CRITICAL FLUX, RESISTANCE, AND REMOVAL OF CONTAMINANTS IN ULTRAFILTRATION (UF) OF NATURAL ORGANIC MATERIALS

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by
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Abstract

Critical flux is defined as the permeate flux of a membrane system under which no or little fouling is observed. Critical flux can be a good indicator for the membrane system to keep its productivity constant with advantage of operational cost. Therefore, it is very important to understand the impact of operating modes (constant flux and constant pressure modes) on the system and the relationship between foulants (NOM and inorganic particles) and critical flux to use it as an indicator of the system performance.

Under sub-critical conditions, operating the system with constant flux mode resulted in better performance than with constant pressure mode. In both the sub-critical and the super-critical flux conditions, the hydraulic resistances of the system with constant flux mode were less than those with constant pressure mode. It was because there was “overfouling” of the system at the beginning of the ultrafiltration under the constant pressure mode.

Aromaticity, which mainly resides in hydrophobic fraction of humic substances, has been known to be the main component that decides the degree of fouling. Molecular weight of NOM also plays an important role in membrane fouling. As the soil-NOM can be differentiated from the water-NOM by its higher hydrophobicity and larger molecular size, the critical fluxes of those two NOM types can also be categorized by their origins. The critical fluxes of the soil-NOM group (117 ~ 268.3 lmh) were much lower than those of the water-NOM (not detected in the operational range of the tests).

Dissolved organic matter (DOM) was a major foulant as well as a pollutant hard to remove with UF membrane. Higher NOM concentration decreased the critical flux as
increased NOM transport to the membrane surface increased the hydraulic resistances and fouling. As the NOM concentration increased, the critical flux of the system decreased.

There was controversy about the role of inorganic particles in the system performance. As the concentration of inorganic particle increased, the critical flux of the system also increased when the NOM concentration was fixed at 0.0, 5.0, or 10.0 mg/L of Aldrich humic acid (AHA). Inorganic particles increased the critical flux of the system as they acted as another adsorbent of the system and inhibited NOM accumulation on the membrane surface.

Fouling is one the biggest obstacles in using membrane filtration in water and wastewater treatment as it increases the hydraulic resistance of the membrane filtration system and, hence, increases operational cost.

Inorganic particle addition was known to reduce fouling of membrane in some cases. Increasing particle concentration can improve the performance of the membrane filtration system. Particles can play a role as an adsorbent of NOM molecules competing with membrane surface to reduce amount of NOM adsorption on the surface or in the pore of the membrane. The hydraulic resistances were affected little by particle concentration changes. The hydraulic resistance after chemical cleaning ($R_{ch}$) which was related to the resistance by adsorbed layer decreased with increasing inorganic particle concentration.

NOM has been known to be a major foulant in membrane filtration for water treatment. It is expected that increasing NOM concentration increases its transport to the membrane which will result in increased deposit layer or adsorption of NOM molecules.
and increased hydraulic resistance of the system. The system with more NOM molecules had higher hydraulic resistance than the system with less NOM.

Among the components of NOM, humic fraction, which is more hydrophobic and larger in its size, causes more fouling because of its adsorptive capacity on the membrane. Though it’s hard to be categorized due to its diversity and heterogeneity, water-NOM can be differentiate from soil-NOM according to its hydrophobicity and molecular size which affect the fouling of the membrane system by each NOM type. The soil-NOM caused more resistance than the water-NOM. Hydrophobicity and molecular weight can be the distinct difference between those two NOM types.

The rejection of dissolved organic matter measured by UV\textsubscript{254} or DOC did not change much with inorganic particle concentration or NOM concentration. When the rejection was studied in terms of different NOM types (water-borne and soil-borne NOM), the rejection was closely related with humic fraction of NOM (UV\textsubscript{254}) as more humic substances were removed from the NOM with higher humic fraction (UV\textsubscript{254}).

Though the ultrafiltration is an efficient treatment process to remove various contaminants, it still has physical and chemical limitations (fouling and dissolved organic matters) in its use for water treatment. Coagulation pretreatment is an effective resort to overcome the obstacles in applying the ultrafiltration system to water treatment.

Dissolved organic matter has been known to be removed by coagulation with metal salts otherwise not be removed by the ultrafiltration alone. In this study, the turbidity removal by the UF was 99% with coagulation. Humic substances represented by UV\textsubscript{254} could be removed completely by the UF with conventional coagulation conditions while little ( < 88%) with unconventional coagulation conditions.
It was hypothesized that though the conventional coagulation condition can be effective to improve the physical and chemical performance of the UF system, there can be other optimum conditions depending on the raw water characteristics. The flocs formed under charge neutralization conditions were less compressible and more permeable than those formed under sweep floc conditions. The hydraulic resistances of the membrane system with charge neutralization conditions were smaller than with sweep floc conditions. In some cases (condition #1, #3 and #4), the hydraulic resistance, an indicator of fouling, was lower with unconventional coagulation conditions than conventional ones.

It can be concluded that the optimum coagulation conditions in conventional water treatment are not always the optimum conditions for UF-with-coagulation system and the unconventional coagulation conditions can be much more effective than the conventional ones in the context of membrane filtration, depending on the raw water characteristics.
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My brethren, count it all joy when ye fall into divers temptations;
Knowing this, that the trying of your faith worketh patience. But
let patience have her perfect work, that ye may be perfect and entire, wanting nothing.

James 1:2 - 4
Chapter 1. Introduction

1.1. General Aspects of Membrane Systems and Statement of Problems

1.1.1. Membrane – Generals

The use of membrane technology has been growing rapidly during the last few decades. New membrane technologies are being developed and existing processes are also being improved to enhance their physical and chemical performance along with economic competitiveness.

Significant improvements have been made in many different aspects of membrane technologies, e.g., membrane materials, membrane process design (hybrid system with GAC\textsuperscript{1}, PAC\textsuperscript{2}, activated alumina, and coagulation), membrane configuration (flat-sheet, hollow fiber, or tubular form), modified membrane properties, and membrane modular design. Currently, membrane technology is used in many different applications and the scale of business related with membrane technology totals over a billion (US) dollars annually (Cheryan, 1995).

\textsuperscript{1} GAC: Granulated Activated Carbon

\textsuperscript{2} PAC: Powdered Activated Carbon
The major membrane processes include microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), dialysis, electrodialysis (ED), and pervaporation (PV) (Table 1.1). The main factors categorizing the membrane processes are the driving force, the separation mechanism and the pore size of the membrane (Figure 1.1).

**Table 1.1. Membrane processes with driving forces and mechanisms of separation**

<table>
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<tr>
<th>Membrane operation</th>
<th>Driving force</th>
<th>Mechanism of separation</th>
<th>Feed Phase</th>
<th>Permeate Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microfiltration</td>
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<td>Sieve</td>
<td>L</td>
<td>L</td>
</tr>
<tr>
<td>Ultrafiltration</td>
<td>Pressure</td>
<td>Sieve</td>
<td>L</td>
<td>L</td>
</tr>
<tr>
<td>Nanofiltration</td>
<td>Pressure</td>
<td>Sieve + diffusion</td>
<td>L</td>
<td>L</td>
</tr>
<tr>
<td>Reverse Osmosis</td>
<td>Pressure</td>
<td>Diffusion</td>
<td>L</td>
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<tr>
<td>Dialysis</td>
<td>Activity</td>
<td>Diffusion</td>
<td>L</td>
<td>L</td>
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<tr>
<td>Electrodialysis</td>
<td>Electrical potential</td>
<td>Ion exchange</td>
<td>L</td>
<td>L</td>
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<tr>
<td>Pervaporation</td>
<td>Activity</td>
<td>Evaporation</td>
<td>L</td>
<td>G</td>
</tr>
</tbody>
</table>

(After Mallevialle et al., 1996)

MF, UF, and NF are pressure driven membrane filtration processes. MF can retain micron size particles (suspended particle of 0.1 µm to 5.0 µm) while UF retains macromolecules or particles larger than 0.001 ~ 0.02 µm. NF membranes have received their names as they have a molecular weight cut-off (MWCO) corresponding to pores of about one nanometer in diameter. Rejection of ions is influenced not only by size but also by the charge relationship between membrane and ions. The operational range of nanofiltration lies between ultrafiltration and reverse osmosis. Though nanofiltration can be applied to various fields, the main application is desalination.
Reverse osmosis (RO) is a pressure-driven membrane process which separates the solvent from most solutes using a dense or “non-porous” membrane. RO can be applied to retain salts and low-molecular-weight solutes.

Dialysis refers to a process in which the driving force is a transmembrane concentration difference. Selective passage of ions and low-molecular-weight solute occurs, while larger colloidal and high-molecular-weight solutes are retained.

Electrodialysis (ED) is an operation by which ions are driven through ion-selective membranes under the influence of an electrical potential.

Pervaporation (PV) is a liquid/vapor separation process in which a liquid is partially vaporized though a dense membrane. The activity difference is generally maintained by creating a partial vacuum on the permeate side in such a way that the pressure is kept below the vapor pressure on the feed side of the membrane.

All membrane processes are subject to resistances against the solution flux and therefore additional energy must be supplied in the form of pressure or activity gradient in order to keep the system performance constant. There are many factors affecting the resistances of membrane system. Generally, the factors can be categorized into three groups, i.e., solution chemistry, membrane properties, and operation conditions. These factors can interact and as a result predicting the resistance can be very complicated.

One of the most important factors is the size of solute particles or molecules. Back transport from membrane to bulk solution increases with particle size. When the particles are extremely small, the adsorption of the particles can be prohibited by electrostatic repulsion between the particles and the membrane when they have same charge. Wiesner et al. (1989) reported that the sum of the Brownian and shear-induced diffusion
coefficients exhibits a minimum for particles with approximately 0.1 µm diameter for flow conditions typical of hollow fiber. Consequently, the relatively low mass transfer coefficients of the particles in this unfavorable size range are predicted to produce minimum permeate flux, while the particles either smaller or larger than this intermediate size are predicted to produce higher permeate fluxes if all other conditions are identical.

Figure 1.1. Pressure driven membrane filtration process. (After Cheryan, 1998)

Shape of the particles (molecules) is another important factor in two aspects; (1) particle size effect and (2) steric interaction. Porter (1990) reported that Dextran 250, a branched polysaccharide with molecular weight of 250 kDa passed through a 50 kDa
MWCO membrane. Linear molecules, such as polyacrylic acid, passed easily through membranes with MWCO far below their molecular weight (Noble and Stern, 1995). The solute molecules can be attracted to or repulsed from membrane by steric interaction. If high molecular-weight, linear macromolecules can be coagulated or attached to the membrane surface, then these molecules can be retained and contribute to additional fouling by polymer bridging.

Several membrane properties affect the performance of membrane systems.

*Hydrophilicity:* When water is the solvent, then hydrophilic (water-attracting) membranes usually result in higher permeate flux. If the membrane is hydrophobic, it will adsorb hydrophobic components and have more fouling.

*Surface roughness:* Membrane surface roughness has been related to fouling. Rough surfaces have protuberances, which can act as hooks for suspended matter in the feed, thus leading to greater fouling.

*Surface charge:* Most membranes are charged negatively in the usual operation conditions. When the feed solution has charged particles, the electrostatic interactions between the membrane and particles play important role in particle transport and in rejection or attachment.

*Pore size:* The relative size of the pores and the particles in the feed solution are very important. Membranes with larger pore size have higher initial flux than membranes with smaller pore size but often have lower flux after long term filtration. It has been demonstrated that if the pores are much smaller than the particles, the particles will not
get caught within the pores but will accumulate on top of the membrane, and this can also result in severe hydraulic resistance.

**Surface modification:** The surface characteristics of membranes can be modified to be less prone to fouling. The methods for surface modification include surface coating by adsorption, free radical or radiation grafting of hydrophilic or polymerizable hydrophilic monomers, microwave or plasma treatment, chemical conversion of polymer side chains to hydrophilic groups, and coating with oriented monolayers (Cheryan, 1998).

Presence of other solutes in the solution can affect the system performance. Smaller solutes with low molecular weight (e.g., sugars, salts) which can pass through membrane pores can be retained within the cake layer when they interact with larger molecules (e.g., proteins, macromolecules). Changes in the operation conditions such as pressure may force larger molecules to form a secondary dynamic membrane that inhibits passage of the smaller solutes, especially when the layer is compressible.

Operating conditions are critical for the efficiency of the system. There have been controversies on the relationship between system performance and operating with constant flux or with constant pressure. Concentration polarization is the accumulation of solutes and particles on the feed side of the membrane. Concentration polarization is more pronounced at higher TMP\(^3\), lower crossflow velocities, and any other conditions which bring solute to the membrane surface very rapidly (e.g., a very porous MF

\(^3\) TMP: Transmembrane Pressure
membrane). In addition, operating time between backwashes or membrane cleanings can be another important factor.

Module configuration, e.g., flat-sheet, hollow fiber, or tubular configuration, can affect performance of membrane systems even with the same membrane and operating conditions.

The permeability of solutes can be affected by pH, ionic strength, and temperature of the solution. The conformation and shape of macromolecules can change with pH and ionic strength. Macromolecules of natural organic material (NOM) tend to be coiled at low pH and high ionic strength, and stretched at higher pH. In addition, pH can change the charge of the solute molecules and of the membrane. The pore size of membranes is known to be decreased by higher ionic strength. The viscosity of water decreases with temperature and the decreased viscosity will result in higher flux.

Fouling is the main problem in most applications of membrane technologies for water and wastewater treatment. Fouling can be defined as a decline in flux with time of operation. The flux decline related to fouling is best observed when all other parameters are set to constant values. When the system is operated under constant pressure mode, fouling is indicated by flux decline. On the other hand, TMP increase will represent the degree of fouling when the system is operated in a constant flux mode. Resistance and fouling are closely related and the factors affecting resistance also play an important role in membrane fouling. According to most definitions, however, membrane fouling is
different from concentration polarization effects and means a decline in flux or an increase in TMP that is irreversible unless the membrane is cleaned.

There have been many studies with the objective of enhancing flux and decreasing fouling by reducing the concentration of solutes and particles or by improving the physical characteristics of the membrane filtration system. This has been attempted by use of chemical treatments such as coagulation pre-treatment or in-line treatment, addition of adsorbents (GAC, PAC, activated alumina, and modified iron oxide such as HIOPs), ozonation, by modification of membrane surface properties, or by control of solution chemistry (pH, ionic strength, and temperature). In addition, physical modifications have been used to increase shear force which prohibits the solute from accessing the membrane surface and increases back transport of the solute from the membrane surface to the bulk solution. Increased back transport can be achieved by adoption of turbulence promoters/inserts/baffles to the membrane system, frequent backflushing of membrane, permeate backpressure, intermittent jets, pulsating flow, ultrasonic vibration, and establishing an electric field near the membrane.

The deterioration of membrane performance can be evaluated by a couple of different parameters. TMP increase of constant flux operation or flux decline of constant pressure operation can be used as the parameters to monitor the system performance. Hydraulic resistance of the membrane is a good parameter to describe system performance.

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HIOPs: Heated Iron Oxide Particles
regardless of the operational conditions. It is still necessary to have a criterion to operate
the system with constant productivity. “Critical flux” is an indicator by which one can
predict the maximum flux that can be achieved without significant deterioration of
system performance. Critical flux has been defined as the highest flux for which no or
little fouling occurs (Field et al., 1995).

1.1.2. Statement of problems

There have been many studies on the parameters that can be an indicator of system
performance, but we still need to have more efficient indicators of the performance not
only to monitor it but also to predict it. One goal of this research is identification of
bench-scale techniques to determine the performance of membrane systems.

As described in the previous section, one of the important issues in membrane
filtration system is reducing the fouling of the system, where fouling is demonstrated by
flux decline or TMP increase with operation time. Though membrane fouling is often
defined as irreversible flux decline (or TMP increase), it may be necessary to consider
reversible fouling due to concentration polarization and formation of a cake layer that can
be removed by hydraulic washing. Therefore, one goal of this research on ultrafiltration
processes is to understand and identify ways to reduce fouling (both reversible and
irreversible) and to keep the system output constant without deterioration of water quality
or increase in energy required for filtration.
Although NOM and inorganic particles have been investigated extensively as the main foulants in water treatment, little has been reported about their combined role in fouling of membrane filtration systems. There needs to be a systematic investigation on the behavior of NOM and inorganic particles in the context of membrane filtration. In addition, there are still controversies about the significance of NOM and inorganic particles in membrane fouling. These issues will be investigated.

There have been many research reports about the coagulation process in the context of membrane filtration but almost all of them used conventional coagulation conditions (sweep floc and/or charge neutralization conditions). Other unconventional coagulation conditions might be advantageous according to the feed water characteristics. To the author’s knowledge, there is no existing report about use of coagulation conditions that are inappropriate for conventional water treatment (settling and/or rapid filtration) for membrane filtration system. This issue will also be investigated in this thesis.

1.2. **Hypotheses**

1.2.1. **Evaluation of critical flux**

The author hypothesizes that “critical flux” can be a good indicator to operate a membrane filtration system with constant productivity. It is hypothesized that membrane systems will have little or no fouling if operated at flux less than the critical flux.
1.2.2. **Origin of NOM**

NOM properties are important parameters to control membrane fouling. Among the properties of NOM, hydrophobicity and aromaticity have been identified as indicators of NOM adsorption onto the membrane surface or within the pores of membranes. It is hypothesized that those properties can be grouped by the origin of the NOM and that the system performance also can be categorized according to the origin of NOM molecules.

1.2.3. **Concentration of NOM and inorganic particles**

NOM concentration has been closely related with fouling of the membrane. I hypothesize that the membrane filtration system will get fouled more easily and severely with higher concentration of NOM molecules in the feed solution as more NOM can be transported to membrane surface and have more chance to deposit or adsorb on the membrane.

Inorganic particles can play a role as a foulant or as an inhibitor of fouling according to its relative size to membrane pore size and its adsorption capacity. It is hypothesized that when the adsorption capacity of the inorganic particles is large enough, then increased concentration of particles can inhibit fouling and decreased resistance due to NOM.

1.2.4. **UF with coagulation process**

I propose coagulation treatment to enhance system performance, with the hypothesis that coagulation under “unconventional” conditions will reduce fouling (increased back
transport), reduce hydraulic resistances (more porous cake layer), and increase removal of NOM.

1.3. Objectives

The specific objectives of the research are:

1. To develop methods to evaluate the critical flux of the system as an indicator of the system performance and, to streamline the method to be applied generally to other membrane filtration systems.

2. To elucidate the effect of NOM on physical performance (resistance, flux, TMP, and critical flux) as well as chemical performance ($\text{UV}_{254}$ and DOC removal) of ultrafiltration systems in terms of NOM origin, i.e., water-NOM and soil-NOM.

3. To study the system performance with varying NOM concentrations and to understand the mechanisms of membrane fouling due to NOM.

4. To examine the performance of ultrafiltration with varying inorganic particle concentrations, and to identify the mechanisms of particle interaction with NOM.
5. To investigate conventional and “unconventional” conditions for coagulation treatment to enhance the performance of the ultrafiltration system.

1.4. Research Overview and Organization of the Thesis

The thesis has six chapters. General information about membrane filtration, statement of problems, the hypothesis, and the objectives are provided in Chapter 1. The general information of materials and methods used for the study is provided in Chapter 2. Chapter 3 covers the evaluation of critical flux with the relation to the system performance. The behaviors of NOM and inorganic particles in terms of fouling of the system are discussed in Chapter 4. In Chapter 5, the results of the study on the coagulation process to enhance the system performance. The research carried out in Chapter 5 is focused on the use of “unconventional” coagulation conditions to improve the system performance. The conclusion of the study is in Chapter 6. The raw data are reported in Appendices.
1.5. References


Chapter 2. Materials and Methods

2.1. Chemicals and apparatus

All the chemicals used in the experiments were reagent grade.

All the glassware used for the experiment were rinsed with tap water and immersed in the acid bath (10% nitric acid) for more than an hour. When it was needed, 1.0 N NaOH was used to remove organic contaminant from glassware. The acid cleaned glassware was rinsed with DI water and immersed in the water bath filled with DI water for more than an hour. After soaking in the DI water, the glassware was rinsed with DI water again and dried in the oven overnight.

The vials for DOC measurement were cleaned through the procedure mentioned above and baked in the furnace at 600 °C for more than 2 hours to oxidize possible organic residuals.

2.2. Membranes
Polyethersulfone (PES) ultrafiltration membranes (PBHK, Millipore, Bedford, MA) and regenerated cellulose (RC) ultrafiltration membrane (YM100, Millipore, Bedford, MA) with a 100 kD molecular weight cut-off (MWCO) were used for the experiments. Jucker and Clark (1994) reported that the same polysulfone membranes had zeta potentials from -5 to -12 mV for pH of 4.5 and 6.5. The pore size of the membrane can be determined from the MWCO by the following equation (Kawakatsu et al., 1993).

\[ d_m = \frac{1.13 \cdot k \times 10^{10}}{\pi \cdot \mu \cdot M_w^{0.48}} \]  

Equation 2.1

where, \( d_m \) is the pore diameter in meter on the membrane surface, \( k \) is Boltzmann’s constant, \( \mu \) is viscosity and \( M_w \) is the molecular weight cutoff. The temperature is assumed 298 K in Equation 2.1. The mean pore diameter calculated with the equation for the PES ultrafiltration membrane was 14 nm. It corresponded well with the previously reported values (9.8 ~ 22 nm) of the UF membrane (PBHK, Millipore, Bedford, MA). Polyethersulfone membrane is frequently used in microfiltration (MF) and ultrafiltration (UF). Polyethersulfone has diphenylene sulfone repeating units in its structure (Figure 2.1). Polyethersulfone is widely used today because of wide range of temperature limits (up to 75°C), wide pH tolerance (from pH 1 to 13), fairly good chlorine resistance (up to 200 ppm chlorine for cleaning and 50 ppm chlorine for short-term storage of the membrane), wide range of pore sizes for UF and MF applications (ranging from 10 Å (1000 D MWCO) to 0.2 μm and good chemical resistance to aliphatic hydrocarbons, fully halogenated hydrocarbons, alcohols, and acids. Disadvantages of Polyethersulfone are
low pressure limit (100 psig with flat sheet and 25 psig with hollow fiber) and hydrophobicity which leads to an apparent tendency of membrane fouling by stronger interactions with a various solutes (Cheryan, 1998).

![Figure 2.1. Structure of Polyethersulfone](http://felix.metsce.psu.edu/papers/BMErwin-APS-02.pdf)

For some preliminary experiments, the regenerated cellulose ultrafiltration membranes (YM100, Millipore, Bedford, MA) with 100 kDa MWCO were used. Regenerated cellulose membranes are very hydrophilic and have exceptional nonspecific protein-binding properties by which membrane fouling and flux decline can be reduced. Regenerated cellulose has good tolerance to temperature up to 75°C and good resistance to some common solvents (Figure 2.2).

![Figure 2.2. Structure of regenerated cellulose](http://www.chem.vt.edu/chem-dept/helm/3434WOOD/notes1/cellulose.pdf)
2.3. **Filtration module**

A commercial stirring cell (Cole Parmer, Model H-02910-42) was used for the membrane filtration module (Figure 2.3). The internal diameter of the cell was 7.2 cm (i.e., 40.7 cm² of filtration surface) and the cell volume was 500 mL with a 1 cm stirring bar. All the experiments were carried out in non-stirred mode.

![Diagram of filtration module](image)

**Figure 2.3. Ultrafiltration module and schematic diagram of the system for constant flux mode experiments. The blue lines are tubing for water flow and the orange lines are data transferring cables.**

The synthetic solution was fed to the module by a peristaltic pump with a pressure dampener to stabilize the pressure fluctuation at the feeding side and suction pressure was added across the membrane by another peristaltic pump at the permeate side. The pressure was controlled by the pressure control valve and dial settings of pumping speed.
Two digital pressure gages at feed side and permeate side collected the data and sent them to the computer. The permeate flux of the system was measured automatically with the digital balance connected to the computer (Figure 2.3). The data collected during the experiments were processed with computer programs written by the author. The experiments were carried out at room temperature.

![Figure 2.4. Ultrafiltration module and schematic diagram of the system for constant pressure mode experiments. The blue lines are tubing for water flow, the green line is tubing for nitrogen gas flow and the orange lines are data transferring cables.](image)

For the UF tests under constant pressure mode, nitrogen gas was used to provide feed solution container with pressure. The permeate side peristaltic pump was removed for the test. The pressure provided by nitrogen gas was controlled by the regulator attached to the tank. The pressure valve was used to stabilize the TMP when it fluctuated. The feed
and permeate side pressures were measured by two digital pressure gages. The flux was measured with the digital balance (Figure 2.4). All the data was collected by computer and analyzed with the computer program.

2.4. Synthetic model water

Model waters were created to supply constant quantity and quality of water sample by simulating real water in a couple of aspects, i.e., organic material, ionic strength, buffer capacity, and naturally occurring multivalent cations.

To investigate the impact of particle and NOM concentration on the critical flux of the membrane system, Aldrich humic acid (Milwaukee, Wisconsin) was used. For the experiments to find out the impact of different NOM characteristics, six different types of organic sources were used: 1) Aldrich Humic Acid (AHA), 2) Summit Hill Soil Humic Acid (SHSHA), 3) Suwannee river fulvic acid (SRF), 4) Leonardite humic acid (LHA), 5) George Town NOM (GTNOM), and 6) Soil Humic Acid (SHA). AHA was made from the commercial humic acid purchased from Aldrich Chemicals (Milwaukee, Wisconsin) and the others were prepared with the organic materials purchased from International Humic Substances Society (IHSS).

All the humic acids and fulvic acids were prepared by dissolving the organic materials in the MilliQ water. The pH of the solution was set to 10 to assure complete
dissolving of humic acid. The solution was filtered through 0.2 µm membrane filter (Supor®-200, Pall Corporation, Ann Arbor, Michigan).

The background solution included 0.2 mM CaCl₂ as a representative of naturally occurring multivalent cations, 0.5 mM NaHCO₃ as a natural buffer system, and Georgia kaolinite and alumina as natural turbidity. The synthetic water was prepared every morning before the experiment started with the stock solution of 100 mg AHA/L, 0.02 M CaCl₂ and 0.05 M NaHCO₃ to maintain constant solution chemistry. The components and characteristics of the synthetic model water were given in Table 2.1.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>NOM</td>
<td>pH 7.74</td>
</tr>
<tr>
<td>Inorganic particles</td>
<td>Temp. 22 C</td>
</tr>
<tr>
<td>Kaolinite 2.5 mg/L</td>
<td>Zeta potential -27.9 mV</td>
</tr>
<tr>
<td>Alumina 2.5 mg/L</td>
<td>Turbidity 3.17 NTU</td>
</tr>
<tr>
<td>Background solution</td>
<td>UV₂₅₄ 0.124 1/cm</td>
</tr>
<tr>
<td>NaHCO₃ 0.5 mM</td>
<td>DOC 1.94 mg C/L</td>
</tr>
<tr>
<td>CaCl₂ 0.2 mM</td>
<td></td>
</tr>
</tbody>
</table>

2.5. Filtration protocols

Before the ultrafiltration test was carried out with the synthetic waters, the pure water flux ($J_0$ in Figure 2.5) was measured for each membrane to get the intrinsic membrane resistance ($R_m$). Before the test for the intrinsic membrane resistance ($R_m$), the membrane was immersed in 1,000 mL of deionized water and the water was changed three times for
an hour, at least. The rinsed membrane was kept in the deionized water in the refrigerator overnight. A 20-minute filtration with pure water was performed before the filtration experiment to compact the new membrane surface (i.e., compaction between membrane surface and supporting layer) and stabilize the permeate flux and pressure. A new membrane was used for each test.

The synthetic water was prepared every morning before a test. If the synthetic water had particles in it (i.e., Georgia kaolinite as the larger size particle and alumina as the smaller size particle), the particles were dispersed in the solution in the ultrasound bath for 20 minutes. The particles were then mixed with NOM for 20 minutes and then the background solutions (NaHCO₃, and CaCl₂) were added. With this order of mixing after particle dispersion, the system can reduce the possibility of precipitation and co-precipitation by complexation. After all the components were added to the synthetic water, the solution was mixed rapidly for an hour with magnetic stirrer.

After an hour of mixing, 150 mL of the solution was taken to measure the raw water characteristics such as pH, temperature, turbidity, zeta potential, UV₂₅₄, DOC and metal concentration.

The membrane was operated for 3 minutes just before the test started to stabilize the flux and pressure with constant permeate flux of about $1.6 \times 10^{-5}$ m/sec (56.5 lmh⁵).

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⁵ lmh: The unit of flux used in membrane filtration. Lm⁻²h⁻¹ where, L is volume of permeate, m² is the effective filtration area of membrane, and h is hour.
The experiments with varying solution chemistry were carried out under constant flux (permeate flux) conditions. The permeate flux was increased stepwise from about $2.0 \times 10^{-5}$ m/sec (72 lmh) to about $10.0 \times 10^{-5}$ m/sec (360 lmh) by 5 steps (2.0, 4.0, 6.0, 8.0 and $10.0 \times 10^{-5}$ m/sec). The filtration was performed for 10 minutes for each step and the permeate flux was kept constant for each step. The experiments to test the impact of operation modes were performed under constant flux and constant pressure conditions.

To evaluate the chemical performance of the system, the samples were collected at the end of each step and analyzed for the parameters such as pH, temperature, turbidity, UV$_{254}$, DOC and metal concentration. The zeta potential of the permeate solution was not measured as there were few particles left in the solution to be seen under the microscope (the turbidity removal after the ultrafiltration was over 98% in all experiments).

The synthetic water used to investigate the impact of operation modes (constant flux and constant pressure) was composed of 2.5 mg kaolinite/L, 2.5 mg alumina/L, 5.0 mg AHA/L, 0.5 mM of NaHCO$_3$ and 0.2 mM of CaCl$_2$. The particles were dispersed in the ultrasound bath for 20 minutes and mixed with NOM. NaHCO$_3$ and CaCl$_2$ were added and mixed for an hour. After the mixing, samples were taken to measure pH, temperature, zeta potential, turbidity, UV$_{254}$, DOC and metals. Samples were collected at 30, 60, 90, and 120 minutes to investigate the changes of solution chemistry with time. The permeate flux was set to four different values around the critical flux of the system (139, 199, 242, and 263 lmh). The tests were carried out for 120 minutes.

The experiments with constant pressure used the same procedures except that the TMP of the system was set to a constant value while the permeate flux changed. The
TMP corresponding to each constant flux was obtained from the previous results of the UF tests under constant flux mode. The fluxes used for the constant flux tests were 139, 199, 242, and 263 lmh and the corresponding TMP’s 1.25, 2.43, 4.57 and 6.19 psi, respectively. The constant pressure across the membrane in the module was maintained by the regulated N₂ gas.

2.6. Evaluation of resistances

The total resistance at the end of filtration test \( R_f \) was calculated with the permeate flux and TMP at the end of each permeate test. The resistance at the end of filtration test \( R_f \) includes the resistance by concentration polarization, cake layer and adsorbed layer.

After ultrafiltration, the membrane was put in 1,000 mL of deionized water and stored in a refrigerator (about 4°C) overnight to remove all possible labile particles from the surface of the membrane (Jones and O’Melia, 2000).

The membrane rinsed with deionized water was used for another pure water flux (PWF) test to evaluate the resistance after hydraulic rinse \( R_{by} \). The membrane was operated for 3 minutes before the PWF test to stabilize the permeate flux and pressure.

The same membrane was then cleaned chemically by filtering 0.05 N NaOH solution for 30 minutes and then followed by another PWF (Pure Water Flux) test for 30 minutes.
The weakly adsorbed NOM is believed to dissolved and flow through the membrane pores. The membrane was stored in the clean deionized water in a refrigerator overnight. Then, the third pure water flux test was performed to determine the resistance after chemical cleaning ($R_{ch}$).

The relationship between TMP and operating parameters (time or permeate flux) were illustrated in Figure 2.5.

Theoretically, the relationship among the flux, the driving force and resistances can be expressed by Darcy’s law as shown in Equation 2.2

\[
J = \frac{\Delta P}{\mu \cdot R}
\]

Equation 2.2

where, $J$ is the flux, $\Delta P$ is the transmembrane pressure, $\mu$ is the viscosity of the permeate solution, and $R$ is the resistance.
Flux decline during filtration.

**Chemical cleaning**

Membrane compaction

Irreversible fouling

Flux, $J$

Filtrate volume or time of operation

$J_0$ is the initial flux of the membrane system after compaction of membrane, $J$ is the flux at the end of the test. (a) Hydraulic resistances of the system under constant pressure operation mode (after Kilduff et al., 2000), (b) Hydraulic resistances of the system with constant step-wise increased flux.

Figure 2.5. Schematic diagram of the filtration protocol employed (fluxes and resistances involved).

After the membrane is fouled, the equation can be changed as Equation 2.3 (Belfort, et al, 1994).
where \( \pi \) is the osmotic pressure by concentration polarization, \( R_m \) is the intrinsic membrane resistance, \( R_{cp} \) is the resistance by concentration polarization, \( R_{cl} \) is the resistance by cake layer, and \( R_a \) is the resistance by adsorbed layer. In ultrafiltration and microfiltration of drinking water, the effect of the osmotic pressure by concentration polarization on the flux was neglected due to low concentration of solute in surface water treatment applications (Mulder, 1991; Hong and Elimelech, 1997; Schäfer et al., 1998). Although it depends on the definition of authors, it can be said that \( R_{ch} \) is closely related with \( R_a \), \( R_{hy} \) with \( R_{cp} \), and \( R_f \) with \( R_{cl} \).

### 2.7. Evaluation of critical flux

The critical flux was evaluated from the change of TMP as a function of the flux. As almost all of the experiments were carried out under the constant flux conditions, the permeate flux was increased stepwise and the change of TMP was recorded. The TMP changes over time was measured and plotted with permeate flux (Figure 2.6 a).

It has been known that the system could have accumulation of particles even with the sub-critical flux operation. But the results could be separated into two flux groups according to their different flux-TMP behaviors, i.e., lower flux group with little or no
fouling and higher flux group with fouling. The authors used the TMP changes with flux (dP/dJ) to differentiate those two groups of data (Figure 2.6 b). Each group was regressed to get the linear equation of line. The intersection of two lines from each group was determined as the critical flux of the system (Figure 2.6 b).

Figure 2.6. Evaluation of critical flux. (a) TMP and flux changes with time and (b) TMP vs. flux to evaluate the critical flux.
10-minute-step-wise flux increasing technique was used to evaluate the critical flux of the system. The flux declines with operating time. The critical flux evaluated with 10-minute-step-wise flux increasing technique had to be corrected according to the operating time.

As the permeate flux declines exponentially with operation time, we assumed the normalized flux declines with power of normalized operation time (Equation 2.4).

The empirical equation for the relationship was given as,

\[
\frac{J_t}{J_{10}} = \left( \frac{t}{t_{10}} \right)^{-n}
\]

Equation 2.4

where \( J_{10} \) is the critical flux in lmh [L·m\(^{-2}\)·hour\(^{-1}\)] evaluated 10-minute-step-wise flux increasing technique, \( J_t \) is the corrected critical flux for operation time of \( t \) in minute, and \( n \) is the constant accounting for system characteristics (membrane pore size and material, solution chemistry, and operating conditions). The constant \( n \) is determined experimentally.

\( J_{10} \) and \( J_{20} \) were 262 and 248 lmh, respectively. As \( n \) was 0.078, \( J_{120} \) was calculated to be 216 lmh. This critical flux of 216 lmh was used as the criterion of sub-critical and super-critical operation conditions with longer term (120 minutes) operation experiments.
2.8. **Analytical methods**

2.8.1. **pH**

The system pH was measured with the Orion pH meter, model 520A. Every morning before the experiments started, the pH meter was calibrated with three standard buffer solutions with pH of 4.01, 7.00, and 10.01.

After using the pH meter, the electrode was stored in storage solution provided by the manufacturer.

Table 2.2. Analytical instruments used for the experiments

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Analytical instrument</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH measurement</td>
<td>Orion pH meter, Model 520A</td>
</tr>
<tr>
<td>Turbidity</td>
<td>Hach Ratio/XR turbidimeter</td>
</tr>
<tr>
<td>UV absorbance</td>
<td>Shimadzu UV-601 UV spectrophotometer</td>
</tr>
<tr>
<td>DOC</td>
<td>Shimadzu TOC-5000A Total organic carbon analyzer</td>
</tr>
<tr>
<td>Zeta potential</td>
<td>Penn Kem Lazer Zee zeta meter Model 501</td>
</tr>
<tr>
<td>Metal</td>
<td>ICP-Atomic Emission spectroscopy</td>
</tr>
</tbody>
</table>

The analytical instruments used were listed in Table 2.2.

2.8.2. **Turbidity**

Turbidity was measured with Hach Ratio/XR turbidimeter. Great care was taken to have clean and smooth surface of turbidity measuring cell.
2.8.3. Zeta potential

After the cell was filled with solution slowly, the cell was left still for 2 minutes to get rid of any movement by hydraulic force provided by solution injection into the cell. Usually, zeta potential measurement was carried out three times for the same solution. The measured zeta potential was corrected for temperature according to Equation 2.5

\[
ZP_{\text{cor}} = ZP_{\text{meas}} \left\{ 1 - 0.02 \cdot (T - 20) \right\} \quad \text{Equation 2.5}
\]

The motion of particles in an electric field is observed microscopically and the velocity is determined. The electrophoretic mobility, \( U \), is defined as the velocity per unit field strength. The zeta potential can be calculated with the Smoluchowski equation according to the particle size range. For particles large compared with the double layer thickness (\( \kappa \cdot a \gg 1 \)),

\[
U = \frac{\varepsilon \cdot \zeta}{\mu} \quad \text{is used}
\]

while, at the other extreme, where particles are very much smaller than the double layer extent (\( \kappa \cdot a \ll 1 \)),

\[
U = \frac{2\varepsilon \cdot \zeta}{3\mu} \cdot f(\kappa \cdot a) \quad \text{is used.}
\]
The function $f(\kappa \cdot a)$ depends on the particle shape.

$\varepsilon$ is permittivity, $\zeta$ is zeta potential, $\mu$ is viscosity, and $1/\kappa$ is the thickness of diffuse layer in electrical double layer model.

Penn Kem Lazer Zee zeta meter Model 501 was used to measure zeta potential.

### 2.8.4. UV absorbance

Ultra violet absorbance at 254 nm has been known to be directly related to the aromatic fraction of NOM (Dilling and Kaiser, 2002; Korshin et al., 1997). 1-cm quartz cell was used for the absorbance at the short (254 nm) wavelength. The MilliQ water (Millipore) was used as the blank. Sample solution was pre-filtered through 0.2 µm membrane (Supore membrane, Millipore). pH was not adjusted and measurement was carried out at room temperature. Shimadzu UV-601 UV spectrophotometer was used for the measurement.

### 2.8.5. DOC

Sample solution was pre-filtered through 0.2 µm membrane. After filtered, the sample solution was acidified to pH 2 with 1 N HCl. Before measurement, the sample solution was purged for 10 minutes to remove inorganic carbon.

The sample solution was stored in the refrigerator at 4 °C until measurement. Shimadzu TOC-5000A Total organic carbon analyzer was used to measure the DOC.
2.8.6. *Metals*

Metal contents were measured by using ICP-Atomic emission spectroscopy. The sample solution was digested with (1+1) HCl and (1+1) HNO₃ before measurement.
2.9. References


Chapter 3. Critical Flux

3.1. Overview

Critical flux is defined as the permeate flux of a membrane system under which no or little fouling is observed. Higher critical flux with low resistance to filtration results in lower capital and operating costs. The objectives of this work were: 1) demonstrate the significance of critical flux on ultrafiltration (UF); 2) describe techniques for determining critical flux, especially in the context of potable water treatment; and 3) determine the effect of the operating mode (constant flux or constant pressure) on resistance to filtration over time.

Critical flux values were determined for several raw waters. When comparing waters from different sources, it was shown that resistance to filtration at sub-critical flux was not directly related to macroscopic parameters such as total organic carbon (TOC) or turbidity. The highest resistance to filtration for sub-critical flux conditions occurred for a spring water that had very low TOC and turbidity, and which was influenced by storm water conditions.

Several methods were evaluated for estimation of critical flux for the synthetic water, and critical flux was evaluated to be 216 lmh for operation using 120 minutes between hydraulic cleaning. Subsequent experiments were run for 120 minutes under sub-critical
and super-critical conditions for either constant flux or constant TMP operational mode. These experiments confirmed that operation under sub-critical flux resulted in small, linear increases in TMP with filtration volume. Operation at super-critical conditions resulted in exponentially increasing TMP with filtered volume.

Operation under constant flux conditions was better than operation under constant TMP conditions for the following reasons: 1) constant flux produced lower resistance than constant TMP for sub-critical conditions (i.e. higher resistance for constant TMP with initial flux of 149.5 lmh compared to constant flux at 199 lmh); 2) the rate of increase in resistance was higher for sub-critical constant TMP than for sub-critical constant flux conditions (same pair of data sets); and 3) constant flux resulted in a larger volume of treated water during 120 minutes than was produced under constant TMP conditions.

Final resistance to filtration ($R_f$) was higher for constant TMP conditions. Resistance after a hydraulic rinse ($R_{hy}$) was similar between the two modes after 120 minutes of filtration, but $R_{hy}$ normalized to the volume of water treated was substantially lower for the constant flux than for the constant TMP conditions. Resistance after chemical cleaning ($R_{ch}$) was always higher for constant flux operation, although in most cases the value was lower for constant flux if normalized by the volume of water that was filtered. A model was proposed to explain the different development of $R_{hy}$ and $R_{ch}$ for the two modes.

Most bench-scale investigations of membrane filtration have been conducted using constant TMP conditions. The results that are presented in this chapter show that some
published conclusions from research using constant TMP conditions might be questionable.

3.2. Introduction

The use of low pressure membrane filtration systems, i.e. microfiltration (MF) and ultrafiltration (UF), has increased exponentially during the last decade for production of potable water (Bacchin et al., 1996; Cho et al., 2000; Choksuchart et al., 2002) The application of the low pressure membrane filtration system to water treatment expanded rapidly, with installations in the United States growing from one utility in 1991, to 218 utilities in 2002 (AWWA Residual Management Research Committee, 2003; Mickley, 2001). Ultrafiltration can remove all particles larger than the pore size, which generally includes removal of turbidity, microorganisms (bacteria, protozoa, algae), and some water-borne viruses. Dissolved organic matter is usually not significantly removed by MF or UF. The biggest obstacle to overcome in application of low-pressure membrane filtration is fouling, i.e., reduction in flux or increase in transmembrane (TMP) during operation due to accumulation of materials within the membrane pores or at the surface of the membrane.

“Critical flux” has been proposed as a method for measuring the maximum flux or TMP that can safely be applied and still keep the system running effectively, i.e. with no or little fouling and with reduced frequency of chemical cleaning.
Field et al. (1995) introduced the concept of critical flux, working on constant flux filtration of yeast cells with MF. They defined the critical flux as the flux below which an increase of TMP with time did not occur. Howell (1995) defined the critical flux as the flux below which there is no deposition of colloids on the membrane.

All the definitions of critical flux are related with fouling of the system. Based on theoretical definitions of mass transport, the critical flux can be defined more generally as the flux at which the hydrodynamic force transporting the particle towards the membrane pore is exactly balanced by the opposing back transport forces (Bowen et al. 1999). It should be recognized, however, that diffusion is a statistical process and that not all particles in a population will follow the same path. As a result, conditions that are believed to prevent the average particle from depositing on a membrane surface will not guarantee that all particles of a particular size and density will remain detached from a surface. This also leads to the inference that there is no such thing as a critical flux at which there will be zero fouling. Rather, critical flux should be considered to be the operating condition that separates slow fouling from rapid fouling.

There several methods to evaluate the critical flux of a filtration system. Chen et al. (1997) detected the critical flux using the hysteresis that occurred when the flux was successively increased and decreased. Li et al. (2000) used direct microscopic observation of deposited materials to evaluate the critical flux. Chan et al. (2002) and Huisman et al. (1999) determined the critical flux by examining deviations from linearity in the plot of TMP versus the permeate flux. Cho and Fane (2002) found that a jump in $dP/dt$ could be used to find the critical flux of the system. Espinasse et al. (2002) used
resistance to filtration to estimate the critical flux, by plotting the normalized resistance against the permeate flux. However, since flux (with constant TMP) or TMP (with constant flux) changes with time, definition of the critical flux using this method was inexact. According to Huisman et al. (1999), reproducibility for this method was about ±15%. Kwon et al. (2000) studied the critical flux evaluated by two methods, based on particle mass balance or based on the increase in TMP required to maintain a constant permeate flux. They found the critical flux evaluated by the former method was lower than by the latter one.

Operating mode can be an important factor in optimizing membrane filtration. Constant flux operation mode has been shown to produce less resistance than constant pressure operation mode (Field et al., 1995; Defrance and Jaffrin, 1999; Decloux and Tatoud, 2000). These observations may be due to operation with an initial pressure that results in supercritical flux. Bowen et al. (1999) disagreed with this opinion and insisted that “critical pressure” could be used as an improved operational indicator for membrane systems. Operation below the critical pressure allowed continuing filtration with only a minor decrease in flux. Vyas et al. (2002) observed that irreversible fouling was greater under constant flux mode than that in constant TMP mode. Burgeois et al. (2001) reported that they could get improved UF performance by allowing flux to decline naturally, rather than using a constant flux mode of operation in their study on crossflow UF of wastewater.
In our research, we usually used the constant flux mode to operate our system as most of the membrane systems are operated with constant flux and as it is critical to guarantee the production of treated potable or waste water. Also, with constant flux operation, overfouling by constant TMP operation can be avoided (Field et al., 1995). Constant pressure mode was also tested to compare its impact on the system performance in longer term operation with the results from the operation with constant flux mode.

Solution chemistry can affect critical flux, especially ionic strength, pH, zeta potential, particle concentration and size, and nature and concentration of organic materials. Increased salt concentration is known to decrease the critical flux (Espinasse et al., 2002; Kwon et al., 2000; Bacchin et al., 1996). Salt concentration can affect deposition kinetics and hydraulic resistance. Ionic strength and especially multi-valent ions affect electrostatic interactions between particles (DLVO theory) and the molecular size of polyelectrolytes such as humic materials.

In general, an increase in pH increases the electrostatic repulsion between the membrane and particles, which are typically negatively charged in natural waters. As a result, higher flux is often observed with an increase in pH (Mänttäri and Nyström, 2000; Metsämuuronen et al., 2002; Chen, 1998). Yuan and Zydney (2000) reported increased hydraulic resistance of humic acid deposited at lower pH.

Conversely, Huisman et al. (1999) investigated critical flux as a function of zeta potential. They found that the critical flux was affected neither by membrane zeta potential nor by particle zeta potential. The size of particle that they used was too large to be affected by zeta potential (0.53 µm silica particle).
In general, the critical flux decreased with increasing concentration of particles (Defrance and Jaffrin, 1999; Li et al., 2000; Gèsan-Guiziou et al., 2002; Kwon et al., 2000; Huisman et al., 1999). However, addition of larger particles resulted in higher critical flux (Defrance and Jaffrin, 1999; Li et al., 2000; Gèsan-Guiziou et al., 2002; Kwon et al., 2000; Huisman et al., 1999).

Generally, the critical flux decreased with increasing concentration of dissolved organic materials (Li et al., 2000; Metsämuuronen et al., 2002; Mänttäri and Nyström, 2000; Chen, 1998). However Defance and Jaffrin (1999) reported that the role of dissolved matter in determining critical flux was small since the difference in fouling resistance was only about 5% for the DOC variation of 300 ~ 1200 mg/L. It has been noted that addition of particles reduced the amount of adsorbed NOM on membrane surface (Champlin, 2000), and this could have an impact on critical flux.

In the study of crossflow ultrafiltration with binary mixture of proteins, Chan et al. (2002) reported that the apparent critical flux measured for their UF system was dominated by concentration changes of the larger protein.

Membrane surface characteristics can affect the critical flux. The critical flux was larger for hydrophilic than for hydrophobic membranes (Defrance and Jaffrin, 1999). Mänttäri and Nyström (2000) reported significant irreversible fouling of the most hydrophobic membrane due to sorption of the organic solutes by hydrophobic interaction with the membrane.

---

6 γ-globulin (150 kDa), lysozyme (14.6 kDa), bovine serum albumin (68 kDa), and β-lactoglobulin (18.4 kDa)
Critical flux is affected by hydraulic conditions. The critical flux increased as crossflow velocity increased due to the erosion of the deposited layer (Espinasse et al., 2002; Howell, 1995; Li et al., 2000; Vyas et al., 2002; Mänttäri and Nyström, 2000; Defrance and Jaffrin, 1999). The impact of Reynolds number and wall shear stress can be understood in same way, i.e. higher Reynolds number (Wu et al., 1999) and wall shear stress (Gèsan-Guiziou et al., 2002) resulted in higher critical flux. Interestingly, Bacchin et al. (1996) reported that crossflow was useless when filtering a destabilized colloidal suspension.

Although sub-critical flux operation can improve system performance by reducing fouling, the operation can still encounter problems. Operation at a very low flux may not be economical. Operation at constant permeate flux can result in local fluxes that are too high in some regions of a filter (Cho and Fane, 2002). However, it seems clear that systems with a high critical flux and with significantly larger particles can benefit from operating below the critical flux (Vyas et al., 2002).

There is controversy on how and why operation mode affects the system performance. Constant flux and constant TMP modes are the operation modes used in membrane filtration system. Defrance and Jaffrin (1999) and Decloux and Tatoud (2000) supported constant flux operation mode while Vyas et al. (2002) recommended constant pressure mode. A system with combination of those two modes was reported to show better
performance when constant TMP operation was followed by low constant flux operation (Vyas et al., 2002).

The objectives of this chapter were: 1) develop an accurate method to evaluate the critical flux of a membrane filtration system; 2) determine the effects of NOM concentration and type, particle concentration, and operational mode on critical flux and on resistance to filtration; 3) determine the effect of operational mode (constant flux or constant TMP) on filter performance; and 4) develop a conceptual model to explain the effects of NOM, particles, and operational mode on critical flux.

3.3. Summary of experimental protocols

Materials and methods pertinent to this chapter were reported in Chapter 2 of this thesis. In summary, polyethersulfone (PES) membranes (PBHK, Millipore, Bedford, MA) with a 100 kD molecular weight cut off (MWCO) were used for the experiments carried out in this chapter. Synthetic waters used for these experiments were prepared using various natural organic materials (NOM), kaolinite and alumina particles, and salts to reproduce alkalinity and hardness values that are typical for many raw waters.

Three series of tests are reported in this chapter, all focused on investigating the causes of fouling and critical flux in UF.
3.4. Results and discussion

3.4.1. Observation of critical flux

Critical flux measurements were made for several raw waters for many synthetic water conditions. In most cases, rapid increase in TMP as a function of permeate flux was observed within the tested range of permeate flux (up to 380 l/mh). In some cases there was no apparent critical flux within the tested range, as described below for aquatic humic materials.

3.4.1.1. TMP, critical flux, and resistance versus flux for natural raw waters

The TMP behaviors and the critical fluxes for a spring water from Chilhowee (VA), a reservoir water from Gardner (MA), and Mississippi River water from East St. Louis (IL) are shown in Figure 3.1. Each data point in Figure 3.1 represents the average TMP during 10 minutes of filtration at a fixed permeate flux, as described in the section “2.6 Evaluation of resistances” of this thesis. The sample of Mississippi River water had higher alkalinity, turbidity, UV$_{254}$, and DOC compared to the other waters (Table 3.1). The critical flux of the system was 334.9 l/mh with Chilhowee water, 129 l/mh with Gardner water, and 102.4 l/mh with Mississippi water (Figure 3.1).
Table 3.1. Characteristics of natural raw waters

<table>
<thead>
<tr>
<th>Raw water</th>
<th>pH</th>
<th>Alkalinity [mg CaCO₃/L]</th>
<th>Turbidity [NTU]</th>
<th>UV₂₅₄ [1/cm]</th>
<th>DOC [mg C/L]</th>
<th>ZP [mV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chilhowee spring water</td>
<td>7.58</td>
<td>66.55</td>
<td>1.56</td>
<td>0.015</td>
<td>0.17</td>
<td>-12.8</td>
</tr>
<tr>
<td>Gardner reservoir water</td>
<td>7.36</td>
<td>14.07</td>
<td>0.529</td>
<td>0.036</td>
<td>2.70</td>
<td>-21.7</td>
</tr>
<tr>
<td>Mississippi river water</td>
<td>7.82</td>
<td>126.18</td>
<td>4.5 – 116.7</td>
<td>0.242</td>
<td>5.34</td>
<td>-16.1</td>
</tr>
</tbody>
</table>

Figure 3.1. TMP changes with step-wise increasing flux and the critical fluxes of the system with different natural raw waters. The critical flux with the Mississippi water was 102.4 lmh, the Gardner water 129 lmh, and the Chilhowee 334.9 lmh. The critical flux of the system with each natural water was shown by the arrow.

The lower critical flux for the Mississippi River water corresponds to poorer water quality, i.e. higher turbidity, UV₂₅₄, and DOC than for the other waters.

The hydraulic resistances that correspond to Figure 3.1 are illustrated in Figure 3.2.

Plots of resistance versus flux illustrate the effects of contaminants on membrane
performance. The hydraulic resistances for sub-critical conditions were relatively constant and the differences among the raw waters were indistinct. On the other hand, the resistance increased with different rate according to the raw water characteristics when the operating flux was higher than the critical value.

The samples from Chilhowie and from Gardner (results described in Figure 3.1) were obtained during episodic events that caused failures at operating full-scale UF facilities. For example, the plot of resistance versus permeate flux for Chilhowie water shown in Figure 3.2 was for a storm event (as shown in Figure 3.1). The results for Gardner water in Figure 3.1 and Figure 3.2 were for the water that was obtained during seasonal overturn of the reservoir.

![Hydraulic resistances with permeate flux](image)

**Figure 3.2.** Hydraulic resistances of different natural raw waters at the given fluxes.
3.4.1.2. **TMP, critical flux, and resistance versus flux for synthetic water**

Similar experiments were run using synthetic water. The composition of the synthetic water was presented in section 2.4 of this thesis.

The data were plotted to show average TMP as a function of the step-wise increasing flux. The data were analyzed and evaluated to determine the critical flux of the system as described in section 2.4. The critical flux of the system with the synthetic water was 262 l/mh (Figure 3.3).

In preparation for subsequent experiments with 120-minute filtration times, similar experiments to those shown in Figure 3.3 were run using 20-minute incremental filtration steps (instead of 10 minute filtration per incremental flux value). The 20-minute critical flux was 248 l/mh. The critical value for 120 minutes was calculated using Equation 2.4 of Chapter 2. The corrected critical flux of the system for 120 minute operation was 216 l/mh.
Figure 3.3. Critical flux of the synthetic water. The solution contained 2.5 mg alumina/L, 2.5 mg kaolinite/L and 5.0 mg AHA/L, 0.5 mM NaHCO₃ and 0.2 mM CaCl₂.

3.4.2. **Longer operation at sub-critical and super-critical fluxes**

3.4.2.1. **Constant flux experiments**

When the filtration experiments were carried out using sub-critical fluxes (139 and 199 lmh), the TMP rose very gradually and in a linear fashion during 120 minutes, as shown in Figure 3.4. When the filtration was performed for 120 minutes at super-critical fluxes (242 and 263 lmh), the TMP increased exponentially with operating time. These results are also shown in Figure 3.4.
Figure 3.4. Transmembrane pressure (TMP) changes with operating time under sub-critical and super-critical fluxes. Permeate flux was held constant for 120 minutes for each of the four experiments.

The exponentially increasing TMP with time for the permeate fluxes that had been determined to be super-critical (263 lmh and 242 lmh) are qualitative and quantitative confirmation of the concept of critical flux and of the values that were reported in the previous section of this thesis for this synthetic water. The resistance change with operation time (not shown) showed the same pattern as the TMP changes.

The exponential increase in TMP or resistance with increasing flux, for super-critical conditions, is an indication of fouling. With super-critical flux, the transport of particles and NOM to the membrane surface will increase and the concentration polarization layer and/or cake layer will become more compact and thicker, which will cause more hydraulic resistance to the flow.
As illustrated in Figure 3.5, the resistances after hydraulic rinse \((R_{hy})\) increased with permeate flux, but the resistance after chemical cleaning \((R_{ch})\) was not significantly affected by flux for this water. The large increase in \(R_{hy}\) with flux would mean that more frequent chemical cleaning would be required for the higher permeate fluxes.

![Resistance after hydraulic rinse and chemical cleaning under constant flux condition](image)

**Figure 3.5.** Resistances \((R_{hy}, \text{resistance after hydraulic rinse, and } R_{ch}, \text{resistance after chemical cleaning})\) of the system under constant permeate flux condition.

### 3.4.2.2. Constant TMP experiments

Similar results were observed for experiments that were run at constant TMP conditions over a range from initially sub-critical to initially super-critical flux. The initial TMP for these experiments were identified from critical flux results that were shown in Figure 3.4. Note that three of the conditions appeared to have super-critical flux and only the lowest TMP resulted in initially sub-critical flux.
The permeate flux decreased linearly and slowly as the TMP of the system increased under sub-critical conditions (1.25 psi) while permeate flux decreased exponentially and rapidly under super-critical conditions (Figure 3.6). Qualitatively, the higher TMP conditions should increase the transport of particles and NOM to the membrane surface and the accumulated layer should become more compact and less permeable than for sub-critical conditions.

Although the initial flux was higher for higher initial TMP, the flux decline rate was also faster with higher TMP. After about 100 minutes of operation, the lowest initial TMP condition produced a higher flux than was obtained with the three super-critical conditions. The order of flux was completely reversed after 100 minutes of operation (Figure 3.7).

These results show that operation of a UF system at super-critical conditions could result in lower production of water than if the system had been initially operated at a sub-critical flux. These results are also pertinent to many prior studies of UF and MF. Many investigators have operated at a high initial TMP and they have frequently suggested that certain solutes or particles were responsible for irreversible fouling, based on their observations of exponentially decreasing permeate flux. It might be important to investigate whether operation at super-critical fluxes might have jeopardized the value of some experimental results that have been reported in the literature.
Figure 3.6. Flux decline with operation time under constant TMP conditions. The TMP conditions 1.25 and 2.43 psi are the conditions corresponding sub-critical conditions while the other two (4.57 and 6.19 psi) are for super-critical conditions. Every test was carried out under the constant TMP condition for 120 minutes.

Figure 3.7. Flux decline with operation time under constant TMP conditions (detailed data between 100 and 120 minutes of operation time). The data were same as the ones used in Figure 3.6. The data was selected from the range between 100 and 120 minutes of operation to illustrate the reversed order of flux clearly.
The hydraulic resistance during each experiment was evaluated, using the flux and the TMP data that were accumulated during the experiment (Figure 3.8). There was no change in resistance for the sub-critical condition (1.25 psi), small linear change in resistance for the condition with barely super-critical initial flux (2.43 psi), and rapidly increasing resistances for the systems with clearly super-critical initial conditions (Figure 3.8 a). Resistances increased exponentially with volume for all of the super-critical initial conditions (Figure 3.8 b).

![Figure 3.8](image_url)

**Figure 3.8.** (a) Resistance variation with operation time under constant TMP conditions and (b) resistance variation with accumulated volume filtered. The TMP conditions of 1.25 psi is the condition corresponding to sub-critical conditions while the others (2.43, 4.57 and 6.19 psi) are for super-critical conditions. Every test was carried out under the constant TMP condition for 120 minutes.
The resistances after hydraulic rinse ($R_{hy}$) increased as TMP increased while the resistances after chemical cleaning ($R_{ch}$) did not change much with TMP (Figure 3.9). As observed from the results with constant flux mode (Figure 3.5), the resistances due to sorption of NOM, which is related with $R_{ch}$, were not affected much by the changes of the physical operating parameters such as TMP and permeate flux.

![Figure 3.9. Resistances (resistance after hydraulic rinse and resistance after chemical cleaning) of the system under constant pressure condition. The resistances of the membranes were determined by measuring the particle-free MilliQ water flux.](image)

3.4.2.3. **Comparison of constant flux with constant TMP operating modes**

The previous results were rearranged so as to better compare the constant flux with the constant TMP operational modes (Figure 3.10, Figure 3.11, and Figure 3.12).

When the permeate flux was less than the critical flux, there was a small and linearly increasing resistance with increasing volume filtered. However, sub-critical flux
operation with constant TMP resulted in higher initial resistance and more rapidly increasing resistance with volume filtered, compared to sub-critical constant flux operation. This result is shown in Figure 3.10 a b, i.e. the initial permeate flux for operation at 1.25 psi was 149.5 l/mh, yet the initial resistance and the rate of increase in resistance with volume filtered were both higher than for initial flux of 199 l/mh under constant flux conditions.

Operation using super-critical conditions (Figure 3.10 b) resulted in higher and more rapidly increasing hydraulic resistances for both operating modes.

A greater volume of treated water was produced using constant flux than constant TMP operation, i.e. the maximum volume produced by constant TMP in 120 minutes was 1283.0 mL while constant flux produced up to 2004.6 mL during 120 min (Figure 3.10).
Figure 3.10. Comparison of the total resistances of the membrane under constant flux mode and constant pressure mode. The flux and pressure are corresponding to each other. (a) includes the results with sub-critical conditions; (b) with super-critical conditions.
The other resistances such as the resistance after hydraulic rinse ($R_{hy}$) and after chemical cleaning ($R_{ch}$) were compared to investigate the differences in the mechanisms of fouling under different operating modes.

As the flux increased, $R_{hy}$ also increased (Figure 3.11 a). There was not much difference between constant pressure and flux modes when the system was operated under sub-critical conditions.

![Graph showing hydraulic resistances under constant flux and TMP modes.](image)

> Figure 3.11. Hydraulic resistances under (a) constant flux mode and (b) constant TMP mode. $R_{hy}$ is the resistance after hydraulic rinse and $R_{ch}$ is the resistance after chemical cleaning. The number in parenthesis is the initial flux [lmh] of the constant flux mode operation.
$R_{hy}$ increased with increasing TMP in constant TMP mode operation (Figure 3.11 b).

$R_{ch}$ was much lower than $R_{hy}$ for all of the experiments (Figure 3.11 a and Figure 3.11 b). The effect of flux on $R_{ch}$ was not clear, but in all cases, the resistances after chemical cleaning with constant flux mode were higher than those with constant pressure mode. This suggests that contaminants were more likely to be bound to the membrane in locations that resisted chemical cleaning for constant flux than for constant TMP operation.

When the resistances were normalized to the volume filtered, it suggested that increased flux or TMP resulted in increased $R_{hy}$. The resistance after chemical cleaning, $R_{ch}$, decreased with increased flux or TMP although the trend was not so clear. The resistances of the system operated under constant TMP mode were always higher than those operated under constant flux mode (Figure 3.12 a and b).

Ho and Zydney (2002) used a pore blockage and cake filtration model to predict TMP profiles for constant flux operation of MF. They assumed that fouling occurred first by pore blocking and that a cake layer was subsequently formed over the blocked area of the membrane. Their model was in good agreement with experimental data.
Figure 3.12. Hydraulic resistances normalized to filtered volume under (a) constant flux mode and (b) constant TMP mode. $R_{hy}$ is the resistance after hydraulic rinse and $R_{ch}$ is the resistance after chemical cleaning. The number in parenthesis is the initial flux [lmh] of the constant flux mode operation.

The experimental results that are shown in Figures 3.10 through 3.12 seem consistent with the Ho and Zydney model, i.e. the constant TMP mode produced very high initial fluxes, which could have produced an initial cake layer that subsequently removed foulants before they could reach the membrane surface. Filtration using constant flux, on the other hand, did not produce as rapid a change in resistance as was observed for the constant TMP experiments. This indicates that the cake layer was less developed for the
constant flux condition, and this might have permitted passage of foulants to the membrane surface. This hypothesis is illustrated in Figure 3.13. The hypothesis is not entirely consistent with experimental observations, since there was a greater volume of water filtered for the constant flux condition in each of the paired experiments.

![Figure 3.13. Conceptual models of resistance build-up under different operating modes.](image)

3.5. Conclusions

Critical flux of a membrane system was investigated as a measure of system performance. Plots of TMP versus flux were divided into two flux groups, i.e., lower fluxes for which there was no or little increase in TMP with time and higher fluxes for
which TMP increased rapidly over time. The lower fluxes were labeled “sub-critical” and the higher fluxes were labeled “super-critical”.

The critical flux depended on the nature of the water that was filtered. Critical flux values were determined for several raw waters. The critical flux of the system with the synthetic model water was evaluated to be 262 lmh for 10-minute filtration at each incremental flux and 248 lmh for 20-minute filtration at each flux. An equation was developed to extrapolate to longer filtration times, and this led to an estimate that the critical flux would be 216 lmh for operation using 120 minutes between hydraulic cleaning. This value was in agreement with an alternative evaluation for critical flux, based on measurement of $dP/dt$ for each incremental flux value.

Experiments were run for 120 minutes under sub-critical and super-critical conditions for either constant flux or constant TMP operational mode. These experiments confirmed that operation under sub-critical flux resulted in small, linear increases in TMP with filtration volume. Operation at super-critical conditions resulted in exponentially increasing TMP with filtered volume.

Operation under constant flux conditions was better than operation under constant TMP conditions for the following reasons: 1) constant flux produced lower resistance than constant TMP for sub-critical conditions (i.e. higher resistance for constant TMP with initial flux of 160 lmh compared to constant flux at 199 lmh); 2) the rate of increase in resistance was higher for sub-critical constant TMP than for sub-critical constant flux conditions (same pair of data sets); and 3) constant flux resulted in a larger volume of treated water during 120 minutes than was produced under constant TMP conditions.
Final resistance to filtration ($R_d$) was higher for constant TMP conditions. Resistance after a hydraulic rinse ($R_{hy}$) was similar between the two modes after 120 minutes of filtration, but $R_{hy}$ normalized to the volume of water treated was substantially lower for the constant flux than for the constant TMP conditions. Resistance after chemical cleaning ($R_{ch}$) was always higher for constant TMP operation, although in most cases the value was lower for constant flux if normalized by the volume of water that was filtered. A model was proposed to explain the different development of $R_{hy}$ and $R_{ch}$ for the two modes.

Most bench-scale investigations of membrane filtration have been conducted using constant TMP conditions. The results that are presented in this chapter show that some published conclusions from research using constant TMP conditions might be questionable.
3.6. **References**


Chapter 4. Foulants: NOM and particles

4.1. Overview

Fouling is one of the biggest obstacles in using membrane filtration in water and wastewater treatment as it increases the hydraulic resistances of the membrane filtration systems and, hence, increases operational cost. Before we try to find methods to decrease fouling, we need to understand what causes fouling in membrane filtration system and how they work.

Among the components of NOM, the humic fraction causes more fouling than any other components because of its high adsorptive capacity on the membrane surface. Although a single source of humic materials can be made up of components that have a broad range of chemical and physical properties, water-NOM can be differentiated from soil-NOM according to UV-absorbance, hydrophobicity, molecular weight etc. These characteristics can indicate the tendency to foul in UF. In these experiments, soil-NOM caused significantly more fouling and resistance to filtration, and lower critical flux, compared to water-NOM.

NOM has been shown to be a major foulant in membrane filtration for water treatment. It is expected that increasing NOM concentration increases deposition on the
membrane. In these experiments, higher hydraulic resistance and lower critical flux was observed with increasing concentration of NOM.

Particles can play a role as an adsorbent of NOM, competing with membrane for sorption of NOM and thus reducing NOM adsorption on the surface or in the pores of the membrane. The resistances by concentration polarization and/or cake layer were affected very little by changes in the alumina concentration.

The rejection of dissolved organic matter was measured by UV$_{254}$ and DOC. Rejection did not change with NOM concentration while rejection increased with increasing alumina concentration.

### 4.2. Introduction

#### 4.2.1. Natural Organic Matter (NOM)

Natural organic matter (NOM) is ubiquitous in natural aquatic systems (river water and groundwater). Humic substances are the most representative part of stable organic carbon in the biosphere, comprising approximately 60~70% of the total organic carbon in soils and 60~90% of dissolved organic carbon in natural waters. They are predominant species of natural organic matter (NOM). The properties of humic substances vary from source to source, because they are heterogeneous mixtures of biochemical degradation products from plant and animal residues, and synthesis activities of microorganisms (Aguer et al, 2002; Wang et al, 2001).
Humic and fulvic acids (HA and FA) are subclasses of the humic substances, which are operationally divided by their solubility at pH ~ 2 (HAs insoluble and FAs soluble in acid). Humic materials are most abundant in the upper 30–60 cm of the Earth’s crust, where they may be formed more rapidly due to the availability of air, water, and active microorganisms (Aguer et al. 2002). Humic substances behave as flexible, linear polyelectrolytes in aqueous solution; Increasing the ionic strength of solution will lead to a continuous change in humic acid conformation from an uncoiled macromolecule (i.e. expanded conformation) at low salt to a fully coiled state (i.e. compact conformation) at high salt concentration (Bob and Walker, 2001a; Ghosh and Schnitzer, 1980).

NOM is a major precursor to the formation of disinfection by products (DBPs), such as trihalomethanes and other halogenated organics. It has been reported that the formation of DBPs is directly proportional to the concentration of total organic carbon (TOC). DBPs are probable carcinogens and short-term exposure can lead to dizziness, headaches, as well as problems associated with the central nervous system. Recent studies have also linked DBPs to increased incidence of miscarriage, rectal and bladder cancer, and neural tube birth defects. As a result, the USEPA has proposed new maximum contaminant levels (MCLs) of 40 and 30 µg/L in finished drinking water for THMs and HAAs, respectively (Bob and Walker, 2001b).
4.2.2. **Natural aquatic system and NOM**

The stability and mobility of colloidal particles in surface water and ground water is known to be affected by the presence of adsorbed NOM. Especially, humic and fulvic acids affect the surface charge of particles in natural aquatic systems.

Tiller and O’Melia (1993) reported that at low ionic strength the adsorption of aquatic NOM increased the stability of hematite particles. In humic acid adsorption onto the surfactant-free amidine polystyrene latex particle, electrostatic interaction was predominant at low ionic strength (Bob and Walker, 2001a). Kretzschmar *et al.* (1998) also reported the same observation in their study on humic acid adsorption on kaolinite at low to medium ionic strength (≤ 0.01 M NaClO₄) that the stabilizing effect of adsorbed humic acid was purely electrostatic. But Kretzschmar *et al.* (1998) added that the steric interaction was also responsible for the increased colloidal stability of clay-humic complexes.

In their study on desorption of humic acid from iron oxide surfaces, Avena and Koopal (1998) hypothesized that electrostatic interactions must be present because both the surface and the particles carry electrical charges and observed that the adsorption was favored by electrostatics at pH < iep of the surface and disfavored at pH > iep. They insisted that specific interactions must also be involved since otherwise humic acid would not adsorb at pH > iep. Specific interactions are usually considered to be complexation reactions of carboxylic and phenolic groups of the humic acid with the surface hydroxyl groups of the oxide (Avena and Koopal, 1998).
4.2.3. **NOM or Inorganic Particles - Performance of membrane system**

NOM has been implicated in fouling problems in the application of membrane technology. As NOM adsorbs onto the surface of oxides easily in natural aquatic system, it is very important to understand the mechanisms of interactions among NOM, inorganic particles and membrane.

Inorganic particle concentration has been related negatively to the membrane performance, i.e. it has been reported that as inorganic particle concentration increases, resistance of the membrane system also increases. In a theoretical investigation on particle deposition onto a permeable surface, Song and Elimelech (1995) showed that strong interplay between permeation drag and electrical double layer repulsion developed by similarly charged particles and surfaces can significantly hinder the rate of particle deposition. Huisman et al. (1998) reported that there was hysteresis in the relationship between flux and TMP which was caused by the silica cake layer formed during crossflow microfiltration and the reversibility of the filter cake depended strongly on the zeta potential of the silica particles when the particles had similar charge with the membrane (i.e., negative charge). When adsorbed on mineral surfaces, dissolved organic matter and anionic surfactants may mask underlying surface charge heterogeneity, thereby reducing particle deposition rates and enhancing colloidal mobility (Song et al., 1994). The observation by Champlin (2000) was opposite to the others’ findings, i.e., adding particles decreased NOM adsorption on the ultrafiltration membrane. Hong et al. (1997) reported increased flux declining rate with increasing particle concentration in
their study on silica (0.10 μm) fouling of zirconia tubular ceramic membrane with average pore size of 0.2 μm.

In general, flux decline of a membrane system is closely related to NOM concentration of the system. Waite et al. (1999) reported that increasing fulvic acid concentration resulted in increasing cake resistance except for the case when the zeta potential of the aggregate (the fulvic acid and hematite) was close to zero, which showed minimum cake resistance. It was reported that the amount of NOM that sorbed onto the membrane was increased with increasing NOM concentration of the feed water (Champlin, 2000), but Mänttäri et al. (2000) reported improved flux with humic acid addition in their study on the crossflow nanofiltration system because of the effect of the negative charge of humic acid.

As NOM (mainly humic substances) has been suspected as one of the main fouling causing materials (foulant), it is critical to understand the impact of different NOM on the system performance in applying the membrane filtration system to water treatment. There have been some contradictory findings in terms of the impact of different NOM type on the membrane filtration performance.

Combe et al. (1999) observed that the hydrophobic/hydrophilic property of the membrane was not changed by fouling in their study of the hydrophobic humic acid adsorption onto the cellulose acetate membrane. Crozes et al. (1993) concluded that a polar molecule was more adsorbable than a non-polar molecule and thus, adsorption
phenomena must be governed by membrane hydrophilicity and organic compound polarity.

According to the results from previous studies, water-NOM such as Suwannee River humic and fulvic acid has higher carboxylic acidity than soil-NOM such as Aldrich humic acid (Hong and Elimelech, 1997). The average molecular weight of soil-NOM is larger than that of water-NOM (Combe et al., 1999; Yuan and Zydney, 2000, Perminova et al., 2003). Chin and co-workers also reported that aquatic humic substances are smaller and less polydisperse (Chin et al., 1994). From the previous observation that the hydrophobicity of humic substance increases with increasing molecular weight and decreasing acidity, Combe et al. (1999) concluded that soil-humic acid is more hydrophobic than water-humic acid.

Fan et al. (2001) reported the order of fouling potential of NOM fraction as hydrophilic neutral > hydrophobic acids > transphilic acids > hydrophilic charged. They attributed high flux decline to high molecular weight fraction of NOM (> 30 kDa) and high aromaticity (hydrophobicity).

Schäfer et al. (2001) observed a different order in flux decline. Regardless of the presence or absence of hematite particles, humic acid (78% decline in flux) had a greater impact on membrane performance compared to fulvic acid (15%) and NOM (37%).

According to the observation of Cho et al. (1999), NOM aromaticity did not affect the flux decline of NF membrane but UF membrane. They suggested UV$_{254}$ and SUVA could be used as indicators of the NOM filtration properties.

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SUVA: Specific Ultraviolet Absorbance [L/mg-m]. SUVA is determined by dividing UV$_{254}$ with DOC.
Alborzfar et al. (1998) reported lower flux decline for the humic acid water than the fulvic acid water though the membrane cleaning could not recover the initial permeate flux completely when the humic acid water was NF filtered while the initial flux of the fulvic acid water was completely recovered. Their observation can be related to humic and fulvic acid fouling in terms of adsorption on the surface and in the pore of the membrane.

Yuan and Zydney (2000) studied the flux decline at the end of humic acid filtration and reported that water-humic acid (Suwannee river humic acid) resulted in greater flux decline than for soil-humic acid (Aldrich humic acid). Their Aldrich humic acid had been pre-filtered using 0.2 µm pore size. They observed no difference in the resistance by adsorbed layer between those two humic acids.

The following hypotheses were proposed, dealing with the physical and chemical performance of the membrane filtration system and the effects of NOM characteristics, NOM concentration, and inorganic particle concentration.

- Among the components of NOM, the humic fraction causes more fouling because of its adsorptive capacity on the membrane. As a result, the impact of NOM on fouling will depend on the origin and characteristics of the NOM. Also, the impact of NOM derived from water should be less than the impact of NOM derived from soil, since soil-NOM is generally retained in that environment due to the tendency to sorb, and the tendency to sorb is related to hydrophobicity and molecular size.
NOM has been known to be a major foulant in membrane filtration for water treatment. It is expected that for a given NOM, increased concentration will increase the hydraulic resistance in UF.

Increasing concentration of sorbents for NOM can improve the performance of UF. In other words, particles can compete with the membrane for the most sorbable fraction of the NOM.

This research is a part of a comprehensive study that sought to understand the interactions among particles, NOM, and membrane, and to find a way to improve both the physical and chemical performance of a membrane filtration system.

In this chapter, we will present the results of the experiments to understand the impact of inorganic particle and NOM molecules on the system performance and provide possible ways to improve the physical and chemical performance of the membrane system.

4.3. **Summary of experimental protocols**

Materials and methods pertinent to this chapter were reported in chapter 2 of this thesis. In summary, polyethersulfone (PES) membranes (PBHK, Millipore, Bedford, MA) with a 100 kD molecular weight cut off (MWCO) were used for the experiments carried out in this chapter. Synthetic waters used for these experiments were prepared
using various natural organic materials (NOM), kaolinite and alumina particles, and salts to reproduce alkalinity and hardness values that are typical for many raw waters.

The adsorption of NOM onto the alumina particles was determined in batch experiments. The pH of the system was kept constant at 7.67 by using a phosphate buffer solution (KH$_2$PO$_4$ and NaOH). The salt concentration for the ionic strength of the system was 0.01 M NaCl. The NOM concentration was 5.0 mg AHA/L and the inorganic particle concentration was 10.0 mg/L alumina.

Kinetic experiments of sorption of NOM onto alumina were also conducted. For the kinetic experiments, samples were taken at 1, 10, 20, 30, 40, 50, 60, 70, 80, 100, and 120 minutes after the addition of AHA to the suspension. The pH, temperature and ZP were measured immediately after taking each sample. The samples for UV$_{254}$ and dissolved organic carbon analyses were prepared at the same time by filtering the solution using 0.2 µm syringe filters. The UV$_{254}$ of the filtered sample solution was measured with Shimadzu spectrophotometer (UV-1601) and dissolved organic carbon (DOC) with Shimadzu TOC analyzer (TOC-5000A). DOC samples were acidified to pH 2.0 with 1.0 N HCl before the measurement. The adsorbed amount was calculated by measuring the depletion in the solution.

Three series of UF tests are reported in this chapter, all focused on investigating the causes of fouling and critical flux in UF. First, the impact of NOM molecules from different origins on the chemical and physical performance of UF was investigated.
Seven different NOM’s were investigated to evaluate relationships between characteristics of the NOMs and the hydraulic and chemical performance of the system. \( \text{UV}_{254} \) and Specific Ultraviolet Absorbance (SUVA) were used to characterize the humic fraction of NOM; \( \text{UV}_{254} \) and SUVA values are related to the aromatic composition and of the humic fraction of the NOM (Korshin, 1997; Cho et al., 2000). Humic materials are generally considered to be the most important of the organic foulants in UF treatment of potable water.

The second series of tests was designed to evaluate the impact of the concentration of the organic material on critical flux and fouling. Aldrich Humic Acid (AHA) purchased from Aldrich Chemicals (Milwaukee, Wisconsin) and was used after initial dissolution at pH 10 followed my MF filtration to remove undissolved particulate material. Five concentrations of AHA were tested, i.e., 0.0, 2.5, 5.0, 7.5 and 10.0 mg AHA/L. All chemical parameters except the concentration of NOM were kept constant during this series of tests (\( \text{NaHCO}_3 \) 0.5 mM, \( \text{CaCl}_2 \) 0.2 mM, kaolinite 2.5 mg/L, and alumina 2.5 mg/L).

The third series of experiments were carried out to test the impact of the relative concentrations of alumina and AHA on the system performance. Five alumina concentrations, 0.0, 2.5, 5.0, 7.5, and 10.0 mg/L and three AHA concentrations, 0.0, 5.0, and 10.0 mg/L were used. All chemical parameters except the alumina and NOM concentrations were kept constant during these tests (\( \text{NaHCO}_3 \) 0.5 mM, \( \text{CaCl}_2 \) 0.2 mM, and kaolinite 2.5 mg/L).
4.4. Results and discussions

4.4.1. Different NOM types

As illustrated in Figure 4.1, two groups of NOM were tested to investigate the impact of NOM characteristics on UF performance. The first group was water-NOM and included Georgetown NOM (GTNOM) and Suwannee River fulvic acid (SRFA). The second group consisted of soil-humic acids and included Summit Hill soil humic acid (SHSHA), Leonardite humic acid (LHA), Soil humic acid standard (SHAstd), and Aldrich humic acid (AHA). Some pertinent characteristics of these NOMs are presented in Chapter 2.

The UV absorbance of the six NOMs for initial NOM concentrations of 2.5 mg/L are shown in Figure 4.1. The water-NOMs had lower UV$_{254}$ and therefore lower SUVA than the soil-NOMs.
Figure 4.1. UV$_{254}$ of the NOMs. The shaded bars represent the water-NOMs while the clear bars are for the soil-NOMs.

4.4.1.1. Critical flux

Critical fluxes for water-NOMs were higher than 360 lmh, which was the highest flux that was tested in these experiments (Figure 4.2).

Figure 4.2. TMP increase with permeate flux of each NOM.
Critical fluxes for the soil-NOMs were between 153 and 268 lmh (Figure 4.3 a). The critical flux decreased with increasing UV$_{254}$ (Figure 4.3 b). It will be shown later in this chapter that the soil-NOMs sorbed more strongly on the membrane, and that this played a significant role in increasing the hydraulic resistance and decreasing the critical flux. Since SUVA and sorption are related to hydrophobicity and aromaticity, it was therefore concluded that the critical flux decreased with increasing hydrophobicity and aromaticity.

Figure 4.3. Critical fluxes of different NOMs (a) plotted as a function of the type of NOM (no critical flux was discovered for the water-NOMs), and b) plotted as a function of UV$_{254}$. 
4.4.1.2. Resistances

Resistances to filtration are plotted in Figure 4.4, where the resistances after completion of the critical flux tests are shown in Figure 4.4 a, the resistances after hydraulic rinse ($R_{hy}$) are shown in Figure 4.4 b, and the resistances after chemical cleaning ($R_{ch}$) are shown in Figure 4.4 c. All experiments were run using 2.5 mg/L of initial NOM and constant concentrations of particles, alkalinity, and hardness. Note that the scales on the y-axes are different for the three plots.

The results presented in Figure 4.4 showed that the soil-NOM group (Summit Hill Soil humic acid, Soil humic acid standard, Leonardite humic acid and Aldrich humic acid) had a much different effect on UF performance than the water-NOM group (GTNOM and Suwannee River fulvic acid). The resistance after the critical flux test much higher for the soil-NOMs than for the water NOMs, and the differences in resistance persisted through all of the cleaning steps.

The results from the experiments carried out by Yuan and Zydney (2000) were different, i.e, they did not observe much difference in the final resistance after UF of a water-NOM (Suwannee River humic acid) and a soil-NOM (Aldrich humic acid). Their system did not have any particulate inorganic materials such as alumina or clay. The particles and the NOM-adsorbed particles seemed to play important role in the hydraulic resistance and the critical flux of the system. Yuan and Zydney (2000) also reported that the water-NOM that had deposited on the membrane surface had a more open packing
and structure and they suggested this was due to greater electrostatic repulsion between the more negatively charged water-NOM.

The significance of the differences in resistances that are presented in Figure 4.4 could be questioned, since super-critical conditions were never reached for the water-NOMs and therefore deposition of materials on the filter should be less for the water-NOMs than for the soil-NOMs. On the other hand, the maximum permeate fluxes for the water-NOM cases were in excess of typical fluxes that are used in operating UF facilities for potable water (typically no more than 200 l/mh). In addition, the percent removal of NOM did not change during the critical flux experiments, i.e. for a given NOM the same removal occurred for either sub-critical or super-critical conditions, as shown in Figure 4.5.
Figure 4.4. Hydraulic resistances after the critical flux experiments: (a) total hydraulic resistance at the end of flux test ($R_f$), (b) resistance after hydraulic cleaning ($R_{hy}$), and (c) resistance after chemical cleaning ($R_{ch}$). Conditions were 2.5 mg NOM/L, 2.5 mg Alumina/L, 2.5 mg Kaolinite/L, 0.5 mM NaHCO$_3$ and 0.2 mM CaCl$_2$. The scales for y-axes are changed in the three plots.
Figure 4.5. UV$_{254}$ removal with flux for each NOM molecule

4.4.1.3. Rejection of NOMs during UF

The removals of UV$_{254}$ and TOC by UF were very different for soil-NOMs compared to water-NOMs. Almost none of the water-NOM was retained by the UF filter (about 1%) while there was substantial removal of the soil-NOMs (15~78%). These results are shown in Figure 4.6 a and b.

Küchler and Miekeley (1994) studied UF of humic compounds using 1 kDa membranes, and reported that HA retention (80–90%) was greater than that of FA (60–70%). Other investigators have studied a wide range of sorbents and have generally demonstrated less sorption of FAs than for HAs, and less sorption for water-NOM than for soil-NOM. Generally, HA has a higher molecular weight, higher carbon content and a smaller proportion of hydrophilic groups than FA (Hayes et al., 1989).

AHA was selected for subsequent experiments that are reported in this chapter, to evaluate the effects of NOM or particle concentration on fouling. The modified AHA that
was used in these experiments (see Chapter 2) was intermediate between the water-NOMs and the soil-NOMs that were investigated, i.e. the removal during UF was less than for the other soil-NOMs (Figure 4.6 a) and the critical flux was higher than for the other soil-NOMs (Figure 4.3 a). In addition, AHA has been previously studied by many other investigators.

Figure 4.6. Removal of UV$_{254}$ (a) as a function of the type of NOM and (b) as a function of the initial UV$_{254}$. 
4.4.2. **NOM adsorption**

4.4.2.1. **Zeta potential of particles**

Zeta potentials (ZP) of particles in the synthetic waters were investigated to gain insight into the effects of NOM and inorganic particle concentration on ZP, and then to determine the effects of ZP on fouling and critical flux. According to the previous study of Schäfer *et al.* (2000), different orders of mixing components (particle, organics, and background solution) resulted in different degrees of coagulation, aggregation, and apparent sorption. Therefore the particles were dispersed into water using an ultrasound bath before adding NOM and then background electrolytes. The methods of addition were reported in Chapter 2.

Fu (1996) previously reported that suspensions with ZP close to zero resulted in higher $R_f$ but lower $R_{hy}$. In some cases, Fu discovered that $R_{hy}$ was greater than $R_f$ for systems with ZP close to zero, presumably due to strong attachment to the surface of the membrane and closer packing of particles during hydraulic cleaning. It should be noted that Fu used a different technique to determine $R_{hy}$ than is used in this thesis. On the other hand, Fu reported that almost all of the incremental resistance ($R_f$) was removed after hydraulic cleaning, when the initial ZP was large.

ZPs are shown in Figure 4.7 a for alumina alone, alumina plus AHA, and alumina and AHA plus alkalinity and hardness species. Similar data are shown for the kaolinite systems in Figure 4.7 b, and for mixed alumina-kaolinite systems in Figure 4.7 c. The ZP values for alumina and for kaolinite were as expected, i.e. pH of the zero-proton-
condition ($pHzpc$) for alumina is about 9.0 to 9.5 and negative ZP for kaolinite over the entire pH range of interest.

In all cases, the ZP became more negative when AHA was added. This has been observed by many other investigators (e.g., Childress and Elimelech, 1996; Childress and Deshmukh, 1998) and is due to adsorption of NOM on the particles. Sorption and decrease of ZP occurred over the entire pH range and for both particles, even when surfaces of the particles were negatively charged. This has been interpreted to mean that there are specific interactions between NOM and particles, e.g. complexation or hydrophobic forces that were stronger that the electrostatic repulsive forces. Bob and Walker (2001b) reviewed the literature and also reported, based on their own studies, that non-electrostatic interactions played a very important role in controlling the sorption of NOM onto a variety of particles.
(a) Zeta potential of particles (alumina) vs. pH

(b) Zeta potential of particles (kaolinite) vs. pH

(c) Zeta potential of particles (alumina+kaolinite) vs. pH

Figure 4.7. Zeta potential of the particle system. (a) Alumina system, (b) kaolinite system, and (c) alumina+kaolinite system. A: Alumina (10 mg/L), K: kaolinite (10 mg/L), AK: alumina+kaolinite, O: NOM (5.0 mg AHA/L), S: background solution (0.2 mM CaCl₂ and 0.5 mM NaHCO₃)
4.4.2.2. Adsorption of NOM onto alumina and kaolinite

Both kinetic and isotherm sorption experiments were conducted, using kaolinite or alumina as the sorbents. Although NOM does sorb onto kaolinite, as demonstrated by the decrease in ZP of kaolinite suspensions upon addition of NOM, the extent of NOM sorption by kaolinite was small.

Sorption of NOM by alumina is shown in Figure 4.8. Kinetic experiments demonstrated that sorption was rapid, as illustrated by soluble UV$_{254}$ and DOC versus time in Figure 4.8 a. The amount of sorbed NOM (again in terms of UV$_{254}$ and DOC) was stabilized around 10% just after the experiment started (Figure 4.8 b). Changes in ZP occurred more slowly than changes in sorbed UV$_{254}$ and DOC, indicating possible rearrangement of AHA on the alumina surface (Figure 4.8 c).
Figure 4.8. Adsorption of AHA onto particles for 2.5 mg alumina/L, 2.5 mg kaolinite/L, 5.0 mg AHA/L, 0.01 M NaCl and pH buffered with KH$_2$PO$_4$ at pH 7.6. (a) UV$_{254}$ and DOC with time, (b) adsorbed UV$_{254}$ fraction with time, and (c) ZP with time.
Since sorption was much more extensive onto alumina than on kaolinite, subsequent sorption data are expressed in terms of mg of NOM sorbed per g of alumina, despite the simultaneous presence of kaolinite in the suspension.

Based on the kinetic experiments, 20 minutes of equilibration was selected for the sorption isotherm experiments. The AHA concentration was varied and the alumina concentration remained constant. The adsorbed concentration was calculated by subtracting the residual dissolved concentration from the initial concentration.

The adsorption of NOM on the inorganic particle appeared to be close to maximum sorption when the NOM concentration reached at about 20.0 mg AHA/L (Figure 4.9 a), when there were 100 mg of sorbed AHA per g of alumina. The ZP dropped to very negative values even for the lowest AHA concentration (Figure 4.9 c). The adsorption isotherm corresponded with Freundlich model (Equation 4.1) which has been used to describe adsorption on non-uniform sites, and the adsorption isotherm constants were 8.37 for $K_f$ and 1.11 for $n$ (Figure 4.9 b and d) when $q_e$ was expressed as mg AHA per g alumina and $C_e$ was expressed as mg/L AHA.

$$q_e = K_f \cdot C_e^{\frac{1}{n}}$$  \text{Equation 4.1}
(a) Adsorbed $\text{UV}_{254}$ and DOC with NOM

(b) NOM Adsorption Capacity

(Figure 4.9 Continues)
Figure 4.9. Adsorption of AHA on alumina for 10.0 mg alumina/L, 2.5 mg kaolinite/L, 0.01 M NaCl and pH of the solution was buffered with KH₂PO₄ at pH 7.6: (a) adsorbed UV₂₅₄ and DOC versus total NOM concentration; (b) raw adsorption isotherm, (d) Freundlich linearization of the isotherm (Kₚ = 8.37 and n = 1.11); and (c) ZP versus total NOM.
4.4.3. Removal of NOM by UF

4.4.3.1. Rejection and inorganic particle concentration

The removal of NOM during UF was investigated using a range of inorganic particle concentrations, in order to investigate the effects of sorption of NOM by particles on critical flux, resistance to filtration, and removal of NOM.

The percent removal of UV$_{254}$ increased with increasing inorganic particle concentration (Figure 4.10 a). The percent removal of DOC also increased with increasing particle concentration (Figure 4.10 b). The difference in NOM concentration (5.0 and 10.0 mg AHA/L) resulted in little difference in the rejection rate of both the UV$_{254}$ and DOC according to statistical analyses.

As more inorganic particles were added to the solution of the UF system, more AHA adsorbed on the inorganic particles and was rejected by the UF membrane.
Figure 4.10. Chemical performance of the system. (a) UV$_{254}$ removal. $t(6) = 0.208$; $p= 0.05$ and (b) DOC removal. $t(6) = 0.313$; $p= 0.05$. As $t_{crt}$($6$) = 1.943 with $p < 0.05$, the data with 5.0 and 10.0 mg AHA/L were not significantly different. 5.0 and 10.0 mg AHA/L concentrations correspond with DOC of 1.6 and 3.4 mg C/L, respectively.
4.4.3.2. Rejection and NOM concentration

The removal of AHA by UF was investigated as a function of the AHA concentration. It was expected that rejection of AHA would increase with increasing AHA concentration.

The UV$_{254}$ rejection rate (18~22%) and the DOC rejection rate (14~17%) were consistent in all the conditions during the experiments (Figure 4.11).

Figure 4.11. Chemical performance of the system. (a) UV$_{254}$ removal and (b) DOC removal of the system.
4.4.4. **Critical flux with NOM and inorganic particles**

4.4.4.1. **Critical flux and NOM**

The critical flux of the system decreased with increasing AHA concentration (Figure 4.12). Kwon et al. (1997) reported that increasing concentration of FA did not result in a decrease in the critical flux. The discrepancy between results shown in Figure 4.12 and the Kwon results might come from the different NOM used for the test. HA is more hydrophobic and has a larger molecular size than FA. Others have reported that the hydrophobic fraction of NOM with large molecular weight is the main cause of fouling or high resistance of membrane systems.

![Graph showing critical flux with different NOM concentrations](image)

**Figure 4.12.** Critical flux of the system with different NOM concentrations (There was no critical flux observed in the range of the experiments when the system has no NOM in it).
4.4.4.2. Critical flux and inorganic particles

The critical flux increased as the inorganic particle concentration increased (Figure 4.13). Kwon et al. (1997) observed that the critical flux in MF decreased with increasing kaolinite concentration (10–100 mg/L). They also reported that there was no significant effect of FA concentration on the critical flux. The discrepancy between the Kwon results and the result reported in Figure 4.13 might come from the different characteristics of the NOM (AHA versus FA), the nature of the particles (i.e., it was demonstrated that kaolinite is not an effective sorbent for AHA), the method to evaluate the critical flux, and different pore size and material of the membrane. Results that are shown in Figure 4.13 and the differences with the Kwon et al. (1997) results are consistent with one of the hypotheses for this chapter, i.e., the critical flux will increase (and the resistance will decrease) when large particles (relative to the pore size) that can sorb the NOM are added to the system.

![Critical Flux with Particle Concentration](image)

Figure 4.13. Critical flux of the system with different inorganic particle concentrations (There was no critical flux observed in the range of the experiments when the system has no NOM in it).
The critical flux decreased when NOM concentration was increased from 5.0 mg AHA/L to 10.0 mg AHA/L (Figure 4.13). No critical flux was discovered for the same synthetic water conditions in the absence of NOM (even for 10 mg/L of alumina). As a result, all of the critical fluxes that are reported in Figure 4.13 represent a decrease in critical flux compared to the same condition in the absence of AHA.

4.4.5. Resistances with NOM and inorganic particles

4.4.5.1. Resistances and NOM

It was expected that increasing the concentration of AHA would increase resistance to filtration due to increased sorption of AHA at the membrane surface. The results shown in Figure 4.14 confirmed the hypothesis with respect to total hydraulic resistance at the end of the flux test ($R_t$) (Figure 4.14 a) and the resistance after hydraulic rinse ($R_{hy}$) (Figure 4.14 b). There was not a clear trend of changing resistance with respect to AHA concentration after chemical cleaning ($R_{ch}$) (Figure 4.14 c). All values for $R_{ch}$ were smaller in the presence of AHA compared to the absence of AHA. In the presence of AHA, the range of values for $R_{ch}$ was only 19 to $32 \times 10^9$ m$^{-1}$, with a possible trend of decreasing $R_{ch}$ with increasing AHA concentration.

Mänttäri et al. (2000) reported improved flux in the pH range 7 – 8 with HA addition and attributed the improvement to alignment of HA on the membrane surface such that the hydrophobic parts of HA were attached to the hydrophobic membrane, and the hydrophilic parts of HA directed towards the solution, resulting in a more hydrophilic
surface which inhibited subsequent attachment of negatively charged particles or hydrophobic materials. Mänttäri et al. (2000) did not have particles in their experiments.

The experimental protocol for this thesis involved equilibration between AHA and alumina or kaolinite prior to the UF tests. Sorption of AHA made the zeta potential of the particles more negative. Both coating of the inorganic particles with AHA and the dissolved concentration of AHA increased with increasing total AHA concentration. It was also observed that $R_{ch}$ changed very little (possibly a slight downward trend) while $R_f$ and $R_{hy}$ increased. These results are consistent with the experimental observations and model developed by Fu and Dempsey (1998). They found that UF of particles that were poorly coagulated due to electrostatic repulsion (and possibly due to steric repulsion in the present case) resulted in high $R_f$, but that a greater percentage of flux was recovered after hydraulic cleaning (which included backwashing in their experiments) than for the coagulated case. In other words, a higher concentration of AHA leads to easier rearrangement and re-packing within the cake layer.
Figure 4.14. Physical performance of the system with constant particle concentration with varying NOM concentration. (a) Total hydraulic resistance at the end of flux test ($R_f$), (b) Resistance after hydraulic rinse ($R_{hy}$), and (c) Resistance after chemical cleaning ($R_{ch}$). The system has varying NOM concentration from 2.5 to 10.0 mg AHA/L with constant particle concentration of 2.5 mg Alumina/L and 2.5 mg Kaolinite/L. The system has 0.5 mM NaHCO$_3$ and 0.2 mM CaCl$_2$ as the background solution. The scale of plot was different from each other to show the trend more clearly.
4.4.5.2. Resistances and inorganic particles

The results from the experiments to investigate the impact of varying alumina concentration on critical flux and resistance are illustrated in Figure 4.15. None of the resistances ($R_f$, $R_{hy}$, or $R_{ch}$) were significantly affected by the alumina concentration when the AHA concentration was either 0 or 5 mg/L. Addition of alumina decreased $R_f$ and $R_{hy}$, for 10 mg AHA/L. $R_{ch}$ did not change with alumina concentration for any of the conditions that were tested (Figure 4.15 c).

It was hypothesized that increased alumina concentration would decrease sorption of NOM onto the membrane and, hence, decrease all of the resistances. The results were consistent with the hypothesis when considering $R_f$ and $R_{hy}$. 
Figure 4.15. Physical performance of the system with constant NOM concentration with varying particle concentration. (a) Total hydraulic resistance at the end of flux test \((R_f)\), (b) Hydraulic resistance after hydraulic rinse \((R_{hy})\), and (c) Hydraulic resistance after chemical cleaning \((R_{ch})\). NOM concentration was set to 0.0, 5.0, and 10.0 mg AHA/L. The solution has 0.5 mM NaHCO\(_3\) and 0.2 mM CaCl\(_2\) as the background solution.
4.5. **Conclusions**

The NOM used for the experiments could be categorized into two groups, water- and soil-NOM groups. The hydraulic resistances for the water-NOM experiments were much lower than for the soil-NOM experiments. Based on available information, the soil-NOM caused increased fouling due to greater removal by sorption onto the membrane. In turn, sorption was related to UV$_{254}$ and SUVA, and these parameters have been shown to be related to molecular weight and hydrophobicity.

The critical flux of the water-NOMs was higher than the maximum permeate flux that was used in these experiments, and higher than reasonable permeate flux that might be used in operating potable water systems. The critical fluxes for soil-NOMs were lower, which was consistent with the previous results and considerations.

Increased concentration of Aldrich HA (AHA) increased the resistances and this was presumed to be due to concentration polarization and a less porous and more deformable cake layer as illustrated in Figure 4.16. $R_{ch}$ decreased with increasing AHA concentration, although the trend was not strong.
The hydraulic resistance were unaffected by alumina concentration for low concentrations of soil-NOM (AHA $\leq$ 5.0 mg/L). Hydraulic resistances decreased with increasing alumina concentration when the solution contained 10.0 mg AHA/L. Increased alumina concentration also increased the critical flux for either 5 or 10 mg AHA/L. The alumina particles did not by themselves foul the membrane, i.e. no critical flux could be identified in the absence of AHA.

These results are consistent with the qualitative model that is shown in Figure 4.17, where it is shown that NOM is adsorbed onto particles thus decreasing sorption of NOM onto the surface of the membrane.
Figure 4.17. Conceptual model to explain the impact of inorganic particle concentration on the physical performance of the system.
4.6. References


15. **Fu, L. Fred**, 1996, *Charge effects in ultrafiltration*, PhD thesis, Penn State University, University Park, PA


29. Song, L., P.R. Johnson, and M. Elimelech, Kinetics of colloid deposition onto heterogeneously charged surfaces in porous media, *Environmental Science and Technology* 28 (1994) 1164 – 1171


Chapter 5. Ultrafiltration with coagulation

5.1. Overview

Though ultrafiltration (UF) is an efficient treatment process to remove various contaminants, there are physical and chemical limitations (fouling and poor removal of dissolved organic matters) in its use for water treatment. Coagulation pretreatment was effective for increasing critical flux, decreasing resistance to filtration, and improving removal of dissolved organic matter and turbidity. Turbidity was removed completely (99%) by UF with coagulation. Humic substances represented by UV$_{254}$ were removed completely by conventional coagulation and UF, while a smaller portion of humic substances was removed with unconventional coagulation conditions and UF; ~ 88% of UV$_{254}$ was removed by “unconventional” coagulation and UF for slightly acidic conditions.

The flocs formed under charge neutralization conditions were less compressible and more permeable than those formed under sweep floc conditions. Hydraulic resistances of the membrane system were lower with charge neutralization conditions than with sweep floc conditions. In some cases (condition #1, #3 and #4) the hydraulic resistance was lower with unconventional coagulation conditions than for conventional conditions.

It was concluded that the optimum coagulation conditions for conventional water treatment are not always the optimum conditions for UF with in-line coagulation. Also, it
was concluded that unconventional coagulation conditions can be much more effective than conventional coagulation ones in the context of membrane filtration, depending on the raw water characteristics.

5.2. Introduction

Membrane filtration – especially, microfiltration (MF) and ultrafiltration (UF) – has been getting more attention in water and wastewater treatment industry due to stricter regulations for finished water quality and due to cost efficiencies.

Though the ultrafiltration can remove particles, turbidity, microorganisms (bacteria, protozoa, algae), and some-viruses, the system still has important chemical and physical problems to overcome, especially removal of dissolved organic matter (NOM and DBPFP\(^8\)) and fouling (flux reduction or transmembrane pressure increase with operation of membrane filtration system).

Several investigators have sought ways to overcome these obstacles to use of membrane filtration for water and waste water treatment. Pre-treatments have been investigated including coagulation, powdered activated carbon (PAC) or granular activated carbon (GAC) adsorption, iron oxides adsorption (Campos et al., 1998; Campos et al., 2000; Li et al., 2003; Matsui et al., 2001a, 2001b; Zhang et al., 2003), ozonation (Bonné et al., 2000; Takizawa et al., 1996), application of rotating membrane

\(^8\) DBPFP: Disinfection by-product formation potential

In case of adsorption pretreatments, PAC or GAC and iron oxides adsorption were known to remove NOM but the added particles themselves could cause membrane fouling while coagulation was known to remove NOM and to reduce fouling at the same time (Carroll *et al.* 2000). According to their data, the rate of fouling by the PAC-treated water was similar to the raw water though the PAC particles themselves did not contribute a resistance to filtration. Bian *et al.* (1998) also reported that the resistances by concentration polarization, cake layer, and adsorbed layer were all higher when the water was treated with PAC than with coagulant. Pretreatment process may constitute up to one-fourth of the total costs of a membrane filtration facility (Gabelich *et al.*, 2002).

Coagulation is one of the most important processes in conventional treatment to produce drinking water. Iron or aluminum salts are added to remove contaminants by associating them with destabilized particles. Conventional water treatment includes coagulation, rapid mix, slow mix, settling, and conventional filtration. In-line coagulation process is a process of adding coagulant before membrane filtration without settling step (Guigui *et al.* 2002).
In-line coagulation is the focus of this investigation, as the pre-treatment to improve physical (fouling) and chemical (NOM removal) performance of the membrane filtration. Coagulation was selected because many water treatment operators have experience using coagulants and existing coagulation facilities could be used for a hybrid system that includes membrane filtration with coagulation.

Even though there have been a lot of researches on the coagulation mechanisms in aqueous environments, it still remains hard to understand the mechanisms in terms of physico-chemical aspect because it is difficult to characterize NOM molecules and structures of aggregates produced from coagulation process. It is usually accepted that two main mechanisms are used for the coagulation process in water and wastewater treatment; charge neutralization and sweep floc coagulation mechanisms.

The removal mechanism of NOM molecules under charge neutralization condition has been reported as both direct precipitation of humic substances by dissolved aluminum species and adsorption, while the major removal mechanism under sweep floc conditions is adsorption of humic substances on solid aluminum hydroxide, Al(OH)$_3(s)$ (Dempsey et al., 1984). Higher alkalinity and coagulant concentrations are needed for sweep floc conditions, and caustic or other alkaline reagents may be required due to the acidity of the coagulant.

Coagulation of particles becomes more effective as the zeta potential of the suspension gets close to zero. Effective coagulation conditions can result in increased particle size, and this can reduce fouling during membrane filtration by reducing adsorption in membrane pores, increasing cake porosity, and increasing transport of
foulants away from the membrane surface (Hwang and Liu, 2002). However, coagulated particles also experienced compaction when the membrane filtration system was pressurized (Antelmi, et al., 2001; Cabane et al., 2002). They observed that aggregates formed under sweep floc condition were more compressible than aggregates that formed under charge neutralization conditions.

Guigui et al. (2002) reported that good coagulation conditions (nature of coagulant, pH and dose) generally used in a conventional coagulation/settling process should lead to good performance in terms of water quality for an in-line coagulation/UF process with dead-end filtration of river water. Lee et al. (2000) provided results from a more detailed investigation on, charge neutralization and sweep floc conditions prior to MF. They found that the specific resistance was smaller with charge-neutralization than with sweep floc. Membrane permeability with charge neutralization was much better than that with sweep floc. They attributed the observation to the formation of less compressible but more porous cake with the charge neutralization condition. They also reported that the coagulated suspension under either condition showed similar steady-state flux under the cross-flow microfiltration mode. Gabelich et al. (2002) observed an adverse effect on RO (decline of flux and salt rejection) due to pre-treatment by alum coagulation (plus sedimentation and rapid filtration). They attributed the negative impact to the coagulant residuals from the pretreatment process. No advantage or disadvantage of coagulation pretreatment with NF or RO system was reported by Wiesner and Lane (1996). Coagulation pretreatment is often used for removal of fouling substances prior to NF or RO. Those systems can remove dissolved contaminants without pretreatment. The
different observations might come from the different membrane characteristics, mainly from the difference in pore sizes.

Judd and Hillis (2001) suggested that floc need to reach a certain critical floc size prior to microfiltration, otherwise membranes can be irreversibly clogged by the flocculant solids. They also reported that a near-zero pressure gradient (stabilized TMP) was observed at the coagulant dose which corresponds to a near-zero zeta potential. The concept of limiting particle size was introduced by Lahoussine-Turcaud et al. (1990), above which particles will not deposit on the membrane. They observed that kaolin (3 µm) and coagulated humic and tannic acids (> 80 µm) did not cause fouling in their studies with MF system.

An optimized coagulant dose reducing membrane fouling depends on the characteristics of original raw water. Bian et al. (1997) suggested that high flux and good water quality after membrane filtration could be obtained when the coagulation was performed with a dose lower than the optimized level for humic substances removal. In another research, Bian et al. (1999) insisted that the optimum coagulation conditions for removing the humic substances in their UF membrane tests was the same as for conventional treatment while the optimum conditions for reducing permeate flux decline were achieved with a smaller amount of coagulant, i.e., 0.5 mg Al/L for removal of humic substances but 0.1 mg Al/L for reducing flux decline.

Carroll et al. (2000) investigated the impact of coagulation pretreatment on the MF of a low-turbidity (3.9 NTU) and high-NOM (9.0 mg DOC/L) surface water. From the observation that coagulation pretreatment by iron or aluminum salt has been known to selectively remove hydrophobic rather than hydrophilic substances, charged rather than
neutral substances, and larger-sized rather than smaller-sized substances, they concluded that small, neutral hydrophilic substances control the rate of fouling as they are the main components of the residual NOM after coagulation treatment (Carroll et al., 2000).

Choksuchart et al. (2002) reported instantaneous destabilization of clay suspensions when ferric chloride was added and they could maintain the desired flux without any other additional method during their UF with clay suspension.

Kim et al. (2001) reported that changes in shear stress did not affect the permeate flux when the yeast feeds were flocculated with cationic polymer. They also observed the shear stress during microfiltration could lead to floc breakup. They found that increasing TMP led to an increase in the driving force for permeation while higher TMP also increased the compaction of the deposited layer, thus reducing permeate flux.

It was thought that the membrane morphology might play a role in determining system performance. When a polypropylene hollow fiber membrane was compared with its modified (grafting with polyacrylic acid) membrane, the modified membrane with more hydrophilic property showed higher permeate flux. However, when the water was treated with alum, the fluxes through the original and modified membranes were similar (Meier-Haack et al., 2003).

From the results from the previous studies, we hypothesized the following.

1. The chemical and physical performance of UF can be improved with coagulation.
   - Coagulated aggregates of particles are larger than primary particles in its size (the aggregates are more easily separated by size exclusion and pore clogging by particles can be reduced).
- The fractal structure of coagulated aggregates retains greater porosity when it deposits on the membrane surface (the hydraulic resistance of the membrane can be reduced).
- Dissolved NOM that cannot be removed by coagulation are unlikely to result in fouling (this fraction of NOM is unlikely to adsorb on the membrane).
- Larger particle aggregates will result in more porous deposits, higher removal of dissolved organic material, and higher critical flux.

2. The system can be optimized with the “unconventional” coagulation conditions according to the characteristics of the solution to be treated.

- Small particles (< 0.1 µm) are significantly affected by their surface charge (or zeta potential). In some instances including small size particle system, the coagulation condition which makes negatively charged particle system can be better than “charge neutralization” or “sweep floc” conditions.

Therefore, the objectives of the present research were to evaluate the effect of coagulation on the chemical and physical performance of UF (removals, resistances, and critical fluxes) and to find the optimized “unconventional” coagulation condition to improve the system performance. The “unconventional” coagulation conditions could be very important as it could save treatment cost by reducing coagulant doses and sludge production.
5.3. **Materials and methods**

5.3.1. **Coagulant**

Commercial (2.17 M Al) liquid alum (Al₂(SO₄)₃·14H₂O) solution was used as the coagulant for most experiments. Aluminum chlorohydrate (ACH) were used in some experiments. ACH has the formula of Al(OH)₂.₄₆(SO₄)ₓ(Cl)ᵧ with basicity of 82%. The major chemical benefit for ACH products is due to the presence of pre-hydrolyzed or pre-polymerized species of Al, especially Al₁₃(OH)₃₂⁷⁺. The polymerization is accomplished by controlled neutralization of the acidity of alum or aluminum chloride using alkaline reagents under specific mixing and temperature conditions. The higher the % basicity, the greater the fraction of Al₁₃(OH)₃₂⁷⁺ in the coagulant, and therefore the more reliable the coagulation process under a variety of temperatures and other conditions. (Dempsey, 1989; Dempsey, 2001)

5.3.2. **Synthetic Water**

The synthetic water contained 2.5 mg/L of Georgia kaolinite, 2.5 mg/L of alumina, 5.0 mg/L of Aldrich humic acid, 0.5 mM of NaHCO₃ and 0.2 mM of CaCl₂. The inorganic particles were dispersed in the ultrasound bath for 20 minutes and then, NOM (AHA) and background solutions (NaHCO₃ and CaCl₂) were mixed and stirred for an hour.

The synthetic water was prepared and its characteristics (pH, zeta potential, DOC, UV₂₅₄, and metal content) were measured every morning before the test started. The alum
was introduced into the synthetic water just under the vortex of the mixing solution to be dispersed completely as soon as it is introduced to the solution as the aluminum hydrolysis reaction occurred so fast.

5.3.3. *Coagulation conditions – Protocol for the jar tests*

Jar tests were performed to characterize and to evaluate the coagulation efficiency according to alum dose and pH. Alum dose varied from 0.59 mg Al/L to 2.93 mg Al/L and the final pH was adjusted from 4.8 to 8.8 by addition of 0.1 N NaOH and 0.1 N HCl prior to addition of the coagulant. Jar tests were performed in 600 mL beakers and stirring was provided with 6-paddle jar tester.

Coagulation, flocculation and sedimentation were performed as follows. The solution was mixed rapidly (60 rpm) for 2 minutes after alum was added. The rapidly mixed solution was mixed slowly (20 rpm) for 15 minutes. The coagulated aggregates were settled for 60 minutes (Table 5.1)

<table>
<thead>
<tr>
<th>Operation step</th>
<th>Speed of mixing [rpm]</th>
<th>Time [min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coagulation (rapid mix)</td>
<td>60</td>
<td>2</td>
</tr>
<tr>
<td>Flocculation (slow mix)</td>
<td>20</td>
<td>15</td>
</tr>
<tr>
<td>Sedimentation</td>
<td>0</td>
<td>60</td>
</tr>
</tbody>
</table>

Samples were collected for each stage to measure pH, temperature, zeta potential, turbidity, DOC and UV$_{254}$. Samples for UV$_{254}$ were handled as described below in the
protocol for UF with coagulation. All samples were filtered through 0.2 µm membrane to remove the “separable phase” materials.

Five (sometimes six) different pH conditions were tested for each coagulant dose. From the results of the jar tests, six different coagulation conditions were selected for the “ultrafiltration with coagulation process” tests.

5.3.4. Membrane

For the main experiments of “UF with coagulation process”, polyethersulfone (PES) ultrafiltration membranes (PBHK, Millipore, Bedford, MA) with 100 kDa molecular weight cut-off (MWCO) were used. Regenerated cellulose ultrafiltration membrane (YM100, Millipore, Bedford, MA) with 100 kDa MWCO were used for the preliminary UF tests with Gardner water. More detailed information about PES UF membranes is given in Chapter 2.

5.3.5. Protocol for UF with coagulation process

Ultrafiltration of coagulated suspensions formed under different coagulation conditions was performed to investigate the effect of coagulation conditions on physical and chemical performance of the membrane system. Six different coagulated solutions from the synthetic water and raw synthetic water were prepared for the UF experiments as in Table 5.2.
Table 5.2. Coagulation conditions for the UF experiments

<table>
<thead>
<tr>
<th>Condition ID</th>
<th>Coagulation regime</th>
<th>Coagulant dose [mg/L as Al]</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>#0</td>
<td>Raw synthetic water</td>
<td>0.00</td>
<td>8.35</td>
</tr>
<tr>
<td>#3</td>
<td>Unconventional condition</td>
<td>0.59</td>
<td>7.47</td>
</tr>
<tr>
<td>#4</td>
<td>Unconventional condition</td>
<td>0.59</td>
<td>8.73</td>
</tr>
<tr>
<td>#1</td>
<td>Unconventional condition</td>
<td>1.17</td>
<td>4.81</td>
</tr>
<tr>
<td>#2</td>
<td>Charge neutralization condition</td>
<td>1.76</td>
<td>5.27</td>
</tr>
<tr>
<td>#5</td>
<td>Sweep floc condition</td>
<td>2.34</td>
<td>6.78</td>
</tr>
<tr>
<td>#6</td>
<td>Sweep floc condition</td>
<td>2.93</td>
<td>7.14</td>
</tr>
</tbody>
</table>

Before adding any other chemicals to make the synthetic water, kaolinite and alumina particles were dispersed in the MilliQ water and the suspension was placed in the ultrasound bath for 20 minutes. Then, the NOM was introduced from the stock solution while the suspension was undergoing rapid mixing. Just after adding NOM, NaHCO₃ and CaCl₂ were added and the suspension was mixed for an hour. As different order of mixing chemicals resulted in different characteristics of particles and solution, the same order of addition was maintained for all the experiments. The pH was adjusted during the mixing step with 1.0 N HCl and 1.0 N NaOH. Alum was added after one hour of mixing. Concentrated alum was introduced just beneath of the vortex of the stirred solution. After 3 minutes of rapid mix, samples were taken to measure pH, temperature, turbidity, and zeta potential. Samples for DOC and UV₂₅₄ samples were filtered through 0.2 µm membrane (Supor-200, Pall Corp., Ann Arbor, MI). DOC samples were acidified with 1.0 N HCl to pH 2 before the measurement. The metal samples were digested with 1+1 nitric acid and 1+1 HCl before analysis. The analytical methods and instruments were given in Chapter 2 in more detail.

The coagulated solution in the feed container was pumped into the membrane module by a peristaltic pump, and through a pressure dampener to stabilize the feeding pressure.
The pumping speed was set to exceed the permeate flux. The speed of feed pump was same for all the tests for this research. Permeate flux was controlled by another peristaltic pump on the permeate side. The permeate flux was increased stepwise (i.e., 57, 156, 255, 304, and 354 l/mh). After 10 minutes of UF operation at one step, the permeate flux was increased to the next higher flux. During the UF test, both the pressures (pressure at feed side and at permeate side) were transferred to a computer. The data for permeate flux were collected by the computer through the balance (Ohaus Navigator balance) using the electronic data transfer function. The data was processed by a computer program written by the author to give the hydraulic resistances and critical fluxes of the system.

5.4. Results and discussion

5.4.1. Observation of advantageous coagulation process

The results from the UF experiments with natural raw water after coagulation with alum and ACH (aluminum chlorohydrate) were illustrated in Figure 5.1. The critical flux of the system increased with increased coagulant dose (Figure 5.1 a and c). The relationship between permeate flux and hydraulic resistance showed the improved system performance (Figure 5.1 b and d) as the resistance with higher coagulant dose (1.46 mg/L Al) did not change much while the raw water without any coagulant or with less amount of coagulant (0.88 mg/L Al) showed rapid increase of the resistance with increasing flux.
(a) Coagulation (alum) and Critical Flux - Gardner water

![Graph showing mean TMP vs. mean permeate flux for different Al concentrations.](image)

(b) Hydraulic resistance with coagulation (alum)

![Graph showing resistance vs. mean permeate flux for different Al concentrations.](image)

(Figure 5.1. Continues)
Figure 5.1. Improvement of UF performance by coagulation: (a) Critical flux of alum-coagulated Gardner water; (b) hydraulic resistance of alum-coagulated water; (c) critical flux of ACH (aluminum chlorohydrate)-coagulated water; and (d) hydraulic resistance of ACH-coagulated water.

Within the limit of the experiments, the coagulation condition of near-zero zeta potential had the highest critical flux (Table 5.3) and the lowest resistance to filtration.

The results of the UF experiments with coagulation provided the motivation for a more systematic study on in-line coagulation with UF.
Table 5.3. Raw water characteristics of Gardner water and zeta potential and critical flux changes with coagulation.

<table>
<thead>
<tr>
<th>Raw water</th>
<th>Membrane</th>
<th>pH</th>
<th>Alk. [mg CaCO₃/L]</th>
<th>Turb. [NTU]</th>
<th>UV₂₅₄ [1/cm]</th>
<th>DOC [mg /L]</th>
<th>ZP [mV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gardner</td>
<td>YM100</td>
<td>7.36</td>
<td>14.07</td>
<td>0.529</td>
<td>0.043</td>
<td>2.70</td>
<td>-21.7</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Coagulant</th>
<th>Dose [mg/L Al]</th>
<th>ZP [mV]</th>
<th>Jₜᵣᵢ [lmh]</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>0.00</td>
<td>-21.7</td>
<td>129.2</td>
</tr>
<tr>
<td>Alum</td>
<td>0.88</td>
<td>-7.6</td>
<td>141.1</td>
</tr>
<tr>
<td>Alum</td>
<td>1.46</td>
<td>-0.5</td>
<td>181.4</td>
</tr>
<tr>
<td>ACH</td>
<td>0.83</td>
<td>-8.8</td>
<td>129.0</td>
</tr>
<tr>
<td>ACH</td>
<td>1.33</td>
<td>0.1</td>
<td>151.0</td>
</tr>
</tbody>
</table>

ZP: Zeta potential  
Jₜᵣᵢ: Critical flux

5.4.2. Jar Test Results

Jar tests with the synthetic water showed that the zeta potential of the synthetic water reached near zero with 2.7 ~ 3.0 mg Al/L of alum dose (Figure 5.2). UV absorbance at 254 nm, DOC, and SUVA (specific UV absorbance) also reached minimum values with the same amount of coagulant (Figure 5.3).

![pH and ZP changes with coagulant dose](image)

**Figure 5.2.** Zeta potential and pH of the synthetic water after various coagulant doses.
As reported in the previous studies and in earlier chapters, the removal of UV$_{254}$ after coagulation and settling was higher than that of DOC (Figure 5.3). When the UV absorbance was normalized with DOC (SUVA), it showed same trend as UV$_{254}$ or DOC removal with coagulant doses (Figure 5.3).

Figure 5.3. UV absorbance at 254 nm (UV$_{254}$), DOC, and SUVA of the synthetic water with various coagulant doses. SUVA was calculated from the ratio of UV$_{254}$ and DOC. Commercial alum (2.17 M Al) was used as the coagulant.
Except for the two cases with alum doses of 2.34 and 2.93 mg Al/L (condition #5 and #6), the particles in the synthetic water had negative zeta potential within the tested pH ranges (Figure 5.4). The slopes of zeta potential changes with pH were similar for the cases with higher coagulant doses while the cases with the lowest alum doses (0.59 mg Al/L for condition #3 and #4; 1.17 mg Al/L for condition #1) showed very negative zeta potentials and relatively flat slope within the pH conditions tested (Figure 5.4).

![Zeta potential changes with pH](image)

**Figure 5.4.** Variation of zeta potential with pH for different coagulant doses. The numbers in the parentheses are the coagulant dose in mg Al/L. The test # represents the condition.

Turbidity removal after 60 minutes of sedimentation was highest between pH 6 and 8 (Figure 5.5). Generally, higher dose of coagulant resulted in higher turbidity removal rate.
Figure 5.5. Turbidity removal after sedimentation as a function of pH and coagulant concentration.

Results from removal of UV$_{254}$ after sedimentation also indicated that the coagulant dose of 0.59 mg Al/L (condition #3 and #4) was inappropriate for conventional water treatment (Figure 5.6). The removal of UV$_{254}$ with coagulant dose of 1.17 mg Al/L also was very low for pH higher than 7.

Figure 5.6. UV$_{254}$ removals as a function of pH and coagulant concentration.
Based on the information from the previous coagulation tests, more than 300 jar tests were conducted on the synthetic water to characterize the ZP and the removal of NOM as a function of pH and coagulant concentration. Based on these tests, coagulation conditions for the UF tests were selected and these conditions were reported in Table 5.2: (1) condition #0 – raw synthetic water (no coagulant); (2) condition #1, #3 and #4 – unconventional coagulation condition; (3) condition #2 – charge neutralization condition; and 4) condition #5 and #6 – sweep floc condition. Although the preliminary jar tests and the characterization of the conditions for the UF experiments were carried out at different times, the results are lumped together in the following figures for convenience. The zeta potential results were plotted in a pC-pH diagram (Figure 5.7). Except for the condition #1, #3 and #4, all the coagulation conditions showed zeta potentials between -5 and +5 mV.
Figure 5.7. Zeta potential as a function of pH and coagulant (alum) dose. Predicted solubility of aluminum hydroxide is indicated by the lines (after Dempsey, 1989). The symbols (◇) represent conditions for the UF tests.
The UV$_{254}$ removals (Figure 5.8) were consistent with the zeta potential information, i.e. more than 80% of UV$_{254}$ removal was achieved after settling for all the conventional coagulation conditions, but lower removals were achieved using the unconventional conditions #1, #3 and #4.

As illustrated in Figure 5.9, over 90% of aluminum was removed after settling under the conventional conditions (#2, #5, and #6). The removal rate under the coagulation condition #3 was much higher (88%) than that under the condition #4 (10%) though the same amounts of coagulant were used (0.59 mg/L as Al). The difference might be due to
formation of very small particles that did not settle and passed through the MF for condition #4.

![Removal of Al](image)

**Figure 5.9. Removal of Al by the conventional (0.2 µm membrane filtered) and the UF system by coagulation condition.**

5.4.3. **Coagulated Turbidity and Removal of UV₂₅₄ using 0.2 µm Filters**

Initial tests were carried out, using the six selected coagulation conditions for the UF tests, to determine the turbidity after coagulation and the removal of UV₂₅₄ after coagulation and filtration through a 0.2 µm membrane filter.

The turbidities of coagulated solutions were highest for conditions #5 and #6 (sweep floc) while conditions #1, #3 and #4 (unconventional coagulation) resulted in lower initial turbidities (Figure 5.10).
Figure 5.10. Turbidities after coagulation of the synthetic water under six coagulation conditions. The turbidity was measured three minutes after the coagulant (alum) was added to the synthetic water.

UV$_{254}$ after 0.2 µm membrane filtration for the conventional coagulation conditions (#2, #5 and #6) were very low (0.010~0.019 cm$^{-1}$) while those values of the unconventional conditions (#3 and #4) were very high (0.111~0.128 cm$^{-1}$) compared with the UV$_{254}$ of the raw water (#0; 0.133 cm$^{-1}$) without coagulant (Figure 5.11). The UV$_{254}$ after 0.2 µm membrane filtration of the unconventional condition #1 was very low.

According to István (1993), the hydrolysis of metal ions occurred just after contacting water. Within the range of the experiments, it was believed that most of the aluminum salts (alum) are in the form of hydroxide before contacting NOM molecules.

The coagulation mechanism involved with the conditions tested were adsorption of organic species on precipitated Al(OH)$_3$(s) (Dempsey et al., 1984; Cheng and Chi, 2002; Duan et al., 2002).
Figure 5.11. UV$_{254}$ of the synthetic water with different coagulation conditions. After the coagulant (alum) was added to the synthetic water, the coagulated solution was filtered through the membrane with pore size of 0.2 µm to separate “separable phase” components from the solution.

5.4.4. Ultrafiltration with coagulation

During the UF experiments under the six different coagulation conditions, the critical flux, the hydraulic resistance, and the rejection of UV$_{254}$ and DOC were measured.
Critical flux with different coagulation condition

Figure 5.12. Critical flux for uncoagulated water and for six coagulation conditions. #0: raw synthetic water without coagulant addition, #1, #3 and #4: unconventional coagulation conditions, #2: charge neutralization condition, and #5 and #6: sweep floc conditions.

The critical flux of the system with different coagulation condition was illustrated in Figure 5.12. The critical flux after unconventional coagulation condition #1 was the same as the critical flux with the charge neutralization condition (#2).

When the solution was coagulated under the sweep floc conditions (#5 and #6), the system showed higher critical flux. The critical flux increased 5% compared with the system with condition #1 while the amount of coagulant added increased 60% to get to the condition #6.
The total hydraulic resistance at the end of the UF test ($R_f$) includes the combined resistances caused by concentration polarization, cake layer, and adsorbed layer (Figure 5.13). The total resistances of condition #3 and #4 were much higher than for the raw synthetic water (#0). The resistance of condition #3 was extraordinarily high ($1.08 \times 10^{12} \text{ m}^{-1}$). As Al(OH)$_3$ precipitates were formed under the condition #3 (0.59 mg Al/L at pH 7.48), parts of the NOM molecules could be associated with the aluminum hydroxide precipitates but the size of aggregates was small. The small aggregates might be adsorbed on the wall of membrane pore and increase the hydraulic resistance of the system. For the condition #4, the size of aluminum hydroxide precipitates or aggregates were so small that they could pass through the membrane.
As it was reported previously (Lee et al., 2000; Antelmi, et al., 2001; Cabane et al., 2002), the compressibility and specific resistance of the flocs produced under sweep floc conditions (#5 and #6) were larger than those produced under charge neutralization conditions (#2) in the membrane filtration system with coagulation process. The relationship among the hydraulic resistances under different coagulation conditions agreed well with the observations in the previous studies.

![Hydraulic resistance after hydraulic rinse](image)

**Figure 5.14.** Hydraulic resistance after hydraulic rinse. #0: raw synthetic water without coagulant addition, #1, #3 and #4: unconventional coagulation conditions, #2: charge neutralization condition, and #5 and #6: sweep floc conditions.

After the pressure in the membrane module was released, the membrane was immersed in the MilliQ water overnight and any labile particles were removed. The PWF test with the membrane after hydraulic rinse can suggest the resistance related with cake layer on the membrane surface. The results from the tests were illustrated in Figure 5.14. The resistances after hydraulic rinse ($R_{hy}$) with the unconventional conditions (#1 and #4)
were lower than the resistances with the conventional conditions (#2, #5, and #6) though the unconventional condition #3 showed much higher resistance ($R_{hy}$) than any other conditions.

The extraordinarily low resistance of the condition #4 might be caused by very small size of aluminum hydroxide precipitates or aggregates which passed though the membrane pore and its very negative zeta potential (-28.8 mV) which might produce larger electrostatic repulsion force. Therefore, when the pressure was released in the module, more particles were removed from the membrane surface and the cake layer got much thinner than any other conditions. Relatively low resistances of the conditions #1, #2, #5, and #6 were due to their larger floc sizes and permeability of the cake layers.

![Hydraulic resistance after chemical cleaning](image)

**Figure 5.15. Hydraulic resistance after chemical cleaning.** 0.05 N NaOH was used for the chemical cleaning process. #0: raw synthetic water without coagulant addition, #1, #3 and #4: unconventional coagulation conditions, #2: charge neutralization condition, and #5 and #6: sweep floc conditions.

The resistance after chemical cleaning is related to the resistance by adsorbed layer which can not be removed by chemical cleaning (Figure 5.15). The resistance of
coagulated solution under charge neutralization condition (#2) showed smallest resistances while the resistances under unconventional conditions (#1, #3 and #4) were comparable with those under sweep floc conditions (#5 and #6). As Judd and Hillis (2001) reported, when the coagulant dose is too low, the aggregation of colloidal particles is incomplete and cause internal fouling and the coagulation condition #3 is believed to be the case.

**Figure 5.16.** Turbidity removal by UF under different coagulation conditions. #0: raw synthetic water without coagulant addition, #1, #3 and #4: unconventional coagulation conditions, #2: charge neutralization condition, and #5 and #6: sweep floc conditions.

Turbidities after the UF tests were between 0.024 and 0.087 NTU and the removal rates were pretty high between 96% and 99% (Figure 5.16). Due to relatively large size (~2 µm) of the inorganic particles, high removal of turbidity could be achieved.
Figure 5.17. UV$_{254}$ removal by UF under different coagulation conditions. #0: raw synthetic water without coagulant addition, #1, #3 and #4: unconventional coagulation conditions, #2: charge neutralization condition, and #5 and #6: sweep floc conditions.

In terms of UV$_{254}$ removal which represents the removal of NOM molecules (humic fraction), the unconventional conditions (#3 and #4) were not successful (9~34%) while with the other condition (#1), over 88% of removal was achieved (Figure 5.17). The UF system with conventional coagulation conditions (#2, #5, and #6) could achieve over 90% of UV$_{254}$ removal. The NOM molecules can be removed by adsorption on aluminum hydroxide (Dempsey et al., 1984; Cheng and Chi, 2002; Duan et al., 2002). The condition #4 was the worst case of all to remove the NOM molecules by those mechanisms as the aluminum hydroxide precipitates were too small.
Variation of TMP with permeate flux under different coagulation condition

As illustrated in Figure 5.18, the TMP increased rapidly for the coagulated solutions under the unconventional coagulation conditions (#3 and #4) as permeate flux increased. The relationship between TMP and flux is an indicator of hydraulic resistance of the system to the solution flux. Under the unconventional conditions #3 and #4, the particle size was smaller, aggregate density was higher, and permeability of deposit layer was lower. The TMP increasing rate of the system with the unconventional coagulation condition #1 was the lowest of all. The system with coagulation process under condition #1 would have least fouling.

As for the TMP increase with conventional coagulation conditions (#2, #5 and #6), the relationship between TMP and flux was close to linear line. The flocs were less dense.
and deposit layer permeability was high for the conventional conditions. Again, the TMP increasing rates of condition #2 (charge neutralization condition) were slower than those of condition #5 and #6 (sweep floc condition). This results can be explained by the difference of compressibility of the aggregates under the two conventional coagulation conditions, i.e., the flocs formed under the charge neutralization condition are less compressible than those under sweep floc condition.

From the chemical (turbidity and UV$_{254}$ removal) and physical (hydraulic resistances) performance analyses, we conclude that the unconventional coagulation conditions can be used for the UF system if the raw water characteristics are considered. For example, the water with high turbidity, low DOC, and high pH, condition #4 can be considered while for the water with low pH, condition #1 can have much more advantage.

Further study is necessary with more diverse solution chemistry as the inorganic particle size (larger or smaller than 0.1 µm), the NOM characteristics (fulvic or humic and water-NOM or soil-NOM), and the divalent ion concentration.

In addition to the diversity of solution chemistry, different membrane operation mode must be studied with the unconventional and conventional coagulation regimes as the impact of coagulated floc structures on the system performance with crossflow mode might be different from that with dead-end mode operation.

There can be other unconventional coagulation conditions which need to be investigated and developed other than the three unconventional coagulation conditions studied (Figure 5.19).
Figure 5.19. Coagulation conditions for the UF with coagulation (plotted on pC-pH diagram with zeta potential). Solubility of Al(OH)$_3$(s) is based on constants provided in Dempsey (1989).
Figure 5.20. Comparison of coagulation results for the synthetic water with coagulation regions described by Amirtharajah and Mills (1982). Solubility of Al(OH)$_3$(s) is from Dempsey (1989).

In Figure 5.20, the coagulation conditions used for the tests are illustrated in the alum coagulation diagram of Amirtharajah and Mills (1982). The charge neutralization zone that is shown from Amirtharajah is for a raw water with negligible concentration of NOM, and therefore very low coagulant demand for charge neutralization. Presence of humic acid (AHA) in the synthetic solution would result in a larger coagulant demand for charge neutralization. For example, the concentration of carboxylic functional groups is approximately 0.007 eq/g AHA, and therefore 5 mg/L AHA results in approximately $3.5 \times 10^{-5}$ eq/L of negative charge that must be neutralized by the positive charge on Al(OH)$_3$(s) precipitates. Edzwald (1986) reported that at pH 5.5, the coagulant demand
for fulvic acid or for NOM in the Grasse River was 0.5 mg $\text{Al}_\text{T}$ per mg of TOC. For 2.5 mg/L TOC (in the experiments using the synthetic water) the coagulant demand for charge neutralization would be approximately 1.3 mg/L as $\text{Al}_\text{T}$, or about $10^{-4.3}$ M $\text{Al}_\text{T}$. This calculation is in agreement with the charge neutralization zone for the synthetic water that is shown in Figure 5.20. Alternatively, some investigators have explained these interactions by stating that the solubility of $\text{Al(OH)}_3(s)$ was increased in the presence of humic materials (Smith and Kramer, 1999; Sutheimer and Cabaniss, 1997; Weng et al., 2002).

**5.5. Conclusion**

Coagulation pretreatment improved the physical and chemical performance of UF with in-line coagulation. It was necessary to use coagulation to increase removal of NOM as removal was poor using UF without coagulation. All the solutions coagulated with conventional coagulation conditions (charge neutralization and sweep floc conditions) showed good performance in particulate and dissolved organic matter removals. The unconventional conditions (#3 and #4) were relatively ineffective for removal of NOM.

Fouling was reduced by coagulation pretreatment. The hydraulic resistances were decreased and the critical fluxes were increased for all in-line coagulation treatments, compared to UF treatment of the untreated water. Although condition #4 resulted in higher resistance after filtration compared to the other coagulation treatments, the
resistance was easily removed for condition #4 by a hydraulic rinse. This result confirms observations by Fu (1996), i.e. the greater ZP seemed to result in easier regeneration of clean-water flux.

The amount of coagulant used for the unconventional condition was 5 times less than that used for the sweep floc condition. Therefore, we can reduce the amount of coagulant dose with the same or better physical and chemical performance if we can select appropriate coagulation condition according to the raw water characteristics. For example, the unconventional coagulation condition #4 can be used to treat the water with high pH, high alkalinity, high turbidity and low DOC.

The system with coagulation condition #1 was the best condition for the treatment of the synthetic model water as the system showed better physical performance and comparable chemical performance compared to the conventional conditions.

The optimum coagulation condition for conventional water treatment is not always optimum condition for the UF with coagulation system.

By adopting the unconventional coagulation conditions into the coagulation treatment regime for the UF system, we can reduce the coagulant dose used for the system, reduce the sludge production and improve the system operation parameters.
5.6. **References**


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Chapter 6. Conclusions and Proposed Studies

6.1. Conclusions

The main objectives of the study were to investigate the impact of dissolved organic matter and inorganic particles on the performance of membrane filtration systems, understand the mechanisms of interactions among solutes, particles, solvent, and membrane, and find ways to enhance the system performance through in-line coagulation and by control of permeate flux.

It was necessary to have methods to evaluate the system performance and to study the impact of solutes and particles and the mechanism of fouling. The performance of membrane systems is typically described using flux decline during constant pressure operation or trans-membrane pressure (TMP) increase during operation with constant permeate flux. Both of these modes were investigated in this research. Hydraulic resistance to filtration was used when it was necessary to compare the two operational modes.

In addition, methods for the measurement of “critical flux” were developed. Field et al. (1995) and others have used “critical flux” as a criterion for testing and operating
membrane systems. Critical flux was measured by measuring TMP with time while after step-wise increases in permeate flux were imposed on the system. Each step-wise flux was typically maintained for 10 minutes. The results confirmed that the critical flux evaluated with the step-wise increasing constant flux method and with the \( \frac{dTMP}{dt} \) method corresponded to the maximum flux that could be sustained without fouling (i.e., rapid increases in TMP).

It has been reported that fouling of membranes is related to the hydrophobicity of natural organic materials (NOM) and that the humic fraction of NOM is particularly important in fouling. In this research, it was shown that the effects of NOM on membrane fouling were considerably different for water-NOM and soil-NOM. The soil-NOM caused more fouling than the water-NOM (lower critical flux, higher hydraulic resistances, and higher and rapid increasing TMP at a given flux). The rejection of humic fraction for the soil-NOM was 15~78% while that for the water-NOM was about 1%. Based on results from membrane cleaning and recovery of clean-water flux, it was concluded that the soil-NOM adsorbed on the surface and in the pores of the membrane. The tendency for sorption of the NOM on the membranes was related with the absorbance UV\textsubscript{254} and the specific ultra-violet absorbance (SUVA) of the NOM. As the UV\textsubscript{254} and SUVA are indicators of the aromaticity and the hydrophobicity of NOM, therefore it was concluded that the most hydrophobic fraction of NOM was the main cause of the fouling in these experiments.
A single humic material (modified Aldrich Humic Acid, AHA) was subsequently used to investigate the impact of NOM concentration on membrane performance. AHA solutions were prepared by dissolution at pH 10 and filtration through 0.2 µm pore-size membranes prior to preparation of the synthetic solutions. Subsequent rejection of AHA during filtration using 100K polysulfone ultrafilters as measured by UV$_{254}$ and DOC were relatively constant around 20% regardless of AHA concentration. System performance deteriorated with increasing AHA concentration, i.e. the critical flux decreased and resistance to filtration (prior to chemical cleaning) increased with increasing AHA concentration when the concentration of particles was kept constant. As described below, addition of particles resulted in increased adsorption of AHA on the particles, and this resulted in improved system performance for a given AHA concentration.

The effects of inorganic particles on the performance of membrane systems depends on the particle size distribution, pore size distribution of the membrane, membrane surface roughness, solution chemistry (pH, ionic strength, and so on), hydraulic conditions, and other operating parameters. In our system, the particle size of the inorganic particle was much larger (number averaged diameter of 2 µm) than the mean pore diameter (averaged diameter of 14 nm). Under the conditions used for our experiments, the inorganic particles were too large to result in pore-blocking. Rather, the particles assisted filtration by sorbing NOM. As a result, increased concentration of inorganic particles consistently improved both chemical performance of the system represented by rejection of UV$_{254}$ and DOC and physical performance as measured by TMP, resistance and critical flux.
Coagulation was evaluated to enhance the physical and chemical performance of the ultrafiltration system. Both “conventional” coagulant doses (adequate for sweep floc or charge neutralization) and “unconventional” coagulation conditions were tested. Unconventional meant lower doses than appropriate for conventional coagulation treatment, both at acidic and alkaline conditions. Most of the unconventional coagulation conditions were found to be effective during membrane filtration for improving critical flux, lowering resistance to filtration, and improving removal of NOM. For slightly acidic pH, the same or better system performance was achieved using 20 ~ 60% of the coagulant dose that would have been required for conventional conditions. The “unconventional” coagulation condition with pH 4.81 and 1.17 mg/L as Al coagulant dose resulted in the best performance.

6.2. Contributions of this Thesis

The results of the research conducted for the dissertation have suggested a couple of strategies for efficient operation of membrane filtration system. The specific contributions are as follows.
1. Critical flux of a membrane filtration system can be used as a good indicator of the performance and the method developed here can be used for general purpose to predict system performance at a given operating condition.

2. Choice of the operating mode of a system, i.e., constant pressure mode and constant flux mode operation, is very important in predicting and improving the performance of the system especially in long term operation. Sub-critical and super-critical operation is also very important in determining system performance along with operating mode of the system. The results from the research suggest that both operating mode and critical condition must be considered for the strategy of long-term operation of a system.

3. The system performance can be enhanced by controlling the source of NOM.

4. It is critical to remove dissolved organic matter (NOM) to avoid or reduce irreversible fouling while inorganic particles can enhance the system performance by acting as an adsorbent of NOM molecules.

5. Coagulation process was helpful to enhance physical and chemical performance of the ultrafiltration system. By using the “unconventional” coagulation conditions, the amount of chemical used for coagulation process could be reduced down to 20 ~ 40% of the amount used for conventional conditions without deteriorating system performance.
6.3. **Publications and Presentations**

The results of the research carried out for the thesis were and will be used for publications and presentations as follows.


6.4. Future works

The future works to extend the results and knowledge from the research will be;

1. To investigate the impact of different inorganic particle characteristics such as particle size, structure and surface charge.

2. To test the impact of more diverse sources of NOM molecules, i.e., from lake, groundwater, reservoir, river, and soil water.
3. To apply the method and the results from the study on UF system with coagulation process, to systems with different operating modes and configurations (cross-flow, hollow fiber, and so on) and to larger scale facilities, i.e., pilot and full scale.

4. To develop mathematical models to predict the performance of a UF system with NOM, inorganic particles and coagulant.

5. To investigate the economic aspect of the system (e.g., cost analysis)
Appendix. Supplement of Chapters

A.1. Data and Information for Chapter 2 & 3

A.1.1. Permeate flux and TMP of the system with the synthetic water used to evaluate critical flux (Figure 2.6 and Figure 3.3)

Permeate flux and TMP changes with operating time

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Mean permeate flux with mean TMP

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A.1.2. **TMP changes with step-wise increasing flux and the critical fluxes of the system with different natural raw waters (Figure 3.1)**

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<th>Gardner</th>
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<td>Flux [lmh]</td>
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<td>195.0</td>
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<td>6.40</td>
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<tr>
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### A.1.3. Hydraulic resistances of different natural raw waters (Figure 3.2)

#### Chilhowee water

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#### Gardner water

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#### Mississippi water

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A.1.4. Transmembrane pressure (TMP) changes with operating time under sub-critical and super-critical fluxes (Figure 3.4, 3.6, 3.7, 3.8, 3.9 and 3.10)

Constant TMP mode
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<td>Flux (Flm)</td>
<td>Flux (Flm)</td>
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Constant flux mode
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A.1.5. Resistances ($R_{hy}$, resistance after hydraulic rinse, and $R_{ch}$, resistance after chemical cleaning) of the system under constant permeate flux condition (Figure 3.5)

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A.1.6. Hydraulic resistances ($R_{hy}$ and $R_{ch}$) and hydraulic resistances normalized to filtrated volume for each operating condition (Figure 3.11 and 3.12)

### Constant flux mode operation

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<th>Flux [lmh]</th>
<th>$R_{hy}$ [1/m]</th>
<th>$^{\text{1Norm.}} R_{hy}$ [1/m-\text{mL}]</th>
<th>$R_{ch}$ [1/m]</th>
<th>$^{\text{1Norm.}} R_{ch}$ [1/m-\text{mL}]</th>
<th>$^{\text{2Vol.}}$ Filtered [mL]</th>
</tr>
</thead>
<tbody>
<tr>
<td>139.3</td>
<td>8.27E+10</td>
<td>8.43E+07</td>
<td>5.85E+10</td>
<td>5.97E+07</td>
<td>981.3</td>
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<td>198.5</td>
<td>2.99E+11</td>
<td>2.14E+08</td>
<td>2.78E+10</td>
<td>1.99E+07</td>
<td>1397.9</td>
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<tr>
<td>241.9</td>
<td>5.50E+11</td>
<td>2.97E+08</td>
<td>3.88E+10</td>
<td>2.10E+07</td>
<td>1849.6</td>
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<tr>
<td>263.0</td>
<td>1.48E+12</td>
<td>7.37E+08</td>
<td>4.36E+10</td>
<td>2.18E+07</td>
<td>2004.6</td>
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### Constant TMP mode operation

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<th>TMP [psi]</th>
<th>$R_{hy}$ [1/m]</th>
<th>$^{\text{1Norm.}} R_{hy}$ [1/m-\text{mL}]</th>
<th>$R_{ch}$ [1/m]</th>
<th>$^{\text{1Norm.}} R_{ch}$ [1/m-\text{mL}]</th>
<th>$^{\text{2Vol.}}$ Filtered [mL]</th>
<th>$^{\text{3J_{ini}}}$ [lmh]</th>
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<td>1.25</td>
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<td>4.19E+08</td>
<td>2.94E+11</td>
<td>3.45E+08</td>
<td>852.57</td>
<td>149.5</td>
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<td>2.43</td>
<td>5.39E+11</td>
<td>4.07E+08</td>
<td>2.75E+11</td>
<td>2.59E+08</td>
<td>1062.4</td>
<td>256.0</td>
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<tr>
<td>4.57</td>
<td>8.7E+11</td>
<td>6.78E+08</td>
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<td>2.17E+08</td>
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<tr>
<td>6.19</td>
<td>1.36E+12</td>
<td>1.2E+09</td>
<td>2.75E+11</td>
<td>2.42E+08</td>
<td>1135.61</td>
<td>812.8</td>
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</tbody>
</table>

1. Normalized resistance to filtered volume [m$^{-1}$-mL$^{-1}$]
2. Accumulated volume filtered through membrane filter [mL]
3. Initial flux for each constant TMP mode
A.2. Data and Information for Chapter 4

A.2.1. $\text{UV}_{254}$, percent removal of $\text{UV}_{254}$, hydraulic resistances and critical flux of each NOM (Figure 4.1, 4.3, 4.4 and 4.6)

<table>
<thead>
<tr>
<th>Organic source</th>
<th>$\text{UV}_{254}$ [1/cm]</th>
<th>$\text{UV}_{254}$ removal</th>
<th>$R_f [10^4 \text{ 1/m}]$</th>
<th>$R_{hy} [10^9 \text{ 1/m}]$</th>
<th>$R_{ch} [10^9 \text{ 1/m}]$</th>
<th>Critical flux [lm/h]</th>
</tr>
</thead>
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<tr>
<td>GTNOM</td>
<td>0.086</td>
<td>1.3%</td>
<td>45.1</td>
<td>23.2</td>
<td>19.0</td>
<td>$&gt;360.0$</td>
</tr>
<tr>
<td>SRFA</td>
<td>0.097</td>
<td>0.9%</td>
<td>35.1</td>
<td>12.7</td>
<td>15.7</td>
<td>$&gt;360.0$</td>
</tr>
<tr>
<td>SHSHA</td>
<td>0.109</td>
<td>35.8%</td>
<td>442.8</td>
<td>62.9</td>
<td>34.1</td>
<td>159.7</td>
</tr>
<tr>
<td>LHA</td>
<td>0.158</td>
<td>53.2%</td>
<td>417.3</td>
<td>68.8</td>
<td>47.5</td>
<td>153.3</td>
</tr>
<tr>
<td>AHA</td>
<td>0.123</td>
<td>14.6%</td>
<td>348.9</td>
<td>51.8</td>
<td>22.1</td>
<td>266.4</td>
</tr>
<tr>
<td>SHAstd</td>
<td>0.175</td>
<td>77.7%</td>
<td>355.1</td>
<td>47.7</td>
<td>51.1</td>
<td>117.0</td>
</tr>
</tbody>
</table>

GTNOM: Georgetown NOM  
SRFA: Suwannee River Fulvic Acid  
SHSHA: Summit Hill Soil Humic Acid  
LHA: Leonardite Humic Acid  
AHA: Aldrich Humic Acid  
SHAstd: Soil Humic Acid standard
### A.2.2. *TMP and flux for different NOMs (Figure 4.2)*

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<td>0.015</td>
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<td>140.2</td>
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<td>1.284</td>
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<td>231.6</td>
<td>2.4</td>
<td>2.187</td>
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<tr>
<td></td>
<td>283.2</td>
<td>5.0</td>
<td>2.742</td>
<td>0.039</td>
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<tr>
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<td>340.3</td>
<td>4.6</td>
<td>3.361</td>
<td>0.038</td>
</tr>
</tbody>
</table>

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<td>0.609</td>
<td>0.022</td>
</tr>
<tr>
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<td>82.9</td>
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<td>0.924</td>
<td>0.024</td>
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<td>1.408</td>
<td>0.032</td>
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<td>166.1</td>
<td>1.5</td>
<td>2.053</td>
<td>0.069</td>
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<td>204.3</td>
<td>2.2</td>
<td>2.942</td>
<td>0.161</td>
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<tbody>
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<td>0.475</td>
<td>0.021</td>
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<tr>
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<td>234.3</td>
<td>4.7</td>
<td>2.117</td>
<td>0.013</td>
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<tr>
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<td>288.7</td>
<td>6.7</td>
<td>2.652</td>
<td>0.027</td>
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<td>349.0</td>
<td>7.1</td>
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<td>0.030</td>
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<td>1.608</td>
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<td>248.8</td>
<td>5.6</td>
<td>2.746</td>
<td>0.048</td>
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<td>302.6</td>
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<td>3.847</td>
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<td>360.9</td>
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<td>5.516</td>
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<td>204.5</td>
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<td>3.280</td>
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<tbody>
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<td>0.761</td>
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<td>0.017</td>
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<td>197.1</td>
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<td>2.949</td>
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### A.2.3. UV254 removal with permeate flux for each NOM (Figure 4.5)

<table>
<thead>
<tr>
<th>GTNOM</th>
<th>Flux [lmh]</th>
<th>UV254 [1/cm]</th>
<th>UV254 removal [%]</th>
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<tbody>
<tr>
<td></td>
<td>0.0</td>
<td>0.086</td>
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<td>57.1</td>
<td>0.084</td>
<td>2.0%</td>
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<td>140.2</td>
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<td>231.6</td>
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</tr>
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<td>283.2</td>
<td>0.085</td>
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</tr>
<tr>
<td></td>
<td>340.3</td>
<td>0.085</td>
<td>0.7%</td>
</tr>
<tr>
<td>SRFA</td>
<td>Flux [lmh]</td>
<td>UV254 [1/cm]</td>
<td>UV254 removal [%]</td>
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<td>138.6</td>
<td>0.095</td>
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<td>234.3</td>
<td>0.096</td>
<td>0.7%</td>
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<td>288.7</td>
<td>0.096</td>
<td>0.6%</td>
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<td>0.096</td>
<td>0.4%</td>
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<tr>
<td>SHSHA</td>
<td>Flux [lmh]</td>
<td>UV254 [1/cm]</td>
<td>UV254 removal [%]</td>
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<td>Flux [lmh]</td>
<td>UV254 [1/cm]</td>
<td>UV254 removal [%]</td>
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<td>UV254 [1/cm]</td>
<td>UV254 removal [%]</td>
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<td>61.3</td>
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<td>148.4</td>
<td>0.1007</td>
<td>18.3%</td>
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<td>248.8</td>
<td>0.1072</td>
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<td>302.6</td>
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<tr>
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<td>360.9</td>
<td>0.1062</td>
<td>13.9%</td>
</tr>
<tr>
<td>SHAstd</td>
<td>Flux [lmh]</td>
<td>UV254 [1/cm]</td>
<td>UV254 removal [%]</td>
</tr>
<tr>
<td>-------</td>
<td>------------</td>
<td>--------------</td>
<td>-------------------</td>
</tr>
<tr>
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<tr>
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<td>50.4</td>
<td>0.044</td>
<td>74.7%</td>
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<td>82.1</td>
<td>0.039</td>
<td>77.5%</td>
</tr>
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<td>120.9</td>
<td>0.039</td>
<td>77.5%</td>
</tr>
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<td></td>
<td>159.8</td>
<td>0.039</td>
<td>77.8%</td>
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<td>0.039</td>
<td>77.8%</td>
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### A.2.4. Zeta potentials of different solution system (Figure 4.7)

Alumina, NOM (AHA), and background solution (Figure 4.7 a)

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<th>System ID: A+O</th>
<th>System ID: A+O+S</th>
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<td>Solution chemistry</td>
<td>Solution chemistry</td>
<td>Solution chemistry</td>
</tr>
<tr>
<td>Particle conc.</td>
<td>Particle conc.</td>
<td>Particle conc.</td>
</tr>
<tr>
<td>Alumina</td>
<td>10.0 mg/L</td>
<td>Alumina</td>
</tr>
<tr>
<td>Ionic strength</td>
<td>0.01 M NaCl</td>
<td>Ionic strength</td>
</tr>
<tr>
<td>NOM conc.</td>
<td>AHA 0.0 mg/L</td>
<td>NOM conc.</td>
</tr>
<tr>
<td>Background solution</td>
<td>CaCl2 0.0 mM</td>
<td>Background solution</td>
</tr>
<tr>
<td>NaHCO3</td>
<td>0.0 mM</td>
<td>NaHCO3</td>
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</table>

<table>
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<tr>
<th>pH</th>
<th>temp</th>
<th>ZP ave [mV]</th>
<th>ZP std [mV]</th>
<th>pH</th>
<th>temp</th>
<th>ZP ave [mV]</th>
<th>ZP std [mV]</th>
<th>pH</th>
<th>temp</th>
<th>ZP ave [mV]</th>
<th>ZP std [mV]</th>
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Kaolinite, NOM (AHA), and background solution (Figure 4.7 b)

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<td>NaHCO₃ 0.0 mM</td>
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<td>ZP std [mV]</td>
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Alumina, Kaolinite, NOM (AHA), and background solution (Figure 4.7 c)

System ID: AK
Solution chemistry
Particle conc.
Kaolinite 2.5 mg/L
Alumina 2.5 mg/L
Ionic strength 0.01 M NaCl
NOM conc.
AHA 0.0 mg/L
Background solution
CaCl2 0.0 mM
NaHCO3 0.0 mM

System ID: AK+O
Solution chemistry
Particle conc.
Kaolinite 2.5 mg/L
Alumina 2.5 mg/L
Ionic strength 0.01 M NaCl
NOM conc.
AHA 5.0 mg/L
Background solution
CaCl2 0.0 mM
NaHCO3 0.0 mM

System ID: AK+O+S
Solution chemistry
Particle conc.
Kaolinite 2.5 mg/L
Alumina 2.5 mg/L
Ionic strength 0.01 M NaCl
NOM conc.
AHA 5.0 mg/L
Background solution
CaCl2 0.02 mM
NaHCO3 0.05 mM

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<th>temp</th>
<th>ZP ave [mV]</th>
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A.2.5. Sorption of Aldrich Humic Acid on alumina (Figure 4.8)

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<th>Temp [°C]</th>
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<th>ZP std [mV]</th>
<th>UV$_{254}$ [1/cm]</th>
<th>UV$_{254}$ std [1/cm]</th>
<th>UV$_{254}$ adsorbed fraction</th>
<th>Ads. Cap. [mg/g]</th>
<th>DOC [mg C/L]</th>
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1. Standard deviation of zeta potential measured [mV]
2. Standard deviation of UV$_{254}$ measured [1/cm]
### A.2.6. Sorption of Aldrich Humic Acid on alumina (Figure 4.9)

<table>
<thead>
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<th>UV$_{254, ini}$ [1/cm]</th>
<th>pH</th>
<th>Temp [°C]</th>
<th>ZP$_{ave}$ [mV]</th>
<th>ZP$_{std}$ [mV]</th>
<th>UV$_{254, ave}$ [1/cm]</th>
<th>UV$_{254, std}$ [1/cm]</th>
<th>q$_e$ [mg AHA/g alumina]</th>
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<td>-48.50</td>
<td>0.10</td>
<td>0.1272</td>
<td>0.0001</td>
<td>37.58</td>
</tr>
<tr>
<td>7.5</td>
<td>0.2063</td>
<td>7.64</td>
<td>22.5</td>
<td>-50.63</td>
<td>0.38</td>
<td>0.1901</td>
<td>0.0004</td>
<td>58.61</td>
</tr>
<tr>
<td>10.0</td>
<td>0.2750</td>
<td>7.63</td>
<td>22.9</td>
<td>-51.57</td>
<td>0.21</td>
<td>0.2550</td>
<td>0.0002</td>
<td>72.73</td>
</tr>
<tr>
<td>15.0</td>
<td>0.4125</td>
<td>7.64</td>
<td>22.6</td>
<td>-53.93</td>
<td>0.15</td>
<td>0.3896</td>
<td>0.0003</td>
<td>83.39</td>
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<tr>
<td>20.0</td>
<td>0.5500</td>
<td>7.65</td>
<td>23.0</td>
<td>-54.53</td>
<td>0.06</td>
<td>0.5220</td>
<td>0.0004</td>
<td>101.70</td>
</tr>
</tbody>
</table>

1. Adsorbate concentration [mg Aldrich Humic Acid/L]
2. Initial UV$_{254}$ of sample with given concentration of Aldrich Humic Acid
3. Mean zeta potential [mV]
4. Standard deviation of zeta potential measured [mV]
5. Mean UV$_{254}$ [1/cm]
6. Standard deviation of UV$_{254}$ measured [1/cm]
A.2.7. *UV*$_{254}$ and DOC rejection, critical flux and hydraulic resistances with varying alumina concentration (Figure 4.10, 4.13, and 4.15)

<table>
<thead>
<tr>
<th>Alumina [mg/L]</th>
<th>$R_{hy}$ [$10^5$ 1/m]</th>
<th>$R_f$ [$10^5$ 1/m]</th>
<th>$R_{ch}$ [$10^5$ 1/m]</th>
<th>Critical flux [l/mh]</th>
<th>$UV_{254, ini}$ [1/cm]</th>
<th>$UV_{254, fin}$ [1/cm]</th>
<th>$UV_{254}$ removal [%]</th>
<th>$DOC_{ini}$ [mg C/L]</th>
<th>$DOC_{fin}$ [mg C/L]</th>
<th>DOC removal [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>51.6</td>
<td>41.6</td>
<td>45.1</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>5.0</td>
<td>12.3</td>
<td>8.5</td>
<td>33.9</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>7.5</td>
<td>21.6</td>
<td>13.1</td>
<td>45.3</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>10.0</td>
<td>36.5</td>
<td>7.3</td>
<td>30.5</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Alumina [mg/L]</th>
<th>$R_{hy}$ [$10^5$ 1/m]</th>
<th>$R_f$ [$10^5$ 1/m]</th>
<th>$R_{ch}$ [$10^5$ 1/m]</th>
<th>Critical flux [l/mh]</th>
<th>$UV_{254, ini}$ [1/cm]</th>
<th>$UV_{254, fin}$ [1/cm]</th>
<th>$UV_{254}$ removal [%]</th>
<th>$DOC_{ini}$ [mg C/L]</th>
<th>$DOC_{fin}$ [mg C/L]</th>
<th>DOC removal [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>115.2</td>
<td>552.5</td>
<td>23.1</td>
<td>262.0</td>
<td>0.124</td>
<td>0.101</td>
<td>18%</td>
<td>1.94</td>
<td>1.67</td>
<td>14%</td>
</tr>
<tr>
<td>5.0</td>
<td>77.8</td>
<td>473.7</td>
<td>22.9</td>
<td>278.0</td>
<td>0.124</td>
<td>0.099</td>
<td>20%</td>
<td>1.01</td>
<td>0.80</td>
<td>21%</td>
</tr>
<tr>
<td>7.5</td>
<td>79.4</td>
<td>492.3</td>
<td>12.6</td>
<td>292.5</td>
<td>0.122</td>
<td>0.095</td>
<td>22%</td>
<td>1.09</td>
<td>0.86</td>
<td>21%</td>
</tr>
<tr>
<td>10.0</td>
<td>110.7</td>
<td>641.1</td>
<td>35.6</td>
<td>297.1</td>
<td>0.122</td>
<td>0.094</td>
<td>23%</td>
<td>1.77</td>
<td>1.25</td>
<td>29%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Alumina [mg/L]</th>
<th>$R_{hy}$ [$10^5$ 1/m]</th>
<th>$R_f$ [$10^5$ 1/m]</th>
<th>$R_{ch}$ [$10^5$ 1/m]</th>
<th>Critical flux [l/mh]</th>
<th>$UV_{254, ini}$ [1/cm]</th>
<th>$UV_{254, fin}$ [1/cm]</th>
<th>$UV_{254}$ removal [%]</th>
<th>$DOC_{ini}$ [mg C/L]</th>
<th>$DOC_{fin}$ [mg C/L]</th>
<th>DOC removal [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>315.3</td>
<td>2800.1</td>
<td>18.9</td>
<td>254.4</td>
<td>0.241</td>
<td>0.1948</td>
<td>19%</td>
<td>3.41</td>
<td>2.88</td>
<td>16%</td>
</tr>
<tr>
<td>5.0</td>
<td>280.6</td>
<td>2600.4</td>
<td>28.3</td>
<td>275.0</td>
<td>0.252</td>
<td>0.1936</td>
<td>23%</td>
<td>3.42</td>
<td>2.75</td>
<td>20%</td>
</tr>
<tr>
<td>7.5</td>
<td>289.1</td>
<td>2213.8</td>
<td>29.7</td>
<td>288.7</td>
<td>0.254</td>
<td>0.1992</td>
<td>22%</td>
<td>3.86</td>
<td>2.86</td>
<td>26%</td>
</tr>
<tr>
<td>10.0</td>
<td>217.7</td>
<td>1725.6</td>
<td>38.8</td>
<td>289.6</td>
<td>0.265</td>
<td>0.1973</td>
<td>26%</td>
<td>2.71</td>
<td>1.76</td>
<td>35%</td>
</tr>
</tbody>
</table>

1. Initial *UV*$_{254}$ before UF  
2. Final *UV*$_{254}$ after UF  
3. Initial DOC before UF
A.2.8. *UV*$_{254}$ and DOC rejection, critical flux and hydraulic resistances with varying AHA concentration (Figure 4.11, 4.12, and 4.14)

Alumina = 2.5 mg/L

<table>
<thead>
<tr>
<th>AHA [mg/L]</th>
<th>$R_{hy}$ $10^6$ [1/m]</th>
<th>$R_{f}$ $10^6$ [1/m]</th>
<th>$R_{ch}$ $10^6$ [1/m]</th>
<th>Critical flux [l/mh]</th>
<th>$^1$UV$_{254,ini}$ [1/cm]</th>
<th>$^2$UV$_{254,fin}$ [1/cm]</th>
<th>UV$_{254}$ removal</th>
<th>$^3$DOC$_{ini}$ [mg C/L]</th>
<th>$^4$DOC$_{fin}$ [mg C/L]</th>
<th>DOC removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>51.6</td>
<td>41.6</td>
<td>45.1</td>
<td>NA</td>
<td>0.000</td>
<td>NA</td>
<td>NA</td>
<td>0.00</td>
<td>0.00</td>
<td>NA</td>
</tr>
<tr>
<td>2.5</td>
<td>86.1</td>
<td>374.3</td>
<td>31.8</td>
<td>291.09</td>
<td>0.069</td>
<td>0.0554</td>
<td>20%</td>
<td>1.61</td>
<td>1.38</td>
<td>14%</td>
</tr>
<tr>
<td>5.0</td>
<td>115.2</td>
<td>552.5</td>
<td>23.1</td>
<td>261.96</td>
<td>0.124</td>
<td>0.1014</td>
<td>18%</td>
<td>1.94</td>
<td>1.67</td>
<td>14%</td>
</tr>
<tr>
<td>7.5</td>
<td>228.4</td>
<td>1408.3</td>
<td>29.3</td>
<td>258.30</td>
<td>0.187</td>
<td>0.1462</td>
<td>22%</td>
<td>2.12</td>
<td>1.75</td>
<td>17%</td>
</tr>
<tr>
<td>10.0</td>
<td>315.3</td>
<td>2800.1</td>
<td>18.9</td>
<td>254.43</td>
<td>0.241</td>
<td>0.1948</td>
<td>19%</td>
<td>3.41</td>
<td>2.88</td>
<td>16%</td>
</tr>
</tbody>
</table>

$^1$ Initial UV$_{254}$ before UF

$^2$ Final UV$_{254}$ after UF

$^3$ Initial DOC before UF

$^4$ Final DOC after UF
### A.3. Data and Information for Chapter 5

#### A.3.1. Improvement of UF performance with coagulation (Figure 5.1)

Source water = Gardner reservoir water (characteristics are given in Table 3.1)

Coagulant = Alum and Aluminum Chlorohydrate (ACH)

<table>
<thead>
<tr>
<th>Raw water</th>
<th>Alum 0.88 mg/L Al</th>
<th>0.88 ZP</th>
<th>0.88 mg/L Al</th>
<th>0.88 ZP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>J [lmh]</td>
<td>0.88</td>
<td>0.88 mV</td>
<td>0.88 mV</td>
</tr>
<tr>
<td></td>
<td>TMP [psi]</td>
<td>ZP</td>
<td>J [lmh]</td>
<td>R [1/m]</td>
</tr>
<tr>
<td>24.6</td>
<td>0.6</td>
<td>6.79E+11</td>
<td>28.4</td>
<td>0.22</td>
</tr>
<tr>
<td>67.1</td>
<td>1.08</td>
<td>4.50E+11</td>
<td>66.8</td>
<td>0.69</td>
</tr>
<tr>
<td>109.2</td>
<td>1.94</td>
<td>4.96E+11</td>
<td>109.1</td>
<td>1.32</td>
</tr>
<tr>
<td>151.0</td>
<td>3.59</td>
<td>6.63E+11</td>
<td>156.3</td>
<td>2.30</td>
</tr>
<tr>
<td>195.0</td>
<td>6.40</td>
<td>9.15E+11</td>
<td>194.5</td>
<td>3.69</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Raw water</th>
<th>ACH 1.46 mg/L Al</th>
<th>1.46 ZP</th>
<th>1.46 mg/L Al</th>
<th>1.46 ZP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>J [lmh]</td>
<td>1.46</td>
<td>1.46 mV</td>
<td>1.46 mV</td>
</tr>
<tr>
<td></td>
<td>TMP [psi]</td>
<td>ZP</td>
<td>J [lmh]</td>
<td>R [1/m]</td>
</tr>
<tr>
<td>24.6</td>
<td>0.6</td>
<td>6.79E+11</td>
<td>26.0</td>
<td>0.35</td>
</tr>
<tr>
<td>67.1</td>
<td>1.08</td>
<td>4.50E+11</td>
<td>66.2</td>
<td>0.92</td>
</tr>
<tr>
<td>109.2</td>
<td>1.94</td>
<td>4.96E+11</td>
<td>107.6</td>
<td>1.57</td>
</tr>
<tr>
<td>151.0</td>
<td>3.59</td>
<td>6.63E+11</td>
<td>153.2</td>
<td>2.65</td>
</tr>
<tr>
<td>195.0</td>
<td>6.40</td>
<td>9.15E+11</td>
<td>201.1</td>
<td>4.17</td>
</tr>
</tbody>
</table>

1. Mean permeate flux, J [lmh]
2. Mean transmembrane pressure, TMP [psi]
3. Hydraulic resistance at the end of UF, R [1/m]
4. Zeta potential of coagulated system [mV]
5. Aluminum chlorohydrate

Critical flux of the raw water = 129 lmh
Critical flux of the coagulated water with 0.88 mg Al/L of alum = 141 lmh
Critical flux of the coagulated water with 1.46 mg Al/L of alum = 181 lmh
Critical flux of the coagulated water with 0.83 mg Al/L of ACH = 129 lmh
Critical flux of the coagulated water with 1.33 mg Al/L of ACH = 151 lmh

### A.3.2. Zeta potential and pH, UV\textsubscript{254}, and DOC of the synthetic water after various coagulant doses (Figure 5.2 and 5.3)

<table>
<thead>
<tr>
<th>(^1)pH (init)</th>
<th>(^2)Dose [mg/L Al]</th>
<th>(^3)pH (fine)</th>
<th>Temp [°C]</th>
<th>(^4)ZP [mV]</th>
<th>(^5)UV\textsubscript{254} [1/cm]</th>
<th>DOC [mg/L C]</th>
<th>(^6)SUVA [L/mg-m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.71</td>
<td>0.00</td>
<td>8.71</td>
<td>22.0</td>
<td>-25.6</td>
<td>0.1206</td>
<td>2.30</td>
<td>5.243</td>
</tr>
<tr>
<td>8.90</td>
<td>1.46</td>
<td>7.15</td>
<td>22.4</td>
<td>-12.7</td>
<td>0.0105</td>
<td>0.42</td>
<td>2.490</td>
</tr>
<tr>
<td>8.89</td>
<td>2.93</td>
<td>6.44</td>
<td>22.5</td>
<td>+5.4</td>
<td>0.0032</td>
<td>0.23</td>
<td>1.412</td>
</tr>
<tr>
<td>8.76</td>
<td>4.39</td>
<td>5.68</td>
<td>22.2</td>
<td>+7.9</td>
<td>0.0027</td>
<td>0.26</td>
<td>1.048</td>
</tr>
<tr>
<td>8.76</td>
<td>1.76</td>
<td>6.96</td>
<td>22.2</td>
<td>-9.0</td>
<td>0.0073</td>
<td>0.36</td>
<td>2.007</td>
</tr>
<tr>
<td>8.76</td>
<td>2.05</td>
<td>6.69</td>
<td>22.4</td>
<td>-6.7</td>
<td>0.0048</td>
<td>0.30</td>
<td>1.623</td>
</tr>
</tbody>
</table>

1. Initial pH of the solution before coagulation
2. Coagulant (alum) dose [mg/L as Al]
3. Final pH of the coagulated solution
4. Zeta potential of the coagulated particles
5. Specific Ultraviolet Absorbance [L/mg·m]
### A.3.3. Zeta potential, turbidity, and UV\textsubscript{254} with different coagulant dose (Figure 5.4, 5.5, and 5.6)

<table>
<thead>
<tr>
<th>Alum dose [mg/L Al]</th>
<th>pH</th>
<th>temp [C]</th>
<th>ZP [mV]</th>
<th>turbidity [NTU]</th>
<th>UV\textsubscript{254} [1/cm]</th>
<th>pH</th>
<th>temp [C]</th>
<th>ZP [mV]</th>
<th>turbidity [NTU]</th>
<th>UV\textsubscript{254} [1/cm]</th>
</tr>
</thead>
<tbody>
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<td>+7.7</td>
<td>5.09</td>
<td>0.0035</td>
<td>5.16</td>
<td>21.5</td>
<td>+8.2</td>
<td>4.77</td>
<td>0.0055</td>
</tr>
<tr>
<td></td>
<td>5.59</td>
<td>21.4</td>
<td>+13.1</td>
<td>5.25</td>
<td>5.81</td>
<td>21.3</td>
<td>+12.4</td>
<td>+2.4</td>
<td>4.99</td>
<td>0.0040</td>
</tr>
<tr>
<td></td>
<td>5.92</td>
<td>22.1</td>
<td>+13.8</td>
<td>0.035</td>
<td>6.13</td>
<td>21.6</td>
<td>+15.4</td>
<td>+1.5</td>
<td>4.15</td>
<td>0.0045</td>
</tr>
<tr>
<td></td>
<td>5.99</td>
<td>21.9</td>
<td>+7.4</td>
<td>5.42</td>
<td>0.0035</td>
<td>6.09</td>
<td>21.4</td>
<td>+6.1</td>
<td>4.06</td>
<td>0.0049</td>
</tr>
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<td>6.15</td>
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<td>6.46</td>
<td>21.6</td>
<td>+5.7</td>
<td>5.25</td>
<td>0.0099</td>
</tr>
<tr>
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<td>6.35</td>
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<td>5.47</td>
<td>0.0034</td>
<td>6.47</td>
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<td>+6.7</td>
<td>4.66</td>
<td>0.0027</td>
</tr>
<tr>
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<td>+6.0</td>
<td>5.55</td>
<td>0.0032</td>
</tr>
<tr>
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<td>-15.6</td>
<td>3.85</td>
<td>0.1213</td>
<td>7.82</td>
<td>21.1</td>
<td>-16.6</td>
<td>3.82</td>
<td>0.1213</td>
</tr>
<tr>
<td>1.465</td>
<td>5.31</td>
<td>22.5</td>
<td>-0.4</td>
<td>5.37</td>
<td>0.0043</td>
<td>5.43</td>
<td>22.8</td>
<td>+1.4</td>
<td>5.61</td>
<td>0.0046</td>
</tr>
<tr>
<td></td>
<td>6.09</td>
<td>22.6</td>
<td>-2.7</td>
<td>5.55</td>
<td>0.0057</td>
<td>6.33</td>
<td>22.7</td>
<td>-0.3</td>
<td>5.18</td>
<td>0.0060</td>
</tr>
<tr>
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<td>6.63</td>
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<td>-13.5</td>
<td>5.72</td>
<td>0.0099</td>
<td>6.65</td>
<td>22.1</td>
<td>-16.6</td>
<td>5.17</td>
<td>0.0146</td>
</tr>
<tr>
<td></td>
<td>2.930</td>
<td>5.99</td>
<td>23.3</td>
<td>+9.6</td>
<td>4.75</td>
<td>0.0142</td>
<td>7.41</td>
<td>22.8</td>
<td>-21.0</td>
<td>4.19</td>
</tr>
<tr>
<td></td>
<td>6.73</td>
<td>22.2</td>
<td>+5.8</td>
<td>5.38</td>
<td>0.0062</td>
<td>6.72</td>
<td>23.2</td>
<td>+5.3</td>
<td>5.05</td>
<td>0.0065</td>
</tr>
</tbody>
</table>

2 min Rapid mix
15 min of Slow mix
60 min of settling
(Table C-3 continued on the next page)
<table>
<thead>
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<th>Alum dose [mg/L Al]</th>
<th>After Rapid mix</th>
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<td>-0.8%</td>
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<tr>
<td>2.930</td>
<td>-22.4%</td>
<td>95.0%</td>
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</tr>
<tr>
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<td>-14.5%</td>
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</tbody>
</table>
A.3.4. Coagulation conditions with the synthetic water (Figure 5.7, 5.8, 5.19, and 5.20)

<table>
<thead>
<tr>
<th>Condition 1</th>
<th>Coagulant dose</th>
<th>1.172 mg/L Al</th>
<th>Condition 2</th>
<th>Coagulant dose</th>
<th>1.758 mg/L Al</th>
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<td>pH</td>
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<td>4.90</td>
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<td>5.31</td>
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<tr>
<td>ZP [mV]</td>
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<td>-10.7</td>
<td>ZP [mV]</td>
<td>-4.6</td>
<td>-3.7</td>
</tr>
<tr>
<td>Turbidity removal [%]</td>
<td>-28.2%</td>
<td>-28.5%</td>
<td>Turbidity removal [%]</td>
<td>-14.5%</td>
<td>-9.2%</td>
</tr>
<tr>
<td>DOC removal [%]</td>
<td>63.2%</td>
<td>65.6%</td>
<td>DOC removal [%]</td>
<td>77.0%</td>
<td>72.4%</td>
</tr>
<tr>
<td>UV_{254} removal [%]</td>
<td>74.7%</td>
<td>77.4%</td>
<td>UV_{254} removal [%]</td>
<td>96.4%</td>
<td>96.5%</td>
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<table>
<thead>
<tr>
<th>Condition 3</th>
<th>Coagulant dose</th>
<th>0.586 mg/L Al</th>
<th>Condition 4</th>
<th>Coagulant dose</th>
<th>0.586 mg/L Al</th>
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</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.48</td>
<td>7.41</td>
<td>pH</td>
<td>8.7</td>
<td>8.22</td>
</tr>
<tr>
<td>ZP [mV]</td>
<td>-22.0</td>
<td>-21.0</td>
<td>ZP [mV]</td>
<td>-24.2</td>
<td>-18.0</td>
</tr>
<tr>
<td>Turbidity removal [%]</td>
<td>4.8%</td>
<td>24.0%</td>
<td>Turbidity removal [%]</td>
<td>15.1%</td>
<td>24.0%</td>
</tr>
<tr>
<td>DOC removal [%]</td>
<td>-6.1%</td>
<td>-21.3%</td>
<td>DOC removal [%]</td>
<td>-3.3%</td>
<td>-2.8%</td>
</tr>
<tr>
<td>UV_{254} removal [%]</td>
<td>-0.8%</td>
<td>-2.3%</td>
<td>UV_{254} removal [%]</td>
<td>-0.3%</td>
<td>-0.1%</td>
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</table>

<table>
<thead>
<tr>
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<th>Coagulant dose</th>
<th>2.344 mg/L Al</th>
<th>Condition 6</th>
<th>Coagulant dose</th>
<th>2.930 mg/L Al</th>
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<tr>
<td>pH</td>
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<td>6.80</td>
<td>pH</td>
<td>7.19</td>
<td>6.90</td>
</tr>
<tr>
<td>ZP [mV]</td>
<td>-6.8</td>
<td>-6.3</td>
<td>ZP [mV]</td>
<td>3.7</td>
<td>-4.0</td>
</tr>
<tr>
<td>Turbidity removal [%]</td>
<td>-4.1%</td>
<td>35.2%</td>
<td>Turbidity removal [%]</td>
<td>-6.7%</td>
<td>2.4%</td>
</tr>
<tr>
<td>DOC removal [%]</td>
<td>84.4%</td>
<td>77.6%</td>
<td>DOC removal [%]</td>
<td>-3.3%</td>
<td>-2.8%</td>
</tr>
<tr>
<td>UV_{254} removal [%]</td>
<td>95.5%</td>
<td>94.9%</td>
<td>UV_{254} removal [%]</td>
<td>97.7%</td>
<td>94.3%</td>
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A.3.5. Residual aluminum concentration with coagulant conditions (Figure 5.9)

<table>
<thead>
<tr>
<th>Cond #</th>
<th>Al_{in}[mg/L Al]</th>
<th>Al (0.2 μm filtered)[mg/L]</th>
<th>Removed Al (0.2 μm filtered)</th>
<th>Al (UF)[mg/L]</th>
<th>Removed Al (UF)</th>
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<td>0.59</td>
<td>0.21</td>
<td>64%</td>
<td>0.07</td>
<td>88%</td>
</tr>
<tr>
<td>4</td>
<td>0.59</td>
<td>0.53</td>
<td>10%</td>
<td>0.51</td>
<td>13%</td>
</tr>
<tr>
<td>1</td>
<td>1.17</td>
<td>0.31</td>
<td>74%</td>
<td>0.24</td>
<td>80%</td>
</tr>
<tr>
<td>2</td>
<td>1.76</td>
<td>0.06</td>
<td>97%</td>
<td>0.06</td>
<td>97%</td>
</tr>
<tr>
<td>5</td>
<td>2.34</td>
<td>0.00</td>
<td>100%</td>
<td>0.00</td>
<td>100%</td>
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<tr>
<td>6</td>
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<td>0.04</td>
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<td>0.02</td>
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<tr>
<td>3</td>
<td>0.59</td>
<td>0.24</td>
<td>59%</td>
<td>0.04</td>
<td>93%</td>
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</table>

1 Coagulation condition. The number matches with the coagulation condition number in Table C-4.
2 Initial Al concentration in the solution
3 Residual aluminum concentration of the solution filtered through 0.2 μm membrane filter
4 Residual aluminum concentration of the solution filtered through 100 kDa UF membrane

A.3.6. Chemical and physical performance of the ultrafiltration system with coagulation (Figure 5.10 ~ 5.17)

<table>
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<th>Chemical performance</th>
<th>1#</th>
<th>Alum dose [mg/L Al]</th>
<th>pH</th>
<th>2ZP [mV]</th>
<th>Temp [°C]</th>
<th>3UV254, ini</th>
<th>4UV254, UF</th>
<th>UV254 removal [%]</th>
<th>5Turb, ini [NTU]</th>
<th>6Turb, UF [NTU]</th>
<th>Turb. removal [%]</th>
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</thead>
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<td>0</td>
<td>0.00</td>
<td>8.35</td>
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<td>0.1329</td>
<td>0.1328</td>
<td>0%</td>
<td>3.96</td>
<td>0.167</td>
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<td>3</td>
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<td>7.47</td>
<td>-50.6</td>
<td>22.4</td>
<td>0.1112</td>
<td>0.0873</td>
<td>34%</td>
<td>4.93</td>
<td>0.054</td>
<td>98.6%</td>
</tr>
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<td>4</td>
<td>4</td>
<td>0.59</td>
<td>8.73</td>
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<td>0.1283</td>
<td>0.1206</td>
<td>9%</td>
<td>4.67</td>
<td>0.038</td>
<td>99.0%</td>
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<td>4.81</td>
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<td>19.9</td>
<td>0.0186</td>
<td>0.0162</td>
<td>88%</td>
<td>5.39</td>
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<td>2</td>
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<td>5.27</td>
<td>-4.3</td>
<td>22.4</td>
<td>0.0096</td>
<td>0.0103</td>
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<td>5.81</td>
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<td>0.0115</td>
<td>0.0112</td>
<td>92%</td>
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<td>0.0129</td>
<td>90%</td>
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<table>
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<th>Physical performance</th>
<th>1#</th>
<th>Critical flux [lmh]</th>
<th>R_m \times 10^{10} m^{-1}</th>
<th>R_t \times 10^{10} m^{-1}</th>
<th>R_{hy} \times 10^{10} m^{-1}</th>
<th>R_{ch} \times 10^{10} m^{-1}</th>
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<td>1.17</td>
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<td>6</td>
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<td>24.69</td>
<td>9.75</td>
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<td>2.34</td>
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</table>

1 Coagulation condition
2 Zeta potential
3 Initial UV254 (filtered through 0.2 µm membrane)
4 Final UV254 after ultrafiltration
5 Initial turbidity
6 Final turbidity after ultrafiltration
# GLOSSARY OF SYMBOLS AND TERMINOLOGIES

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<tr>
<th>Symbol</th>
<th>Description</th>
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<tr>
<td>AHA</td>
<td>Aldrich humic acid</td>
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<tr>
<td>DBP</td>
<td>Disinfection by-product</td>
</tr>
<tr>
<td>DBPFP</td>
<td>Disinfection by-product formation potential</td>
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<td>DOC</td>
<td>Dissolved organic carbon</td>
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<td>ED</td>
<td>Electrodialysis</td>
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<tr>
<td>FA</td>
<td>Fulvic acid</td>
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<td>GAC</td>
<td>Granular activated carbon</td>
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<td>GTNOM</td>
<td>Georgetown NOM</td>
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<td>HA</td>
<td>Humic acid</td>
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<tr>
<td>HAA</td>
<td>Haloacetic acid</td>
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<td>HIOP</td>
<td>Heated iron oxide particle</td>
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<tr>
<td>IEP</td>
<td>Iso-electric point</td>
</tr>
<tr>
<td>kDa</td>
<td>Kilo Dalton</td>
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<tr>
<td>LHA</td>
<td>Leonardite humic acid</td>
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<td>lmh</td>
<td>The unit of flux used in membrane filtration. ([\text{Lm}^{-2}\text{h}^{-1}]) where, (L) is volume of permeate, (m^2) is the effective area of membrane for filtration, and (h) is hour.</td>
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<td>Maximum contaminant level</td>
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<td>Microfiltration</td>
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<td>MWCO</td>
<td>Molecular weight cut-off</td>
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<td>Abbreviation</td>
<td>Description</td>
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<td>Natural organic matter</td>
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<td>Powdered activated carbon</td>
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<td>Polyethersulfone</td>
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<td>Pervaporation</td>
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<td>Point of zero charge</td>
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<td>RC</td>
<td>Regenerated cellulose</td>
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<td>RO</td>
<td>Reverse osmosis</td>
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<td>Soil humic acid standard</td>
</tr>
<tr>
<td>SHSHA</td>
<td>Summit Hill soil humic acid</td>
</tr>
<tr>
<td>SRFA</td>
<td>Suwannee River fulvic acid</td>
</tr>
<tr>
<td>SUVA</td>
<td>Specific ultraviolet absorbance</td>
</tr>
<tr>
<td>THM</td>
<td>Trihalomathane</td>
</tr>
<tr>
<td>TMP</td>
<td>Transmembrane pressure</td>
</tr>
<tr>
<td>TOC</td>
<td>Total organic carbon</td>
</tr>
<tr>
<td>UF</td>
<td>Ultrafiltration</td>
</tr>
<tr>
<td>UV\textsubscript{254}</td>
<td>Ultraviolet absorbance at the wavelength of 254 nm [1/cm]</td>
</tr>
<tr>
<td>ZP</td>
<td>Zeta potential [mV]</td>
</tr>
<tr>
<td>ZPC</td>
<td>Zero point of charge</td>
</tr>
</tbody>
</table>
\( \kappa \) \hspace{1cm} \text{Debye (reciprocal) length, Debye-Hückel parameter [m]}

\( \mu \) \hspace{1cm} \text{Absolute viscosity of permeate solution [Pa\cdot sec or kg\cdot m\(^{-1}\)\cdot sec\(^{-1}\)]}

\( \varepsilon \) \hspace{1cm} \text{Permittivity [C\(^2\)\cdot cm\(^{-1}\)\cdot J\(^{-1}\)]}

\( \zeta \) \hspace{1cm} \text{Zeta potential [mV]}

\( \Delta P \) \hspace{1cm} \text{Transmembrane pressure [Psi or Pa]}

\( a \) \hspace{1cm} \text{Radius of sphere [m]}

\( J \) \hspace{1cm} \text{Permeate flux [lmh or m\cdot sec\(^{-1}\)]}

\( J_0 \) \hspace{1cm} \text{Initial permeate flux [lmh or m\cdot sec\(^{-1}\)]}

\( R \) \hspace{1cm} \text{Resistance [m\(^{-1}\)]}

\( R_a \) \hspace{1cm} \text{Resistance by adsorption layer [m\(^{-1}\)]}

\( R_{ch} \) \hspace{1cm} \text{Resistance after chemical cleaning [m\(^{-1}\)]}

\( R_{cl} \) \hspace{1cm} \text{Resistance by cake layer [m\(^{-1}\)]}

\( R_{cp} \) \hspace{1cm} \text{Resistance by concentration polarization [m\(^{-1}\)]}

\( R_f \) \hspace{1cm} \text{Resistance at the end of a filtration test [m\(^{-1}\)]}

\( R_{hy} \) \hspace{1cm} \text{Resistance after hydraulic rinse [m\(^{-1}\)]}

\( R_m \) \hspace{1cm} \text{Intrinsic membrane resistance [m\(^{-1}\)]}

\( T \) \hspace{1cm} \text{Temperature [K]}

\( U \) \hspace{1cm} \text{Electrophoretic mobility [\mu m\cdot sec\(^{-1}\)\cdot V\(^{-1}\)\cdot cm]}

\( ZP_{cor} \) \hspace{1cm} \text{Corrected zeta potential [mV]}

\( ZP_{meas} \) \hspace{1cm} \text{Measured zeta potential [mV]}
Curriculum Vitae

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PUBLICATIONS AND PRESENTATIONS
1. Kevin Y. Choi and Brian A. Dempsey, In-line coagulation with microfiltration (MF),
   The 75th ACS Colloid and Surface Science conference, Pittsburgh, PA (2001)
2. Kevin Y. Choi and Brian A. Dempsey, Ultrafiltration of mixtures of particles, humic
   materials, and coagulants, The 77th ACS Colloid and Surface Science conference,
   Atlanta, GA (2003)
   oxide controls the solubility of Fe(III) in hematite suspension?, The 77th ACS Colloid
4. Kevin Y. Choi and Brian A. Dempsey, Design of low pressure membrane filters using
5. Kevin Y. Choi and Brian A. Dempsey, Foultants of UF membrane filtration: Particles
   and/or NOM (in preparation; plan to submit July, 2003)
6. Kevin Y. Choi and Brian A. Dempsey, Critical flux of ultrafiltration system and its
   variation with different solution chemistry and operational conditions (in
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   of coagulation conditions (in preparation; plan to submit July, 2003)

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