Impact of Low Coagulant Dosages on Protein Fouling of Ultrafiltration Membranes

by

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ABSTRACT

Ultrafiltration fouling in drinking water treatment has been primarily attributed to the biopolymer fraction (e.g., proteins) of organic matter in source waters. This bench-scale study examined the use of coagulation to mitigate fouling in three model protein solutions. Similar to results from studies conducted with natural waters, a low coagulant dose ($2\ \mu\text{M}$ Al) was identified to significantly reduce membrane fouling relative to zero coagulant addition for two proteins (BSA and ovalbumin). It is hypothesized that the low dosages alter the surface hydrophobicity of proteins in both the bulk solution and fouling layer, resulting in weakened intermolecular interactions, reducing fouling.

The impacts of applying coagulation only during the initial stages of a permeation cycle (phased coagulation) on membrane fouling were investigated at pilot-scale. Coagulant application during the first half of the cycle resulted in fouling rates similar to that of continuous addition, which could translate to significant cost savings.

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NOMENCLATURE

%	Percent
°C	Degree(s) Celsius
<	Less than
≤	Less than or equal to
>	More than
μ	Viscosity
~	Approximate
±	Plus or minus
a.u.	Arbitrary units
Al	Aluminum
ANS	1-anilinonaphthalene-8-sulfonate
BLG	β-lactoglobulin
BSA	Bovine serum albumin
C	Concentration
CEB	Chemically enhanced backwash
CIP	Clean in place
cm	Centimetre(s)
DOC	Dissolved organic carbon
FEEM	Fluorescence excitation-emission matrix
g	Gram(s)
h	Hour(s)
HCl	Hydrochloric acid
Hz	Hertz
in	Inches
J	Flux
KHP	Potassium hydrogen phthalate
kPa	Kilopascal(s)
L	Liter(s)

LC-OCD	Liquid chromatography-organic carbon detection
L/h	Liter(s) per hour
LMH	Liter(s) per square metre per hour
L/min	Liter(s) per minute
m	Metre(s)
M	Molar
m ²	Squared meter(s)
mg/L	Milligram(s) per liter
min	Minute(s)
mL/min	Milliliter(s) per minute
mm	Millimeter(s)
mm ²	Millimeter(s) squared
mM	Millimolar
m/s	Meter(s) per second
mV	Millivolt(s)
NaOCl	Sodium hypochlorite
NaOH	Sodium hydroxide
NF	Nanofiltration
nm	Nanometer
NOM	Natural organic matter
ON	Ontario
OVA	Ovalbumin
Pa	Pascal(s)
PACl	Polyaluminum chloride
pH	Negative log of the hydrogen ion concentration; - log{H ⁺ }
PRODAN	6-propionyl-2-(N,N-dimethyl-amino)naphthalene
psi	Pounds per square inch
psig	Pounds per square inch gauge
PVC	Polyvinyl chloride

PVDF	Polyvinylidene difluoride
QC	Quebec
R	Resistance
R ²	Coefficient of determination
R _{irr}	Irreversible resistance
R _m	Intrinsic membrane resistance
RO	Reverse osmosis
rpm	Revolutions per minute
R _{rev}	Reversible resistance
R _T	Total resistance
TMP	Transmembrane pressure
TOC	Total organic carbon
TX	Texas
UF	Ultrafiltration
μL	Microliters
μM	Micromolar
UV	Ultraviolet
UV ₂₅₄	UV absorbance at 254 nm
WTP	Water treatment plant
ZW500	ZeeWeed® 500 membrane
ZW1000	ZeeWeed® 1000 membrane

1 Introduction

1.1 Background

Ultrafiltration (UF) has become increasingly prevalent in drinking water treatment due to its ability to consistently remove pathogens and particulates while having a footprint smaller than conventional media filters. However, fouling caused by the accumulation of solutes on the surface and within membrane pores impedes permeate flow, adversely impacting efficiency (Zularisam et al., 2006). Although resistance due to fouling is largely reversible via hydraulic backwashing, hydraulically irreversible fouling necessitates the periodic use of chemical cleaning reagents that can permanently alter membrane properties (Abdullah and Bérubé, 2013). Therefore, there exists a demand for methods that can improve the reversibility of fouling for greater efficiency.

Natural organic matter (NOM) is a significant source of UF fouling in drinking water treatment, particularly the large macromolecules (proteins and polysaccharides) that comprise the biopolymer fraction (Amy, 2008; Zheng et al., 2012). While most studies report the contribution of the biopolymer fraction as a whole to UF fouling, several studies have identified proteins to be primarily responsible for hydraulically irreversible fouling (Peiris et al., 2010; Peldszus et al., 2011; Peleato et al., 2017). Therefore, it is worth elucidating the properties and mechanisms of proteins relevant to UF fouling which can potentially lead to the development of effective fouling mitigation strategies.

Coagulation is the most popular pretreatment method to mitigate UF fouling in drinking water treatment. While conventional treatment optimizes coagulation for turbidity or dissolved organics removal, it may be advantageous to select conditions to maximize biopolymer/protein removal prior to UF to mitigate fouling instead. Previous studies have reported reduced fouling at low coagulant doses (< 1 mg metal/L) (Peleato et al., 2017; Tabatabai et al., 2009), which has been associated with the point of diminishing returns for biopolymer removal (Wray and Andrews, 2014). However, the impact of coagulation, particularly at low dosages, on protein fouling remains unclear. Changes in protein conformation (Peleato et al., 2017) as well as particle size (Ma et al., 2015) have been identified as a result of coagulation with low dosages.

1.2 Objectives

The main objectives of this study were to:

1. Examine the impact of low coagulant dosages on protein fouling of UF membranes
2. Assess the impact of coagulation on the properties of proteins relevant to UF fouling
3. Examine the impact of phased coagulation with respect to membrane fouling at pilot-scale

1.3 Description of Chapters

- **Chapter 2** provides background information regarding ultrafiltration in drinking water treatment, membrane fouling and coagulation pretreatment as a fouling control strategy
- **Chapter 3** describes the methodology used to evaluate the effect of low coagulant dosages on protein-related fouling of UF membranes. Details regarding the model solution, experimental design, bench- and pilot-scale apparatus, and analytical methods are provided
- **Chapter 4** presents the results of the bench-scale experiment about the impacts of low coagulant dosages on protein fouling of UF membranes, as well as an analysis of protein properties at different coagulant dosages
- **Chapter 5** presents the results of the pilot-scale experiment regarding the impact of phased coagulation on membrane fouling and the associated cost savings
- **Chapter 6** summarizes the results of this study and provides recommendations for future research
- **Chapter 7** lists the references mentioned in this study
- **Chapter 8** presents the appendices containing analytical procedures and raw data

2 Literature Review

2.1 Ultrafiltration Overview

Ultrafiltration (UF) is a low pressure membrane filtration method that is commonly used in drinking water treatment because it is more economical than high pressure systems such as nanofiltration (NF) and reverse osmosis (RO) (Gao et al., 2011). They also have a smaller footprint when compared to conventional media filters, making them a popular choice for retrofits. Low pressure membranes operate via a sieving mechanism that removes any constituents larger than the membrane pores. As a result, UF membranes have been shown to be very effective in removing pathogens (*Giardia* and *Cryptosporidium*) and particulates (AWWA, 2008). Since they operate via size exclusion, UF membranes do not require precise control of water chemistry for effective removal unlike conventional filters. As a result, UF membranes are commonly implemented into newly constructed or retrofitted treatment facilities (Gao et al., 2011).

2.2 Membrane Fouling

Membrane fouling is the primary limitation for the broader application of UF (Gao et al., 2011). The accumulation of foulants on the membrane can form a cake/gel layer on the surface and/or narrow or block pores (Figure 2-1). As a result, fouling leads to greater energy consumption and increases maintenance frequency, all of which adversely impact efficiency (Kimura et al., 2014).

Figure 2-1: Types of ultrafiltration fouling (a) cake layer formation, (b) pore narrowing, and (c) pore blocking

When membranes are operated under constant flux, fouling is quantified by the change in transmembrane pressure (TMP) during permeation. Fouling is often expressed using resistance (R) which is calculated according to equation [2.1]:

$$R = \frac{TMP}{J \cdot \mu} \quad [2.1]$$

where, R is resistance (m^{-1})

TMP is the transmembrane pressure (Pa)

J is the permeate flux ($\text{m}^3 \text{m}^{-2} \text{s}^{-1}$)

μ is the viscosity of water (Pa s^{-1})

2.2.1 Types of UF Fouling

Fouling is typically characterized as reversible or irreversible and can be further classified as hydraulically or chemically reversible and irreversible. Hydraulically reversible fouling is readily removed by physical cleaning methods such as backwashing and air sparging and is often associated with cake layer formation (Taniguchi et al., 2003). Foulants that remain on the membrane after physical cleaning, which is typically a result of adsorption or pore blocking/narrowing (Belfort et al., 1994), is defined as hydraulically irreversible and is often removable by chemical cleaning (i.e., chemically reversible fouling). Chemically irreversible fouling can cause permanent reduction in the permeable area of the membrane.

Membrane fouling is often modeled using the resistance-in-series model, which defines the total membrane resistance (R_T) as the sum of intrinsic membrane resistance (R_m) and resistance due to fouling, both reversible (R_{rev}) and irreversible (R_{irr}) (equation [2.2]). Relative contributions of reversible and irreversible fouling resistance can be determined by removing the reversible fouling layer, either hydraulically or chemically. A representation of the different resistances contributing to total resistance for the typical operation of a hollow fibre UF for drinking water is presented in Figure 2-2.

$$R_T = R_m + R_{rev} + R_{irr} \quad [2.2]$$

Figure 2-2: Representation of contributions of intrinsic membrane resistance (R_m), reversible fouling resistance (R_{rev}), and irreversible fouling resistance (R_{irr}) during UF with continuous permeation and backwash cycles

2.3 Identification of Foulants

Natural organic matter (NOM), particularly the dissolved fraction ($< 0.45 \mu\text{m}$), has been identified as the predominant source of membrane foulant when considering drinking water treatment (Amy, 2008; Howe and Clark, 2002). Ubiquitous in natural waters, NOM is a complex mixture of compounds ranging in size, shape, and character. Extensive research has been conducted to identify the components of NOM that are responsible for UF fouling. In particular, the biopolymer fraction has been reported to be the major source of UF foulants (Amy, 2008; Zheng et al., 2012). These include large macromolecules ($>10 \text{ kDa}$) such as proteins and polysaccharides that are often larger than membrane pores. While the concentration of biopolymers is of importance when predicting membrane fouling, the composition of the biopolymer fraction should be considered as well (Hallé et al., 2009). Most existing research has only examined the contribution of the biopolymer fraction as a whole towards membrane fouling. It is therefore worth investigating the types of compounds that comprise the biopolymer fraction and their relative contributions to fouling since they may have unique properties that influence fouling behaviour.

Previous studies have identified proteins via fluorescence spectroscopy to be responsible for irreversible fouling (Peiris et al., 2010; Peldszus et al., 2011; Peleato et al.,

2017). Protein-related fouling of UF membranes occurs in two stages. Initially, a monolayer of proteins is adsorbed onto the membrane surface which is largely governed by protein-membrane interactions (Huisman et al., 2000). Subsequently, deposition and/or adsorption onto this monolayer occurs, such that protein-protein interactions become significant (Wang et al., 2013). It is therefore beneficial to gain an understanding of the physicochemical properties of proteins, including size, surface charge and hydrophobicity, since these govern protein interactions (i.e., fouling potential) with both the membrane and the fouling layer (Gao et al., 2011). Fouling mechanisms can be complex as it is the result of a combination of competitive phenomena such as size exclusion, electrostatic attraction/repulsion, and hydrophobic interactions (Huisman et al., 2000). Therefore, elucidating the characteristics and mechanisms responsible for UF fouling can potentially lead to the development of effective fouling mitigation strategies.

2.4 Fouling Control Strategies

2.4.1 Hydraulic Backwashing

Hydraulic backwashing is a common component of routine membrane maintenance in which the flow of water is reversed to remove any foulants that have deposited onto the surface of the membrane (i.e., hydraulically reversible fouling). Treated water is typically used for backwash but can also be chemically-enhanced to provide more effective cleaning. Backwash frequency, flux (or pressure), and duration can be adjusted to maximize efficiency. Backwash frequency must be often enough to prevent excessive fouling resistance, but sufficiently low to minimize the volume of treated water used to perform backwashing (Li et al., 2014). However, backwashing often does not fully restore permeability and are usually supplemented with other physical and/or chemical cleaning methods.

2.4.2 Chemical Cleaning

Another common component of a membrane maintenance program is chemical cleaning. Two procedures are typically applied at full-scale facilities: chemically enhanced backwash (CEB) and clean in place (CIP). CEB is often performed daily with oxidants such as sodium hypochlorite. CIP is performed less frequently (< 10 times/year) and often exposes the membrane to a variety of chemicals for intensive cleaning (Woo et al., 2013). A variety of chemicals can be used, each targeting different foulants as shown in Table 2-1 (Porcelli and

Judd, 2010). Although chemical cleans are effective in restoring membrane permeability, its applications should be minimized because it can adversely impact membrane properties (Abdullah and Bérubé, 2013). Chemical cleans have been reported to lower the yield strength of membranes, which can result in membrane rupture allowing contaminants that otherwise would have been rejected to pass (Wang et al., 2010). Oxidants such as sodium hypochlorite have been shown to remove any surface modifications from PVDF membranes, resulting in a more hydrophilic surface that can be more prone to NOM fouling (Puspitasari et al., 2010). Therefore, methods that improve the hydraulic reversibility of fouling can reduce the frequency of chemical cleaning, which consequently increase membrane service life and lead to substantial cost savings (Li et al., 2014).

Table 2-1: Types of chemical used for membrane cleaning and foulants targeted

Chemical Type	Examples	Target Foulants
Acid	HCl, Citric Acid	Metals
Alkali	NaOH	Acidic organics (phenols and carboxyls)
Oxidant	NaOCl	Organics

2.4.3 Coagulation

Chemical coagulation is the most popular UF pretreatment employed to reduce fouling (Matilainen et al., 2011). In principle, coagulation decreases UF fouling by agglomerating small NOM molecules via charge neutralization or sweep flocculation to prevent them from blocking or narrowing membrane pores and/or creating a looser cake layer of floc thereby allowing easier removal during backwash (i.e., greater hydraulic reversibility) (Barbot et al., 2008). Moreover, the increases in cake layer porosity was reported to decrease cake layer resistance (Lee et al., 2000).

Full-scale UF facilities often utilize inline coagulation, which does not include a sedimentation step after flocculation in order to reduce plant footprint (Zheng et al., 2012). An optimum coagulant dose for minimizing UF fouling may not be the same as that applied during conventional treatment, which often seeks to maximize dissolved organics or turbidity removal. In fact, it is advantageous to select a dose that preferentially targets UF foulants including

biopolymers. When considering coagulant addition, Wray et al. (2014) determined that the point of diminishing returns for biopolymer removal (0.5 mg/L alum) to be much lower than the dose required to achieve charge neutralization. Furthermore, studies have reported UF fouling to be minimized at low coagulant doses (< 1 mg metal/L) (Peleato et al., 2017; Tabatabai et al., 2009). Excess coagulant dosages typically associated with sweep flocculation have been shown to adversely impact membrane fouling. Through field emission scanning electron microscopy, Wray et al. (2016) observed aluminum precipitate deposits on the membrane surface which contributed to increase cake resistance. Moreover, it has been reported that sweep flocculation promotes a more compressible and less porous (i.e., more resistive) cake layer when compared to one under lower coagulant dosages (Lee et al., 2000).

Unfortunately, limited research exists regarding optimizing coagulation for protein removal or mitigating protein fouling. Moreover, the impact of coagulation on protein character and its fouling mechanisms is still unclear. Peleato et al. (2017) suggest that coagulation addition induces a conformational change in the protein that makes it more hydrophilic and thus less prone to fouling. Conversely, Ma et al. (2015) observed that fouling with synthetic bovine serum albumin (BSA) solutions was most severe at low coagulant concentrations due to changes in the particle size which was closer to the diameter of the membrane pores.

While coagulant dose can have a significant impact on fouling mitigation, it is also worth considering how coagulation is applied. A bench-scale experiment conducted by Pronk et al. (2016) suggested that applying ferric chloride inline only during the first half of a permeation cycle, instead of applying continuously, does not worsen fouling which in turn would reduce coagulant costs. Lok et al. (2017b) applied this strategy to a pilot-scale system using polyaluminum chloride (PACl) and observed similar results. However, their results were highly variable which necessitates long-term (>2 days) filtration tests to comprehensively evaluate the benefits of phased coagulation.

3 Materials and Methods

3.1 Experimental Protocol

3.1.1 Water Selection

Bench-scale studies were conducted with synthetically prepared solutions containing model proteins. Natural water matrices were not selected to avoid any potential interference from non-protein constituents from impacting protein fouling mechanisms. All solutions were prepared using distilled water (Elix[®] Advantage, Millipore Sigma). Bovine serum albumin (BSA, 66.4 kDa), ovalbumin (OVA, 42.7 kDa), and β -lactoglobulin (BLG, 18.4 kDa) were chosen as the model proteins (Millipore Sigma, Oakville, ON) due to their range in size and are commonly used as model membrane foulants in literature (Ko et al., 1993; Ma et al., 2014; Marshall et al., 1993). 20 mg/L BSA and 10mg/L BLG were dissolved in a 1 mM NaCl buffer while 20 mg/L OVA was dissolved in 10 mM NaCl. Buffer concentrations were chosen to maximize protein surface hydrophobicity while remaining within the typical range of ionic strengths reported for natural waters (Haskard and Li-Chan, 1998; Luey et al., 1991). It was anticipated that increased protein surface hydrophobicity would strengthen interactions with the hydrophobic UF membrane and accelerate fouling.

3.1.2 Coagulation

Aluminum sulphate (alum, General Chemical) was selected as the coagulant for bench-scale studies because it is the most commonly used coagulant in drinking water treatment which provides a good comparison to results reported in previous studies. Dosages (Table 3-1) were selected based on those identified in previous studies that minimized UF fouling (Peleato et al., 2017; Wray and Andrews, 2014), as well as values commonly applied at full-scale UF facilities (Wray et al., 2016). Inline coagulation was simulated by the addition of alum into the feed tanks which were continuously rapid mixed to prevent floc settling that may alter feed water quality between permeation cycles. pH was adjusted to 7.0 ± 0.2 using HCl and NaOH to counteract any reduction following coagulant addition, as protein fouling is known to be influenced by pH (Marshall et al., 1993). Mixing speed was monitored and adjusted if necessary throughout the experiment to avoid excessive foaming, which implies denaturation of proteins. Protein concentrations in the feed were monitored throughout the experiment and

were verified to not have change by more than 9% between samples suggesting consistent water quality.

Table 3-1: Alum dosages examined for model protein solutions

Alum Dose	
μM Al	mg/L
0	0
2	0.3
10	1.7
40	6.8

At pilot-scale, polyaluminum chloride (PACl, PAX-XL1900, Kemira Water Solutions) was selected since the same is used at full-scale at Barrie Surface WTP. PACl is injected into the feed stream prior to flocculation (inline coagulation) before it reaches the membrane.

3.2 Bench-Scale System

Membrane fouling was studied at bench-scale using commercially available hollow fibre membranes (ZeeWeed® 500, SUEZ Water Technologies & Solutions, Oakville, ON) composed of reinforced polyvinylidene fluoride (PVDF). Adapted from Lok et al. (2017a), the bench-scale system (Figure 3-1) was automated via a PLC program (WinLDR, IDEC Corporation) to cycle through the steps of a permeation cycle as follows: : 1) A solenoid valve opening to fill the membrane tanks via gravity with approximately 1 L of water, 2) a peristaltic pump (Masterflex L/S 07528-30, Cole-Parmer) drawing feed water through the membrane, 3) reversing the flow direction of the peristaltic pump for backwash, and 4) draining the membrane tanks. Four bench-scale systems were operated in parallel to allow for multiple trials could be conducted simultaneously. TMP and permeate flux were recorded every 30 s (0.033 Hz) with a pressure transducer (PX-26, Omega Engineering, St-Eustache, QC) and an analytical balance (Symmetry 20000-41, Cole-Parmer, Montreal, QC), respectively via data logging software (LabView Signal Express 15.0, National Instruments, Vaudreuil-Dorion, QC). A five-point calibration (-5, -1, 0, 1, 5 psig) of the pressure transducers was performed prior to each trial with a Druck DPI 611 (GE Digital Solutions).

A new, 25-cm long membrane fibre was used for each trial, which has an area of approximately 0.0016 m² and a nominal pore size of 0.04 μm. One end of the membrane was sealed while a 2 mm diameter PVC tubing (McMaster Carr, Cincinnati, OH) was attached to

the other end with epoxy. The fibre was then cleaned by permeating an 800 mg/L NaOCl solution for 3 h following by soaking in the same solution overnight. The integrity of each fibre was tested at the beginning and end of each trail using a bubble test at 35 kPa (~5 psi). If leaks were detected in the fibre, they were either resealed with epoxy or discarded. Cleaned membranes were then stored in 50 mg/L NaOCl solution at 4 °C until use.

The pure water permeability (PWP) measures the maximum flux attained by a virgin membrane which in turn provides a measure of the intrinsic membrane resistance. The TMP of a membrane permeating distilled water at three different fluxes (approximately 20, 30, and 40 LMH) for 2 h each was recorded and averaged. The PWP is estimated as the slope of the flux vs. TMP plot. PWP of membranes were ensured to be within 15% of each other to minimize the impact of intrinsic properties of the membrane (e.g., pore number and size) on fouling mechanisms. Sample calculations are shown in Section 8.1.

Figure 3-1: Schematic of typical bench-scale UF system

3.3 Pilot-Scale System

Pilot-scale experiments were conducted at the Barrie Surface WTP (Barrie, ON). Previously described by Wray et al. (2016), the pilot plant contains a full ZeeWeed® 1000 membrane module (Figure 3-2). It was fully automated to mimic full-scale treatment including inline coagulation with polyaluminum chloride (PACl, PAX-XL1900, Kemira Water Solutions), backwashing, and air sparging. Transmembrane pressure (TMP), feed and permeate turbidity, temperature, pH, and particles counts were recorded every 5 minutes. Between each experimental trial, the membrane module was cleaned with 500 mg/L NaOCl and 200 mg/L citric acid for 6 h each. A membrane integrity test was also conducted after every trial to identify any leaks in the system.

Figure 3-2: Schematic of pilot-scale UF system at Barrie Surface WTP

3.4 Analytical Methods

3.4.1 Protein Quantification

Protein concentrations were approximated using a colorimetric assay (Micro BCA Kit, Thermo Fisher Scientific, Whitby, ON) as per manufacturer's instructions (microplate method). Each sample was prepared in duplicate. Calibration curves were obtained for each protein investigated (Figure 3-3).

Figure 3-3: Example calibration curve for protein quantification via colorimetric assay

3.4.2 Protein Size and Surface Charge

The hydrodynamic radius (nm) and zeta potential (mV) of proteins were measured using a Horiba SZ-100 (Mississauga, ON) with disposable carbon electrode cells. Analysis consisted of 10 pulse measurements with a 5 s delay between measurements. Three measurements were made per sample and were all analyzed at 25 °C.

3.4.3 Fluorescence Spectroscopy

Fluorescence excitation-emission matrices (FEEMs) were collected using a Cary Eclipse fluorescence spectrophotometer (Agilent, Mississauga, ON) with a quartz cuvette. Excitation and emission wavelength ranges (ex/em) were 230-380 nm (5 nm increments) and 280-400 nm (2 nm increments) respectively. Instrument conditions such as photomultiplier tube (PMT) voltage (450 V) and slit widths (10 nm) were kept constant to maintain

comparability between samples. Cuvettes were rinsed with Milli-Q® water between samples. The collected spectra were smoothed with Savitzky-Golay filter with a window size of 7 to reduce data noise (Savitzky and Golay, 1964) (Figure 3-4).

Figure 3-4: Raw and processed (via Savitzky-Golay filter) sample spectra of BSA fluorescence emission at 230 nm excitation

3.4.4 Protein Surface Hydrophobicity Fluorescence Assay

The surface hydrophobicity of a protein was measured using a fluorescence assay using 1-anilinonaphthalene-8-sulfonate (ANS) as a fluorescent probe. Upon binding of ANS to the hydrophobic areas of a protein, an increase in fluorescent intensity and blue shift is observed (Figure 3-5). Adapted from the procedure performed by Haskard and Li-Chan (1998), samples were serially diluted using the same buffer solution into 5 mL aliquots of different concentrations in test tubes. 20 μ L of 8 mM ANS was added into each test tube and gently mixed before left to stand for 10 min. The fluorescent intensity of each sample at ex/em 370/490 nm was measured in a quartz cuvette at a 750 V photomultiplier tube voltage and 10 nm slit width. Cuvettes were rinsed with Milli-Q® between samples. Sample calculations are detailed in Section 8.2.

Figure 3-5: Variation in fluorescence emission spectrum of ANS (ex 370 nm) at various OVA concentrations (0 – 20 mg/L). Increasing concentration (darker colour) corresponds to blue shift and increase in intensity.

3.4.5 Dissolved Organic Carbon

Dissolved organic carbon (DOC) was analyzed using a wet oxidation method based on the Standard Method 5310D on an O-I Corporation Model 1010 Analytical TOC Analyzer with a Vial Multisampler (OI Analytical, College Station, TX). Samples were first filtered through a 0.45 μm filter to remove particulates before being collected into 40 mL amber vials and sealed with Teflon-lined septum screw caps. All samples were prepared on the day of collection, stored at 4 °C, and analyzed within a week. A summary of instrument conditions and reagents are presented in Table 3-2 and Table 3-3, respectively.

Table 3-2: DOC analyzer conditions

Parameter	Description
Acid	200 μL of 5% phosphoric acid
Oxidant	1000 μL of 100 g/L sodium persulphate
Sample Volume	15 mL
Rinses per sample	1
Volume per rinse	15 mL
Reaction time	2 min 30 sec
Detection time	2 min
Purge gas	Nitrogen
Loop size	5 mL

Table 3-3: List of reagents used in DOC analysis

Reagent	Supplier and Purity
Sulphuric acid	VWR, 98+%
Potassium hydrogen phthalate	Sigma, 98+%
Sodium persulphate	Sigma, 98+%, anhydrous
Phosphoric acid	Sigma, ≥85%

DOC concentrations were determined using anhydrous potassium hydrogen phthalate (KHP) as a calibration standard. The calibration solution was prepared at 10 mg/L before the analyzer dilutes it to concentrations of 5, 2.5, 1.25, 0.625, and 0 mg/L to form a 6-point calibration (Figure 3-6). Check standards (3 mg/L) and Milli-Q® blanks were analyzed after every 10 samples to ensure the calibration remains valid.

Figure 3-6: Example DOC calibration curve using potassium hydrogen phthalate

3.4.6 Liquid Chromatography-Organic Carbon Detection

Liquid chromatography-organic carbon detection (LC-OCD) was used to characterize DOC based on size and structure. LC-OCD fractionates DOC into five categories: biopolymers, humic substances, building blocks, low molecular weight acids, and low molecular weight neutrals. These classifications allow for the identification of NOM components that are responsible for UF fouling and subsequently be used to evaluate their removal with fouling control strategies such as coagulation.

Water samples were filtered through a 0.45 µM filter, collected in 40 mL carbon-free (via heat treatment in muffle furnace) sample vials and stored in 4 °C until analysis (within two weeks). The samples were analyzed at the University of Waterloo following the procedure described by Huber et al. (2011) and the collected data was processed using customized software (ChromCALC, DOC-LABOR, Karlsruhe, Germany).

3.5 Statistical Methods

A linear regression was used to model fouling (total, irreversible, or reversible) as a function of permeation time. A two-tailed t-test was used to determine significant differences between the fouling rate of protein solutions with and without coagulant addition at a 5% confidence level ($\alpha = 0.05$). A 15% confidence interval was selected for pilot-scale experiments to reflect the greater variability between replicates. The t-statistic was calculated in Microsoft Excel according to equation [3.1]:

$$t = \frac{b_1 - b_2}{\sqrt{SE_1^2 + SE_2^2}} > |t_{\alpha, n_1 + n_2 - 4}| \quad [3.1]$$

where, b_1, b_2 are the slopes of the two linear models

SE_1, SE_2 are the standard errors of the slopes

n_1, n_2 are the number of points in each model

The 95% confidence intervals (CI) of the slopes were calculated using equation [3.2]:

$$CI_1 = b_1 \pm t_{0.05, n_1 - 2} \cdot SE_1 \quad [3.2]$$

4 Impact of Low Coagulant Dosages on the Protein Fouling of Ultrafiltration Membranes

4.1 Introduction

Ultrafiltration (UF) has become increasingly prevalent in drinking water treatment, however, its broader application is primarily hindered by fouling. Fouling increases the resistance to flow, which in turn increases energy requirements needed to ensure constant water production. Although hydraulic backwashing is regularly performed to remove accumulated foulants (i.e., hydraulically reversible fouling), it typically does not fully restore permeability. Applying chemical cleaning can remove hydraulically irreversible fouling, however, this process typically involves the use of harsh chemicals that may compromise membrane integrity (Porcelli and Judd, 2010). Thus, there is a demand for sustainable strategies to improve the hydraulic reversibility of fouling which maximizes membrane efficiency.

Natural organic matter (NOM) significantly contributes to reversible and irreversible fouling of UF membranes when applied to drinking water treatment (Howe et al., 2006). In particular, the biopolymer fraction (proteins and polysaccharides) has been identified as containing primary UF foulants (Amy, 2008; Zheng et al., 2012). While the concentration of biopolymers is of importance when predicting membrane fouling, the specific composition of biopolymers should be considered as well (Hallé et al., 2009); most existing research has only examined the contribution of the biopolymer fraction as a whole (Kimura et al., 2014; Siembida-Losch et al., 2015; Wray and Andrews, 2014). It is therefore worth investigating the types of compounds that comprise the biopolymer fraction and their relative contributions to fouling, since they may each have unique properties that influence fouling behaviour. Previous studies have demonstrated that proteins are primarily responsible for hydraulically irreversible fouling (Peiris et al., 2010; Peldszus et al., 2011; Peleato et al., 2017).

Protein-related fouling of UF membranes occurs in two stages. Initially, a monolayer of proteins is adsorbed onto the membrane surface which is largely governed by protein-membrane interactions (Huisman et al., 2000). Subsequently, deposition and/or adsorption onto this monolayer occurs, such that protein-protein interactions become significant (Wang et al., 2013). It is therefore beneficial to gain an understanding of the physicochemical properties of proteins, including size, surface charge and hydrophobicity, since these govern

protein interactions (i.e., fouling potential) with both the membrane and the fouling layer (Gao et al., 2011). Fouling mechanisms can be complex as a combination of competitive phenomena often exist such as size exclusion, electrostatic attraction/repulsion, and hydrophobic interactions (Huisman et al., 2000). Therefore, elucidating the characteristics and mechanisms responsible for UF fouling can potentially lead to the development of effective fouling mitigation strategies.

Applying chemical coagulation prior to UF is believed to reduce fouling by aggregating NOM to form a less resistive and more hydraulically reversible fouling layer (Barbot et al., 2008). An optimum coagulant dose for minimizing UF fouling may not be the same as that applied during conventional treatment, which often seeks to maximize turbidity removal. Previous studies have reported that UF fouling is minimized at coagulant dosages much lower (< 1 mg metal/L) than what is required to achieve charge neutralization (Peleato et al., 2017; Tabatabai et al., 2009; Wray and Andrews, 2014). Furthermore, a low coagulant dose (< 0.5 mg/L alum) has been associated with the point of diminishing returns for biopolymer removal (Wray and Andrews, 2014). Unfortunately, limited research exists regarding the effect of coagulation on protein fouling of UF membranes. Moreover, the impact of coagulation, particularly at low doses, on protein character and its fouling mechanisms is still unclear. Peleato et al. (2017) suggest that coagulation addition induces a conformational change in the protein that makes it more hydrophilic and thus less prone to fouling. Conversely, Ma et al. (2015) observed that fouling with synthetic bovine serum albumin (BSA) solutions was most severe at low coagulant concentrations due to changes in the particle size which was closer to the diameter of the membrane pores.

The main objective of this study was to specifically examine the impact of coagulation on protein fouling of UF membranes. By using synthetic protein solutions, it can be confirmed whether low coagulant doses are capable of altering the protein fraction to reduce fouling, as suggested by previous studies (Peleato et al., 2017; Wray and Andrews, 2014). Additionally, trials conducted over the course of 48 h with periodic backwashing allowed for better mimicking of full-scale conditions and evaluation of the effect of coagulation on the hydraulic reversibility of protein fouling.

4.2 Materials and Methods

4.2.1 Model Solutions

Feed waters containing 20 mg/L bovine serum albumin (BSA), 20 mg/L ovalbumin (OVA), or β -lactoglobulin (BLG) were prepared as described in Section 3.1.1. These globular proteins were selected to provide a range in size and are commonly used as model membrane foulants in literature (Ko et al., 1993; Ma et al., 2014; Marshall et al., 1993).

4.2.2 Membrane Filtration

Bench-scale modules were fabricated in-house using commercially available hollow fibre membranes (ZeeWeed® 500, SUEZ Water Technologies & Solutions) composed of reinforced polyvinylidene fluoride (PVDF). The membrane area in each 25 cm-long fibre was approximately 0.0016 m² and with a nominal pore size of 0.04 μ m. New membranes used for each trial were prepared according to the steps outlined in Section 3.2. Intrinsic permeability of each fibre was determined (Section 8.1) to ensure that membranes were within 15% of each other. This step helped minimize the intrinsic differences among fibres from influencing the types of fouling mechanisms during permeation.

Four bench-scale systems (Figure 3-1) were operated in parallel; each was automated to cycle through the steps of a permeation cycle as described in Section 3.2. Each trial consisted of 12 permeation cycles (total of 48 h of permeation) or until transmembrane pressure (TMP) reached 40 kPa. Permeation and backwash flux was kept constant at 30 L m⁻² h⁻¹. TMP and permeate flow were recorded every 30 s. Feed, permeate, and reject (water drained from membrane tank at the end of a permeation cycle) samples were collected at 24 and 48 h during each trial. Each trial was conducted in duplicate except for BLG which was only conducted once.

Membrane fouling during each permeation cycle was quantified using a resistance-in-series model that has previously been used in fouling studies (Peleato et al., 2017; Wray et al., 2014). This model defines total resistance (R_T) as the sum of the intrinsic membrane resistance (R_m) and resistance due to fouling (R_f), both irreversible (R_{irr}) and reversible (R_{rev}). As shown in Figure S2, irreversible fouling is defined as the resistance that cannot be removed at the end of a backwash relative to the intrinsic membrane resistance. Conversely, reversible fouling is

defined as the fouling resistance that was removed by backwash at the end of a permeation cycle.

4.2.3 Inline Coagulation

Inline coagulation conditions (coagulation and flocculation only) were simulated by addition of alum (General Chemical; 0.043 mg Al/mg coagulant added), which was continuously rapid mixed to prevent floc settling that may alter feed water quality between permeation cycles. Coagulant doses (Table 3-1) were selected based on those identified in previous fouling minimization studies (Peleato et al., 2017; Wray and Andrews, 2014), as well as values commonly applied at full-scale UF facilities that utilize inline coagulation pretreatment (Wray et al., 2016).

4.2.4 Protein Characterisation

Zeta potential of the feed solution was measured as described in Section 3.4.2. Surface hydrophobicity of proteins in the feed, permeate, and reject was determined by a fluorescence assay using 1-anilinonaphthalene-8-sulfonate (ANS) as a fluorescent probe (Section 3.4.4)

4.3 Results

4.3.1 Membrane Fouling

When considering BSA and OVA solutions, a 2 μ M Al dose (0.3 mg/L alum) contributed to a significant reduction ($p < 0.05$) in hydraulically reversible and irreversible fouling rates when compared to no coagulant addition (Figure 4-1, see Section 8.4.1 for resistance values). Increasing coagulant dose (10 and 40 μ M Al) was shown to exacerbate fouling, which may be indicative of alum and its hydrolysis products being a membrane foulant (Kimura et al., 2008). These results also indicate that irreversible fouling generally develops at a faster rate than reversible fouling. Protein fouling is a predominantly irreversible phenomenon, which is in agreement with previous membrane studies (Peiris et al., 2013; Peldszus et al., 2011). Interestingly, similar results of a low coagulant dose being effective in mitigating fouling were observed in membrane studies conducted on natural surface water (Peleato et al., 2017; Tabatabai et al., 2009; Wray and Andrews, 2014). This similarity in fouling trends between model solutions and natural waters suggests that proteins are the

predominant membrane foulants in natural waters which is in agreement with previous studies (Peiris et al., 2013; Peldszus et al., 2011; Zheng et al., 2012).

Figure 4-1: (a) Hydraulically irreversible and (b) reversible fouling rates associated with 20 mg/L of bovine serum albumin (BSA), 20 mg/L ovalbumin (OVA), and 10 mg/L β -lactoglobulin (BLG) for a range of coagulant doses. Vertical bars represent the 95% confidence interval calculated from the standard error of the fouling rate ($n = 11$).

Contrasting fouling trends were observed for BLG where dosages of 40 μM and 2 μM resulted in the least and most fouling, respectively. A potential explanation may lie in the difference in character when comparing BLG and BSA/OVA. It is common for proteins to undergo conformational changes upon adsorption to a solid surface to minimize free energy

(Rabe et al., 2011). As such, it is possible that the proteins in the surface cake layer have different properties than proteins in the bulk solution which ultimately impacts fouling behaviour. Intermediate size proteins including BSA and OVA have been reported as being ‘soft’, implying that they are more likely to undergo structural alterations upon surface contact unlike ‘hard’ proteins such as BLG (Pérez-Fuentes et al., 2017). Therefore, differences in cake layer properties may be responsible for varying fouling trends. Nonetheless, the contrasting results demonstrate that proteins do not always respond consistently to coagulant addition. Furthermore, it highlights the complexity of NOM, whereby even within the biopolymer fraction there exists a wide assortment of compounds, each with their own unique properties and response to treatment.

4.3.2 Protein Rejection

Proteins rejected (as %) by the membrane for a range of alum doses after 24 h of permeation indicated that BSA and OVA passes through to the greatest extent when 2 μM Al is added (Figure 4-2a), suggesting that interactions between proteins in the bulk solution and the membrane surface/fouling layer are at a minimum. Similar trends were observed after 48 h of permeation as well, but not shown (see Section 8.4.2 for concentration values). As shown in Figure 4-2b, increased rejection significantly increases irreversible fouling for OVA ($p = 4 \times 10^{-4}$), in agreement with trends suggested by Marshall et al. (1993). However, the relationship is not significant for OVA ($p = 0.056$). Nonetheless, their trends suggest less fouling comes at the expense of lower protein removal. Once again, contrasting results were observed with BLG in which an increasing alum dose was associated with greater, albeit insignificant ($p = 0.20$), protein rejection. This difference in trends suggests that the predominant fouling mechanism for BLG differs from that of BSA and OVA. It is also interesting that the magnitude of irreversible fouling for BLG is relatively lower despite similar removals as BSA and OVA, which implies a difference in fouling layer.

Figure 4-2: (a) Rejection of proteins (%) by UF for a range of alum dosages (as μM Al) after 24 h of permeation. Similar trends were seen after 48 h of permeation (not shown). Vertical bars of BSA and OVA represent the standard deviation of duplicate trials. Vertical bars of BLG represent the standard deviation of duplicate analyses. (b) Relationship between rejection of proteins by UF and irreversible fouling resistance gained during a permeation cycle. Bold R^2 values indicates a significant correlation ($p < 0.05$, $n = 7$ or 8).

4.3.3 Protein Properties

The underlying rationale for explaining why a low coagulant dose may be effective in mitigating protein fouling likely rests in how a protein interacts with the membrane surface. While the characteristics of a membrane are important when considering protein-membrane

interactions, a stronger focus may be needed when considering protein properties (e.g., size, surface charge, and hydrophobicity) and how they may change following coagulation. Ma et al. (2014) demonstrated that increasing AlCl_3 dose increases the average particle size of a synthetic BSA solution. With this in mind, it is anticipated that increasing coagulant dose should reduce fouling, but this was not apparent in the results of the current study where the highest coagulant doses (10 and 40 μM Al) resulted in the most fouling. Thus, it is unlikely that size exclusion is the fouling mechanism being impacted by low coagulant doses.

Alum addition introduces aluminum cations into the water matrix which can alter the overall surface charge of proteins and its electrostatic interactions with the membrane. An inspection of zeta potential indicates that increasing coagulant dose (i.e., cation addition) generally reduces the overall surface charge of the proteins (Figure 4-3, see Section 8.4.3 for raw values). As a result, the reduced magnitude typically increases the electrostatic attraction between proteins which promote aggregation and deposition onto the membrane surface, causing more severe fouling (Choi and Dempsey, 2004). However, the fouling observed at a 2 μM Al dose was less than that with no coagulant which contradicts this trend. Moreover, the change in zeta potential of OVA with increasing alum dose is lower than that of BSA despite similar fouling trends. Thus, changes in the overall surface charge attributed to coagulation do not appear to be responsible for the observed fouling trends.

Figure 4-3: Zeta potential of BSA and OVA as a function of coagulant dose. Vertical bars represent standard deviation of triplicates. Values for BLG were not collected. Lines illustrate overall trends between measurements.

Protein structure is highly sensitive to the polarity of its environment (Vivian and Callis, 2001). Thus, changing the ionic environment via coagulant addition can induce structural changes in proteins which can then affect their surface properties. An assessment of the surface hydrophobicity of BSA in the feed, permeate, and reject (Figure 4-4, see Section 8.4.4 for values) indicate that the proteins in the permeate tend to be more hydrophilic, which is supported by the fact that hydrophilic compounds interact less with the hydrophobic PVDF membrane. Interestingly, the hydrophobicity of permeate proteins reaches a maximum at 2 μM Al, which should imply greater interactions with the membrane and more fouling, however, this was not the case. A potential explanation may be attributed to interactions between the protein and the fouling layer, not the membrane surface. Since each trial was conducted over the course of 48 h, it is likely that the protein-protein interactions associated with the second stage of fouling as described by Huisman et al. (2000) became dominant, dictating irreversible fouling (Wang et al., 2013). Upon adsorption, proteins often undergo conformational changes to reduce the free energy in the system (Marshall et al., 1993). Therefore, the properties of proteins in the fouling layer differ from those in the bulk solution or the properties of a clean membrane surface. Peleato et al. (2017) observed that following the addition of low coagulant doses, the surface fluorescence of fouled membranes exhibited greater tryptophan intensity than those under high doses. The increase in tryptophan intensity is associated with greater exposure of tryptophan residues, which implies increased hydrophilicity. As such, the permeate proteins under the influence of 2 μM Al will interact with the fouling layer the least, resulting in less deposition and irreversible fouling.

Unfortunately, the ANS fluorescence assay did not provide observable results for OVA and BLG. A possible explanation may be that the protein concentrations in this experiment were less than half of those reported in other studies that perform ANS fluorescence assays (Alizadeh-Pasdar and Li-Chan, 2000; Cardamone and Puri, 1992; Delahaije et al., 2013; Haskard and Li-Chan, 1998). Compounded by the fact that quantum yield of ANS after binding with OVA and BLG is lower than that with BSA (Alizadeh-Pasdar and Li-Chan, 2000; Cardamone and Puri, 1992), the fluorescence response of OVA and BLG became insufficient. Laligant et al. (1991) also reported that ANS is not sensitive enough to study BLG hydrophobicity due to its low binding affinity to BLG. Although surface hydrophobicity may offer an explanation as to why low inline coagulant doses are effective in reducing UF fouling,

further investigation into the properties of the fouling layer, the membrane surface, and the bulk protein under low coagulant dose conditions is needed.

Figure 4-4: Surface hydrophobicity of BSA in feed, permeate, and reject determined using ANS fluorescence assay. Vertical bars represent the standard error of the slopes of the fluorescence intensity vs. protein concentration plot ($n = 5$). Lines illustrate overall trends between measurements.

4.4 Conclusions

Ultrafiltration of three model protein solutions were conducted to better understand the fundamental mechanisms associated with membrane fouling. Results indicated that the addition of low amounts of coagulant (0.3 mg/L alum or 2 μM Al^{3+}) significantly reduced hydraulically irreversible and reversible fouling for BSA and OVA solutions when compared to no coagulation. Previous studies focused on natural surface water have suggested that proteins may be the predominant foulant when considering biopolymers and are preferentially impacted by low coagulant dosages (Peleato et al., 2017; Wray and Andrews, 2014). Furthermore, this suggests that BSA and OVA may serve as suitable surrogates for proteins in natural waters. Although contrasting results were observed for BLG, it highlights the complexity of protein structure and how they can respond differently under the same conditions. An optimal low coagulant dose was observed, as further alum addition was shown to exacerbate reversible and irreversible fouling. Irreversible fouling was associated with greater transmission of proteins, implying fouling mitigation was not due to the formation of a more porous fouling layer. Moreover, this tradeoff must be considered when designing a treatment process, as increased organics concentrations in the UF permeate may adversely impact downstream processes.

Through the use of ANS fluorescence assays, it was observed that proteins that permeate through the membrane tend to be hydrophilic. This is likely due to the fact that hydrophilic compounds weakly interact with the hydrophobic PVDF membrane. A low coagulant dose appears to alter bulk protein conformation which in turn likely alters the character of the monolayer adsorbed onto the membrane surface. Thus, interactions between the bulk proteins and the fouling layer were weakened, resulting in less fouling. Nonetheless, further investigation into the properties of proteins and fouling layer under the influence of a low coagulant dose is necessary to better understand the complexities of protein fouling when considering UF membranes.

5 Impact of Phased Coagulation on Membrane Fouling

5.1 Introduction

Ultrafiltration (UF) has become increasingly popular in drinking water treatment for its small footprint relative to conventional media filters and its ability to remove particulates and microorganisms consistently (Gao et al., 2011). However, its efficiency is largely constrained by fouling. The adsorption or deposition of feed water constituents onto the membrane surface reduces permeability and increases energy consumption. Thus, a significant portion of operating costs of UF is devoted to fouling control and removal strategies such as hydraulic backwashing, chemical cleaning, and coagulation.

Natural organic matter (NOM) is a major source of reversible and irreversible fouling for UF membranes. Previous research has identified biopolymers and humic substances (Jermann et al., 2007) as the primary classes of NOM responsible for UF fouling. It is suggested that UF fouling occurs in two stages. Initially, a monolayer of foulants adsorb onto the membrane surface through electrostatic and hydrophobic interactions between the foulants and the membrane surface. Afterwards, additional foulants deposit on top of this adsorbed monolayer throughout permeation (Huisman et al., 2000). Although cake resistivity increases as a result, it has been suggested that the fouling layer can also alter the selectivity of the membrane to remove smaller organic components and reduce irreversible fouling (Wray et al., 2016).

Coagulation is considered to be the most effective pretreatment method for membrane fouling reduction (Huang et al., 2009). The addition of a coagulant into feed water results in the formation of cationic species that agglomerates with the negatively charged NOM into large, settleable particles. However, coagulation pretreatment for UF membranes is often applied without flocculation and/or sedimentation (i.e., inline coagulation) to reduce the footprint of the facility (Choi and Dempsey, 2004). Inline coagulation has been shown to inhibit adsorption of foulants onto the membrane surface and increase cake layer porosity (Barbot et al., 2008). Since the sedimentation step is omitted, it is important to select a coagulant that does not have a strong affinity to the membrane surface, while ensuring the dose is sufficiently high to destabilize NOM.

Much research has been conducted on selecting the appropriate coagulant and dose for UF applications, but little is known about how the coagulant should be applied. Previous work suggests that applying coagulant only during the first half of a permeation cycle limits fouling to a similar extent as applying coagulant throughout the cycle (Lok et al., 2017b; Pronk et al., 2016). Previous studies have reported that pre-coating coagulant precipitates onto the membrane surface prior to permeation establishes a protective layer that inhibits pore blocking (Park et al., 2002; Salinas-Rodriguez et al., 2016). It has been postulated that applying coagulant only during the initial phase of permeation is sufficient in establishing a protective fouling layer and further coagulation is not necessary (Lok et al., 2017b).

This study further investigates the effect of applying inline coagulation at different segments of a permeation cycle (phased coagulation) on membrane fouling rates. The optimization of phased coagulation can potentially reduce coagulant consumption while maintaining the same level of fouling reduction as when coagulant is applied continuously.

5.2 Materials and Methods

5.2.1 Membrane Filtration

Experiments were conducted at the pilot plant (Section 3.3) located in the Barrie Surface Water Treatment Plant (Barrie WTP) using water collected from Lake Simcoe. Each experimental trial consisted of 72 h of continuous permeation and backwashing. Permeation cycles were extended from 30 min (full-scale operation) to 2 h to accentuate fouling (36 cycles total). A summary of operating conditions is detailed in Table 5-1. Before each trial, a membrane integrity test (pressure hold test) was performed to ensure no breaches in the membrane fibres. Subsequently, the membrane module was chemically cleaned by soaking in 500 mg/L NaOCl followed by 200 mg/L citric acid for a total of 6 h to restore permeability. Temperature fluctuated throughout each trial, so its effects on resistance were accounted for in the viscosity term (μ) according to equation [5.1] (Zheng et al., 2010):

$$\mu = \frac{0.497}{(T + 42.5)^{1.5}} \quad [5.1]$$

where T is the feed water temperature ($^{\circ}\text{C}$).

Inline coagulation with 2 mg/L polyaluminum chloride (PACl) (PAX-XL1900, Kemira Water Solutions Canada, Inc.) was applied prior to membrane filtration. PACl was applied during the initial 10, 30, 60, or 120 minutes of each permeation cycle (Figure 5-1). The phased coagulation conditions studied expanded on the those studied by Lok et al. (2017b). A trial without coagulation addition was also be performed to determine the relative impact of coagulation on fouling control.

Table 5-1: Operating parameters for pilot-scale filtration experiments

Operating Parameter	Value
Total Permeation Time	48 h
Permeation Time per Cycle	4 h
Permeate Flux	40 L/m ² ·h
Coagulant Dose	2 mg/L PACl
Backpulse Time	10 min
Backpulse Air Flow	60 L/min
Backpulse Bubble Type	Continuous coarse

Figure 5-1: Phased coagulation conditions of pilot-scale trials

5.2.2 Water Quality and Membrane Fouling

Feed, permeate, and reject (after backwash) samples were collected after 24, 48, and 72 h. Samples were be filtered through a 0.45 µm filter prior to dissolved organic carbon (DOC) analyses as detailed in Section 3.4.5. The ultraviolet absorbance at 254 nm (UV₂₅₄) of the filtered samples was measured using a UV/Vis Spectrophotometer (Agilent, Mississauga, ON). Liquid chromatography-organic carbon detection (LC-OCD) was also performed to characterize NOM and is further explained in Section 3.4.6. The proportion of each NOM fraction deposited onto the membrane following backwash (*A*) was calculated using equation [5.2]:

$$A = \left(1 - \frac{C_{perm}V_{perm} + C_{reject}V_{reject}}{C_{feed}V_{feed}} \right) \times 100\% \quad [5.2]$$

where *C* is the concentration of the respective NOM fraction and *V* is the total volume of the respective water accumulated over the permeation cycle.

Membrane fouling was quantified using the resistance-in-series model as described in Section 2.2. The resistance values were adjusted to account for feed water temperature fluctuations that occur during each trial. Two-tailed t-tests will be used to determine any significant differences in fouling rate (as determined via linear regression model) with respect to continuous coagulation at an 85% confidence level. Cost estimates associated with premature membrane replacement due to chemical cleaning were performed according to the steps outlined by Li et al. (2014).

5.3 Results

5.3.1 Membrane Fouling

The impacts of phased coagulation on membrane fouling rates were assessed by applying PACl during the first 0, 10, 30, 60, or 120 minutes of a 120-minute permeation cycle (see Section 8.4.5 for resistance values). The reduction in coagulation application time does not significantly increase ($p > 0.15$) irreversible and total fouling rates with respect to continuous (120 min) application (Figure 5-2). In other words, any amount of coagulation addition during the permeation cycle effectively mitigates irreversible fouling. A similar result was reported by Pronk et al. (2016) whereby applying ferric chloride during the initial 50% of a filtration cycle resulting in similar fouling performance as continuous coagulation. Despite the lack of statistical significance, irreversible and total fouling rates generally increased with decreasing coagulation time. However, the total and irreversible fouling rates following 60 minutes of phased coagulation were very close to that of continuous coagulation ($< 15\%$). Nonetheless, long-term experiments (i.e. weeks to months) is necessary to better assess the impacts of phased coagulation, particularly with application times below 30 minutes. In contrast, no coagulant addition significantly increases ($p = 0.03$) irreversible fouling rate, which supports previous studies that indicate inline coagulation improves the reversibility of UF fouling. Permeate turbidity generally remained constant (~ 0.01 NTU) regardless of coagulation time.

Biopolymers comprised of the majority of DOC retained by the membrane according to LC-OCD (see Section 8.4.6 for concentrations), which is consistent with previous results (Pronk et al., 2016; Wray et al., 2016). Over 60% of biopolymers were rejected by the membrane regardless of coagulation time while the other fractions were not well retained (Figure 5-3). Moreover, biopolymer removal remained constant over the course of the experiment (60-70%), which suggests that the irreversible fouling layer did not alter the selectivity of the membrane. To further investigate the reversibility of fouling, the fraction of DOC remaining on the membrane after backwash was calculated by a mass balance of DOC in the feed, permeate, and reject water. No trends in DOC or biopolymer deposition between different coagulation times were observed (Figure 5-4).

Figure 5-2: (a) Hydraulically irreversible and (b) total fouling rate of a ZW1000 UF membrane as a function of phased coagulation time. Vertical bars indicate the 85% confidence interval of the estimated slope.

Figure 5-3: Removals of NOM fractions characterised via LC-OCD at various phased coagulation conditions after 24 h of permeation. Negative removals were reported as 0%.

Figure 5-4: DOC and biopolymers deposited (as % of total DOC and biopolymers in the feed solution, respectively) on the membrane after backwash after 24 h of permeation

5.3.2 Cost Analysis

Chemical cleaning methods, such as clean in place (CIP) and chemically enhanced backwash (CEB), are often used to remove hydraulically irreversible foulants. However, they have been shown to adversely affect membrane properties, leading to shortened operational lifespan (Puspitasari et al., 2010). Since coagulation has been shown to mitigate irreversible membrane fouling, it is expected that the costs of UF operation are reduced due less frequent cleaning. The recommended cumulative lifetime chemical exposure of ZW1000 membranes is 500,000 ppm·h (Cote et al., 2012). Values used in cost estimates were taken from Li et al. (2014) and sample calculations can be found in Section 8.3. Assuming CIP frequency is 6 times/year when no coagulation is applied, both continuous coagulation and 60-minute phased coagulation reduces CIP frequency by almost half (3.2 times/year), leading to a 27% reduction in replacement costs (Table 5-2). There are likely further costs savings when considering reduced total fouling rates would result in lower energy consumption from less pumping and lower use of treated water to perform backwash. In addition, utilizing a 60-min phased coagulation regime can halve coagulant costs relative to continuous coagulation which could save approximately \$10,000 annually for a facility similar to the one considered in this study (Lok et al., 2017b).

Table 5-2: Comparison of cleaning frequency, operational lifetime, and replacement costs of different phased coagulation conditions

Coagulation Condition	Irreversible Fouling Rate ($\times 10^9 \text{ m}^{-1} \text{ h}^{-1}$)	CIP Frequency (times/year)	Operational Lifetime (years)	Replacement Costs (\$/year)
No Coagulation	3.43	6.0	11.5	\$124,143
Continuous	2.07	3.2	15.7	\$90,956
60 min	2.36	3.3	15.7	\$91,262
30 min	3.16	6.1	11.4	\$125,638
10 min	2.71	3.8	14.7	\$97,395

5.4 Conclusions

Pilot experiments were conducted to assess the impact of phased coagulation on the fouling of UF membranes. Results indicate that reducing coagulation times does not significantly increase total and irreversible fouling rates with respect to continuous coagulation. On the contrary, not adding coagulant exacerbated fouling which highlights the reported benefits of inline coagulation in fouling mitigation. Through LC-OCD analysis, biopolymers were shown to be the predominant membrane foulant but no trends in its removal or accumulation could be established. Cost analysis estimates that applying coagulation continuously or during the first 60 minutes will result in almost a 50% decrease in chemical cleaning frequency and a 27% reduction in replacement costs with respect to no coagulant addition. More savings are anticipated due to the reduced energy requirements associated with reduced rates of total fouling resistance as well as reduced coagulant costs from phased coagulation.

6 Summary, Conclusions, and Recommendations

6.1 Summary

A bench-scale study was conducted to investigate the impact of coagulation on the fouling of three model protein solutions (BSA, OVA, and BLG) on hollow fibre UF membranes. Four coagulant doses were studied, which include dosages that were reported to mitigate UF fouling as well as those applied at full-scale UF treatment facilities. The irreversible and reversible fouling rates were compared between the various coagulation conditions. Comparisons in the surface charge and fluorescence of the proteins (with and without ANS) were made between different conditions to explain fouling trends.

A pilot-scale study was conducted to determine the impacts of phased coagulation on membrane fouling. Coagulant was applied inline for different durations of the permeation cycle and the fouling rates were compared to the continuous coagulation condition. NOM in feed, permeate, and reject water were characterized via LC-OCD and a cost analysis was conducted to estimate the savings associated with fouling mitigation.

6.2 Conclusions

Adding a low coagulant dose (2 μM Al or 0.3 mg/L alum) resulted in a significant reduction in irreversible and reversible fouling rate when compared to no coagulant addition. On the contrary, dosages above this level (10 and 40 μM) exacerbated fouling. Concentrations of proteins in the feed and the permeate indicate that less hydraulically irreversible fouling is due to the greater transmission of proteins through the membrane, implying the fouling mitigation was not primarily a function of a more porous fouling layer. Trends in particle size and zeta potential as a function of coagulant dose did not appear to explain fouling trends. However, an analysis of surface hydrophobicity suggests that low coagulant dosages induce conformational changes in bulk proteins as well as the adsorbed monolayer on the membrane surface to become less interactive with one another, leading to reduced fouling.

Phased coagulation was shown to have no significant impact on membrane fouling, whereas no coagulant addition exacerbated it. Biopolymers were shown to be the predominant membrane foulant, but no trends in their removal or accumulation on the membrane as a function of coagulation time could be observed. As a result of reduced irreversible fouling, the

frequency of chemical cleaning for membranes under continuous or phased coagulation (first half of cycle) is expected to be approximately half of that for membranes without coagulant addition. Consequently, the reduced chemical exposure is estimated to reduce annual replacement costs by 27%.

6.3 Recommendations for Future Research

The results of this work call for further investigation in the following areas:

1. Membranes with larger areas (i.e. flat sheet membranes or a longer hollow fibre) should be used to minimize the variance caused by intrinsic differences between membranes. This should lead to more reproducible and comparable results. The greater area would also allow for greater magnitude of protein adsorption, which will make it easier to observe an accumulation of proteins in the system via mass balance.
2. The experiment should be repeated with membranes with different properties (e.g., hydrophobicity, surface charge, functional groups). If hydrophobicity is indeed the driving force of fouling trends, then its effects should be more pronounced if a more hydrophobic membrane was used. Conversely, opposite fouling trends could be observed when using a hydrophilic membrane.
3. The reasons why the fluorescence assay did not produce results with OVA and BLG should be investigated, as it is a relatively simple and non-destructive tool to evaluate protein hydrophobicity. Testing the procedure with higher concentrations of proteins, different buffer chemistries, or a different fluorescent probe (e.g. cis-parinaric acid, PRODAN) may result in improved reproducibility. However, it must be noted that optimal conditions for fluorescence assays may not result in appreciable membrane fouling.
4. Further work should be completed to characterize the protein fouling layer under different coagulation conditions, either through qualitative (e.g. scanning electron microscopy) or quantitative (e.g., atomic force microscopy) means. There are also methods to characterize bulk proteins as well, such as circular dichroism, or nuclear magnetic resonance spectroscopy.

5. The duration of pilot-scale experiments investigating phased coagulation should be much longer than 3 days (and preferably at full-scale condition of 30 min permeation cycles) to clearly assess the long-term feasibility of this strategy.

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8 Appendices

8.1 Procedure and Sample Calculation for Pure Water Permeability of a Membrane

This section outlines the procedure and sample calculation followed to determine the pure water permeability of the ZW500 hollow fibre membranes used in bench-scale studies.

1. The TMP of each fibre permeating distilled water over the course of 2 h at three different permeate flow rates was collected

Table 8-1: Measured TMP as a function of permeate flow/flux

Membrane	Area (m ²)	Flow (mL/min)	Flux (LMH)	TMP (kPa)
1	1.56×10^{-3}	0.53	20.5	3.5
		0.79	30.4	5.5
		1.06	40.7	7.3
2	1.55×10^{-3}	0.53	20.4	3.7
		0.79	30.7	5.6
		1.05	40.7	7.4
3	1.56×10^{-3}	0.54	20.8	3.7
		0.79	30.4	5.6
		1.06	41.0	7.5
4	1.53×10^{-3}	0.52	20.6	3.5
		0.78	30.7	5.4
		1.04	40.7	7.3

An example calculation of permeate flux (J) of Membrane 1 at a TMP of 3.5 kPa was is as follows:

$$\begin{aligned}
 J &= \frac{0.53 \text{ mL}}{\text{min}} \times \frac{60 \text{ min}}{\text{h}} \times \frac{L}{1000 \text{ mL}} \\
 &\quad \frac{1}{1.56 \times 10^{-3} \text{ m}^2} \\
 &= 20.5 \frac{L}{\text{m}^2 \cdot \text{h}}
 \end{aligned}$$

2. Plot permeate flux as a function of TMP as shown in Figure 8-1 to determine the slope of the line, which is the PWP

Figure 8-1: Permeate flux as a function of TMP for four ZW500 membrane fibres

3. Compare the PWP of each fibre to the average PWP and verify if it is within 15%. The calculation for membrane 2 is as follows:

$$\begin{aligned}
 \% PWP \text{ Diff} &= \left| \frac{PWP_i - PWP_{avg}}{PWP_{avg}} \right| \times 100\% \\
 &= \left| \frac{5.372 - 5.33}{5.33} \right| \times 100\% \\
 &= 1\%
 \end{aligned}$$

8.2 Procedure and Sample Calculation for Surface Hydrophobicity of Proteins

This section outlines the procedure and sample calculation followed to determine the surface hydrophobicity of model proteins using ANS as a fluorescent probe. Values used to calculate BSA surface hydrophobicity can be found in Section 8.4.4.

1. Dissolve 2.5310 g of ANS ammonium salt in 1 L (8 mM) of Milli-Q[®] water
2. Make a series of dilutions of the sample protein solutions to a total of 5 mL in test tubes with caps (Table 8-2)

Table 8-2: Example dilution scheme for ANS fluorescence assay

Final Protein Concentration (mg/L)	Vol. of Sample (mL)	Vol. of Buffer (mL)
20	5	0
16	4	1
12	3	2
8	2	3
4	1	4
0	0	5

3. Add 20 μ L of 8 mM ANS solution to each vial
4. Invert test tube gently once to mix solutions
5. Let stand for 10 min
6. Set fluorometer to measure at ex/em 350/490 nm at a sufficiently high photomultiplier tube voltage (~750 V)
 - Alternatively, the fluorescence spectrum from 400-600 nm emission at 350 nm excitation can be collected
7. Measure or zero instrument using the 0 mg/L sample
8. Measure the fluorescence of each sample three times, taking the average
9. Calculate the slope of the fluorescence intensity vs. protein concentration (Figure 8-2)

Figure 8-2: Example fluorescence intensity of BSA in the permeate as a function of protein concentration at different coagulant dosages

8.3 Cost Savings Estimation Procedure

The following assumptions were made to determine the costs savings associated with membrane replacement costs due to the reduced frequency of chemical cleaning (clean in place and chemically enhanced backwash):

1. Chemically enhanced backwash was performed daily for 0.5 h each with 100 ppm sodium hypochlorite
2. Clean in place was performed 6 times/year when no coagulant is applied with 500 ppm sodium hypochlorite and 200 ppm citric acid, for a total of 6 h each
3. Membrane will be replaced when chemical exposure has reached 500,000 ppm·h (total cost is \$1,428,571)

-
1. CIP frequency is proportional to the irreversible fouling rate. For continuous coagulation:

$$\begin{aligned}\frac{Fouling\ Rate_{continuous}}{CIP\ Frequency_{continuous}} &= \frac{Fouling\ Rate_{none}}{CIP\ Frequency_{none}} \\ CIP\ Frequency_{continuous} &= \frac{(2.07 \times 10^9 m^{-1}h^{-1})(6\ times/year)}{3.43 \times 10^9 m^{-1}h^{-1}} \\ &= 3.2\ times/year\end{aligned}$$

2. Calculate the annual chemical exposure for CIP and CEB for continuous coagulation:

$$\begin{aligned}CIP\ Exposure &= Frequency \times Concentration \times Duration \\ &= (3.2\ times/year)(700\ ppm)(6\ h) \\ &= 13,440\ ppm \cdot h\end{aligned}$$

$$\begin{aligned}CEB\ Exposure &= (365\ times/year)(100\ ppm)(0.5\ h) \\ &= 18,250\ ppm \cdot h\end{aligned}$$

3. Calculate operational lifetime:

$$Lifetime = \frac{500,000\ ppm \cdot h}{(13,860 + 18,250)\ ppm \cdot h/year} = 15.7\ years$$

4. Calculate replacement costs:

$$Replacement\ Cost = \frac{\$1,248,571}{15.7\ years} = \$90,956/year$$

8.4 Raw Data

8.4.1 Protein Solution Fouling Resistance

Figure 8-3: (a) Total, (b) irreversible, and (c) reversible resistance during 1st trial of ultrafiltration of 20 mg/L BSA with respect to permeation time for different coagulant dosages (μM Al)

Figure 8-4: (a) Total, (b) irreversible, and (c) reversible resistance during 2nd trial of ultrafiltration of 20 mg/L BSA with respect to permeation time for different coagulant dosages (μM Al)

Figure 8-5: (a) Total, (b) irreversible, and (c) reversible resistance during ultrafiltration of 10 mg/L BLG with respect to permeation time for different coagulant dosages ($\mu\text{M Al}$)

Figure 8-6: (a) Total, (b) irreversible, and (c) reversible resistance during 1st trial of ultrafiltration of 20 mg/L OVA with respect to permeation time for different coagulant dosages ($\mu\text{M Al}$)

Figure 8-7: (a) Total, (b) irreversible, and (c) reversible resistance during 2nd trial of ultrafiltration of 20 mg/L OVA with respect to permeation time for different coagulant dosages ($\mu\text{M Al}$)

8.4.2 Protein Concentrations

Table 8-3: Concentrations (mg/L) of BSA in feed, permeate, and reject water during 1st trial

Time (h)	0	24			48		
Water Dose	Feed	Feed	Permeate	Reject	Feed	Permeate	Reject
0 μM	22.2	23.3	12.6	25.0	24.2	12.4	27.5
2 μM	21.9	23.0	19.3	21.7	21.6	19.1	22.9
10 μM	22.9	23.0	18.6	23.4	22.2	18.2	22.8
40 μM	22.8	22.9	16.2	23.8	22.8	10.3	25.5

Table 8-4: Concentrations (mg/L) of BSA in feed, permeate, and reject water during 2nd trial

Time (h)	0	24			48		
Water Dose	Feed	Feed	Permeate	Reject	Feed	Permeate	Reject
0 μM	27.3	28.2	26.6	27.8	27.5	22.9	25.6
2 μM	25.0	27.5	24.5	28.2	28.5	26.1	30.4
10 μM	25.1	26.5	23.1	26.2	26.1	0.0	27.5
40 μM	24.8	26.8	14.6	28.0	28.0	4.6	Not Collected

Table 8-5: Concentrations (mg/L) of BLG in feed, permeate, and reject water

Time (h)	0	24			48		
Water Dose	Feed	Feed	Permeate	Reject	Feed	Permeate	Reject
0 μM	12.1	11.6	10.6	12.0	11.6	9.9	11.2
2 μM	11.6	11.6	10.2	11.2	9.9	7.5	10.1
10 μM	10.7	11.1	9.0	11.1	11.1	8.4	10.7
40 μM	11.2	11.2	7.1	10.0	10.9	7.3	9.5

Table 8-6: Concentrations (mg/L) of OVA in feed, permeate, and reject water during 1st trial

Time (h)	0	24			48		
Water Dose	Feed	Feed	Permeate	Reject	Feed	Permeate	Reject
0 μM	21.8	22.1	19.7	21.8	20.7	17.9	20.2
2 μM	21.4	22.3	20.8	22.9	20.9	20.2	22.9
10 μM	21.7	22.0	19.9	21.3	21.3	19.2	21.0
40 μM	21.5	20.4	16.1	20.4	20.8	16.8	21.0

Table 8-7: Concentrations (mg/L) of OVA in feed, permeate, and reject water during 2nd trial

Time (h)	0	24			48		
Water Dose	Feed	Feed	Permeate	Reject	Feed	Permeate	Reject
0 μM	25.4	25.7	22.3	25.8	26.0	23.3	25.9
2 μM	25.6	24.8	23.5	24.9	24.7	23.9	24.8
10 μM	26.0	25.8	23.1	24.2	24.2	21.5	24.4
40 μM	25.8	24.1	19.6	23.8	23.5	20.2	24.5

8.4.3 Zeta Potential

Table 8-8: Zeta potential (mV) of BSA for different coagulant dosages

Replicate Dose	1	2	3
0 μM	-65.4	-55.4	-59.7
2 μM	-50.0	-50.3	-52.9
10 μM	-42.0	-44.5	-45.6
40 μM	-12.5	-12.7	-12.6

Table 8-9: Zeta potential (mV) of OVA for different coagulant dosages

Replicate Dose	1	2	3
0 μM	-23.3	-22.0	-22.1
2 μM	-21.8	-19.9	-20.7
10 μM	-18.3	-18.6	-21.3
40 μM	-24.9	-24.2	-20.3

8.4.4 ANS Fluorescence Assay

Table 8-10: Fluorescent intensity at ex/em 370/490 nm (average of triplicate measurements) of BSA solutions titrated with ANS

	Sample Time (h)	0	24			48		
	Conc. (mg/L)	Feed	Feed	Perm	Reject	Feed	Perm	Reject
0 μM	2	0.57	2.67	0.72	3.23	2.35	0.91	3.00
	4	2.34	4.27	1.23	4.55	4.27	1.33	4.44
	6	3.64	5.97	1.71	6.48	5.51	1.75	6.14
	8	5.62	6.78	2.71	7.10	6.72	2.19	8.07
	10	5.52	7.22	3.11	9.19	6.97	3.05	9.43
2 μM	2	0.78	3.21	1.51	3.03	2.53	1.65	2.38
	4	2.74	4.81	2.83	4.17	3.35	3.06	3.41
	6	4.06	6.18	3.96	6.48	4.14	3.91	5.07
	8	6.53	7.78	4.89	6.82	6.29	4.87	6.27
	10	8.06	8.93	5.62	8.44	6.61	6.26	7.16
10 μM	2	0.71	2.53	0.97	3.05	2.69	1.72	3.22
	4	2.81	4.16	2.33	5.09	5.05	3.05	4.53
	6	4.49	6.00	3.25	6.86	6.36	4.21	6.71
	8	7.04	7.31	4.33	7.90	7.12	5.37	8.35
	10	8.32	8.34	5.81	9.37	8.42	5.88	10.35
40 μM	2	0.92	2.68	0.72	2.34	2.79	0.93	2.53
	4	2.50	3.47	2.23	4.39	4.43	1.39	4.17
	6	3.35	5.88	2.43	5.65	6.21	1.74	5.54
	8	6.06	6.83	4.21	6.54	6.85	2.24	7.34
	10	7.47	7.02	5.16	8.72	7.96	3.06	8.43

*Blank intensity already subtracted from values

8.4.5 Pilot-Scale Fouling Resistance

Figure 8-8: Total fouling resistance for (a) continuous, (b) 60 min, (c) 30 min, (d) 10 min, and (e) no coagulant addition times during each permeation cycle

Figure 8-9: Irreversible fouling resistance for (a) continuous, (b) 60 min, (c) 30 min, (d) 10 min, and (e) no coagulant addition times during each permeation cycle

8.4.6 LC-OCD Results

Table 8-11: Concentration ($\mu\text{g/L}$) of NOM fractions (via LC-OCD) in feed, permeate, and reject water for different phased coagulation conditions

	Sample-Time	DOC	Biopolymers	Humic Substances	Building Blocks	LMW Neutrals	LMW Acids
Continuous	Feed 24	4150	554	2244	783	323	104
	Perm 24	3516	174	2104	684	337	146
	Reject 24	18689	14434	2768	854	827	117
	Feed 48	4038	604	2259	736	287	113
	Perm 48	3560	172	2261	752	308	95
	Reject 48	18012	14096	2685	798	854	202
	Feed 72	3999	520	2358	735	292	106
	Perm 72	3656	186	2184	785	280	99
	Reject 72	15956	11613	2503	886	986	225
60 min	Feed 24	4185	578	2203	764	320	99
	Perm 24	3767	186	2215	738	284	94
	Reject 24	10196	6778	2386	712	934	118
	Feed 48	3967	529	2262	733	279	97
	Perm 48	3712	187	2187	765	255	94
	Reject 48	9124	5909	2412	574	732	87
	Feed 72	4099	585	2231	730	273	95
	Perm 72	3682	174	2198	721	255	94
	Reject 72	9724	6818	2352	703	571	106
30 min	Feed 24	3965	599	2134	880	409	91
	Perm 24	3790	213	2078	870	276	105
	Reject 24	10785	8362	2412	620	524	109
	Feed 48	4116	574	2227	754	296	95
	Perm 48	3743	244	2149	815	250	97
	Reject 48	12721	10043	2362	722	441	113
	Feed 72	4235	577	2241	735	290	97
	Perm 72	3773	182	2175	790	259	99
	Reject 72	Analysis Omitted					
10 min	Feed 24	3991	544	2189	789	307	92
	Perm 24	3700	187	2166	744	297	90
	Reject 24	12552	8234	2760	767	834	106
	Feed 48	3968	486	2175	790	346	96
	Perm 48	3640	185	2173	733	241	90
	Reject 48	13502	12024	2646	969	669	94
	Feed 72	4048	559	2244	778	308	87
	Perm 72	3710	186	2257	770	260	87
	Reject 72	13737	11177	2720	908	500	94

	Sample-Time	DOC	Biopolymers	Humic Substances	Building Blocks	LMW Neutrals	LMW Acids
0 min	Feed 24	4206	562	2177	810	338	92
	Perm 24	3785	157	2160	797	297	97
	Reject 24	16454	13565	2703	800	720	95
	Feed 48	4051	493	2198	740	311	94
	Perm 48	3674	187	2111	793	280	92
	Reject 48	16332	11894	2543	828	874	105
	Feed 72	4113	528	2235	742	293	94
	Perm 72	3693	173	2248	723	233	92
	Reject 72	17707	12850	2672	940	735	105