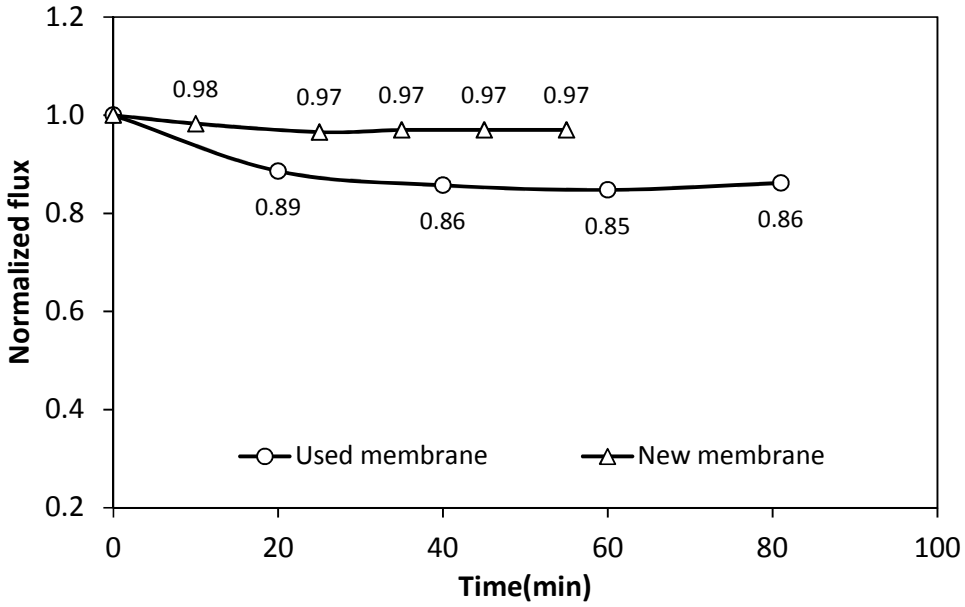

Figure C-1. Normalized flux decline for used and new membranes due to DI water

Appendix D: Flux Decline by Different Types of Water

In addition to the comparison of natural water (TOC=3mg/L) and dechlorinated tap water (DTW) with nutrients described in Chapter 3, the effect of 4 different water types on flux decline was evaluated: DTW with 1 mgC/L of acetate, natural water (TOC = 3.5mg/L) , natural water (<1K Dalton, TOC=3.5mg/L), and DI water. The membranes used were not new, but old membranes. The membranes were operated without adding microorganisms under standard operating conditions. Figure C-1 shows the normalized flux decline for different water types. All water types' fluxes declined in the beginning due to the membrane compaction. It is likely that membrane compaction ended at around 35 hours, given the DI water's flux decline behavior. Other than DI water, all water types showed similar flux decline at 70 hours. It was interesting that the fractionized natural water didn't reduce flux decline in that there was no difference in flux decline between natural water (TOC 3.5mg/L) and fractionized natural water (<1K Dalton, TOC 3.5mg/L).

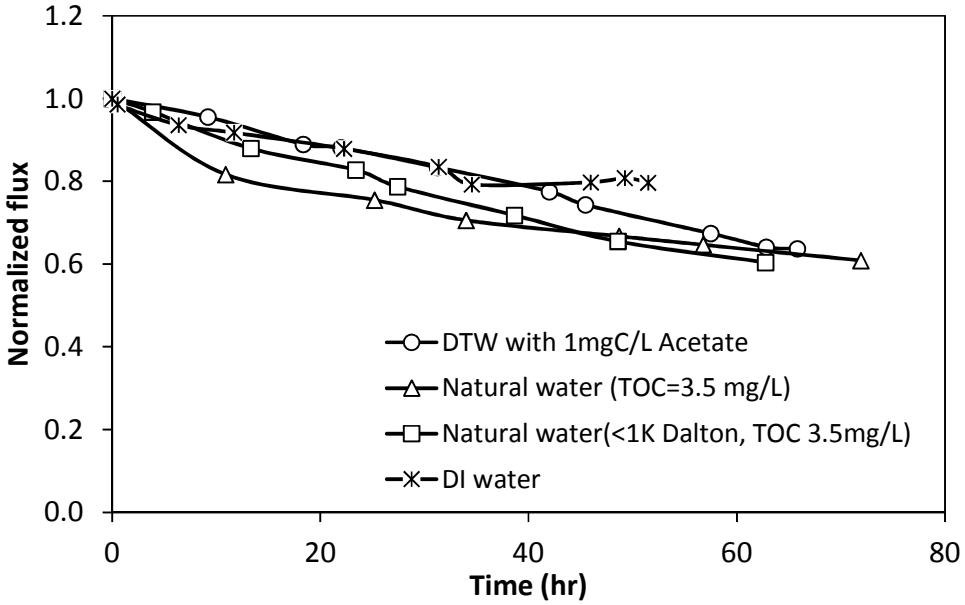

Figure D-1. Normalized flux decline for different water types

Appendix E: The Effect of Ionic Strength on Membrane Flux

It is described in Section 4.1 that when switching from DI water to DTW water, the flux increased around by 20% because of the increase of ionic strength. To make sure that the flux increase was caused by the ionic strength, sodium chloride (NaCl) was added to the DI water to match total dissolved solids (TDS) of DTW; that is, 70 mg/L of NaCl was added to the DI water to match TDS of DI water with DTW water (TDS of DI: 0.7 mg/L, TDS of DTW: 70.8 mg/L). Normalized flux decline for DI water with 70 mg/L of NaCl is shown in Figure E-1. After adding NaCl to the DI water, the flux increased around by 20% which is the same result as the Section 4.1. This flux increase is likely caused by the compression of electrical double layer due to the increase of ions on membrane surface.

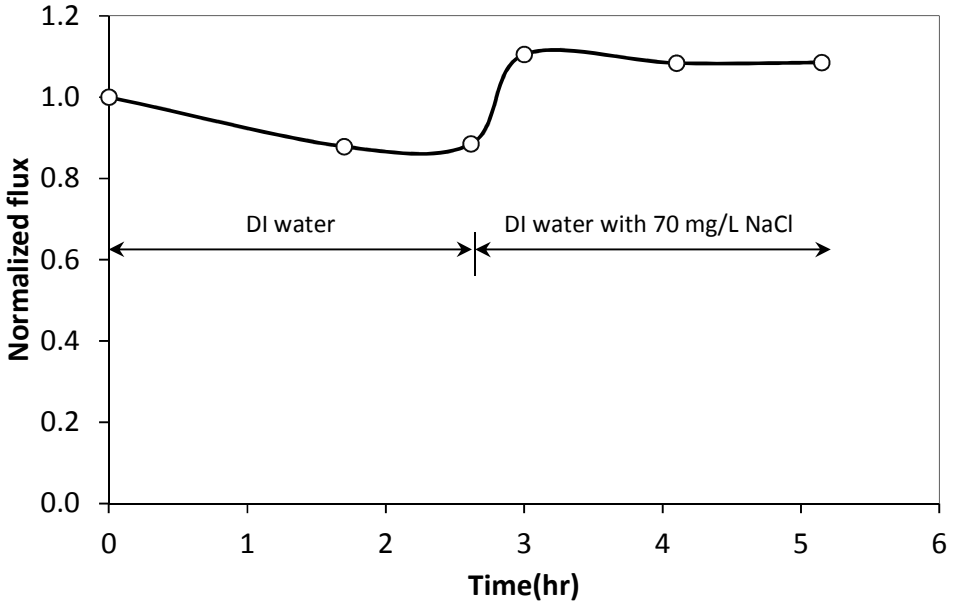

Figure E-1. Normalized flux decline for DI water with 70 mg/L of NaCl