IN-LINE COAGULATION TO REDUCE HIGH-PRESSURE MEMBRANE FOULING IN AN INTEGRATED MEMBRANE SYSTEM

by

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ABSTRACT

Membrane fouling is a chronic problem for many nanofiltration (NF) membrane plants. Foulant material can range from colloidal, particulate, inorganic minerals and natural organic matter (NOM) (Schäfer et al., 2006). This research project worked with a small community integrated membrane facility (low-pressure membrane followed by high-pressure) in Nova Scotia with membrane fouling concerns associated with dissolved NOM as the primary foulant. Membrane autopsies conducted in our laboratory have demonstrated that NOM deposits on the NF membrane decreased pore space on the membrane (Lamsal et al., 2012). The membrane fouling resulted in a requirement for increased pressure to produce a constant permeate flow.

By adding in-line coagulation prior to low-pressure filtration in an integrated membrane system, the goal was to remove more organic material by MF thereby improving the quality of the feed-water entering the NF membranes. Previous work has shown that for some IMS installations there is a need to reduce the amount of dissolved organic matter prior to NF (Cho et al., 2000; Lamsal et al., 2012; Nilson and DiGiano, 1996; Schäfer et al., 2001). An improved membrane feed-water quality reduces fouling on the membrane and membrane operating cost, and increases productivity and lifespan of the membrane (Choi, 2008). A negative aspect to adding in-line coagulation is it adds another step to the treatment process and sludge removal is required.

This study examined the use of in-line coagulation using coagulants aluminum sulphate, ferric chloride and polyaluminum chloride to improve membrane feed-water quality. The addition of in-line coagulation prior to microfiltration will remove NOM with the MF producing improved feed water quality for NF. After determining the optimal dose of each coagulant, 20 L of post-coagulation MF permeate was batched and run through the bench-scale NF membrane for 200 hours. The water quality of the feed tank, concentrate and permeate were monitored constantly as well as the operational properties of pressure and flow. To simulate a full-scale plant the operating conditions of Collins Park water treatment plant on Fletchers Lake were used in the bench-scale set-up. After the 200h NF run time the membranes were analyzed to assess the fouling on the membrane and the performance of each coagulant. Coagulation was found to reduce NF pressure fouling by reduction of NOM in the NF feed-water. Ferric chloride was found to perform best of the three coagulants at a low dose of 0.5mg/L of Fe at a pH of 5.0.

LIST OF ABBREVIATIONS AND SYMBOLS USED

%/min	Percent per minute
Alum	Aluminum Sulfate
Alum/MF	In-line coagulation of aluminum sulfate prior to microfiltration
AWWA	American Water Works Association
CA	Cellulose acetate
Ca^{2+}	Calcium ion
CIP	Clean-in-place
cm	Centimeter
CO_3^{2-}	Carbonate
Da	Daltons
DAF	Dissolved air flotation
DBP	Disinfection by-product
DOC	dissolved organic carbon
EDS	Energy-dispersive X-ray spectroscopy
$FeCl_3$	Ferric chloride
$FeCl_3$/MF	In-line coagulation of ferric chloride prior to microfiltration
GFD	Gallons per square foot of membrane per day
H_2SiO_3	Silicic acid
HP-SEC	High performance-size exclusion chromatography
Hrs	hours
ICP-MS	Inductively coupled plasma-mass spectrometry
IMS	Integrated membrane system

kDa	kilodalton
kV	Kilovolt
L	Liter
m^3/day	Cubed-meters per day
MF	Microfiltration
µA	Microampere
µm	Micrometer
MFI	Modified fouling index
Mg^{2+}	Magnesium ion
mL	milliliter
mL/min	mL/min
mV	Microvolts
MW	Molecular weight
MWCO	Molecular weight cut-off
NF	Nanofiltration
nm	Nanometer
NOM	Natural organic matter
NTU	Nephelometric turbidity units
PA	Poly amide
PACl	polyaluminum chloride
PACl/MF	In-line coagulation of polyaluminum chloride prior to microfiltration
psi	pressure per square inch
Pt.Co	Platinum-Cobalt scale

RO	Reverse osmosis
rpm	Revolutions per minute
SDI	Silt density index
SEM	Scanning electron microscopy
SO_4^{2-}	Sulfate
SUVA	Specific ultraviolet absorbance
TMP	Trans membrane pressure
TOC	Total Organic Carbon
UF	Ultrafiltration
UV_{254}	Ultraviolet absorbance at 254nm
WTP	Water treatment plant

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CHAPTER 1 INTRODUCTION

1.1 Background

The removal capacity of high-pressure membranes in integrated membrane systems (IMS) make them increasingly attractive for drinking water treatment as they are able to meet the increasingly stringent Canadian Drinking Water Guidelines for disinfection by-products (DBP) (Hyung Kim & Yu, 2005; Lamsal, 2012). Decreasing source water quality and invasion of saline waters into fresh water aquifers requires the implementation of membrane treatment to produce high-quality potable water (Lee et al, 2005; Hyung Kim & Yu, 2005). Furthermore, membranes are capable of removing a wide range of contaminants while maintaining a small footprint (Mosqueda-Jimenez et al, 2006).

Several economic challenges arise with membrane operation due to membrane fouling. Membrane fouling is characterized by increased trans-membrane pressure (TMP) and decreased membrane performance (Contreras et al, 2009). Membrane fouling results in increased operational costs, decreased membrane life and permeate quality (Choi et al, 2005; Zhang et al, 2005). Membrane fouling and its effects can be mitigated by improving the quality of the membrane feed-water via pre-treatment or operational parameters (Volk et al, 2000; Contreras et al, 2009). Natural organic matter (NOM) is a dominant membrane foulant and removal of NOM with pre-treatment results in more efficient and sustainable membrane operation (Combe et al, 1999; Mosqueda-Jimenez et al, 2006; Yu et al, 2011).

In surface waters, NOM concentrations are typically high and increase seasonally in the spring and autumn as a result of heavy run-off in the and decomposition of organic matter (Hyung Kim & Yu, 2005; Lee et al, 2005). These seasonal contributions result in high concentrations of terrestrial aromatics and other fractions of NOM, which are comprised of several fractions that vary in molecular weight (MW), hydrophilicity and fluorescence (Lee et al, 2004; Kim et al, 2006; Her et al, 2007; Montreuil, 2011).

Reduction of NOM through feed-water pre-treatment is required for successful operation of high-pressure membranes (Combe et al, 1999; Lee et al, 2004). Types of pre-treatment that are effective in mitigation of NOM fouling include filtration, coagulation and advanced oxidation (Guigui et al, 2002; Geraldes et al; 2008; Lamsal, 2012). Coagulation has been favored for NOM removal due to cost effectiveness and high removal capacity of humic matter (Judd & Hillis, 2000; Guigui et al, 2002; Geraldes et al, 2008).

1.2 Project Rationale

This research evaluated an integrated membrane system for drinking water treatment with the addition of in-line coagulation prior to low-pressure filtration to mitigate high-pressure membranes fouling. Mitigation of nanofiltration (NF) membrane fouling would decrease operation costs and increased efficiency in water treatment facilities.

1.3 Project Objective

1) The main objective of this research was to determine if low-dose in-line coagulation prior to low-pressure membrane filtration was an effective pre-treatment for NF.
2) The secondary objective was to analyze the effectiveness of in-line coagulation with three coagulants (ferric chloride, aluminum sulphate and polyaluminum chloride) followed by microfiltration (MF) as a pre-treatment.

To determine the effectiveness of coagulation/MF pre-treatment for high-pressure membranes, three stages of experiments were conducted:

a) Determination of Optimal Coagulant Dose and pH

Jar tests were performed, followed by microfiltration to determine the three optimal doses and pH of each of the three coagulants using dissolved organic carbon (DOC) as a metric. The three optimal dosages where then analyzed by silt density index (SDI) method to determine the optimal dose for NF membrane feed-water pre-treatment.

b) Bench-Scale Operation of NF Membrane

The optimal dose for each of the three coagulants followed by MF was batched in the feed-water tank of the bench-scale NF membrane set-up. NF permeate was collected at a constant flux for 200hrs with variable feed pressure (TMP). The natural organic matter concentration and classification of the NF permeate and feed-water qualities were monitored as well as the physical flow characteristics including temperature.

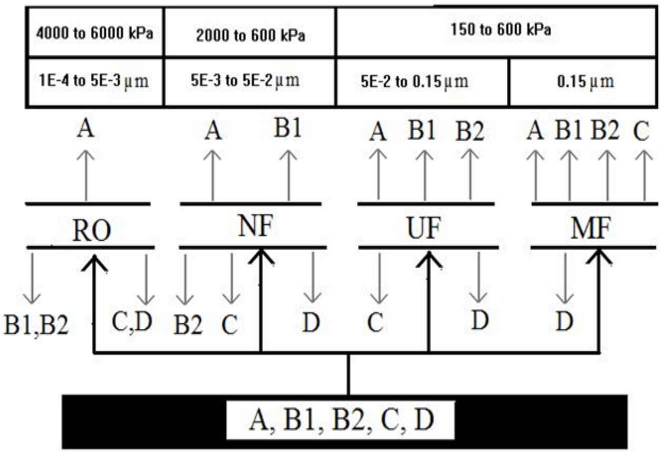
c) Membrane Analysis

Membrane analysis was performed on both the virgin and fouled membranes. The type of membrane analysis that was implemented was scanning electron microscopy (SEM). A mass balance of NOM within the bench-scale system was conducted to identify retained high-pressure membrane foulants.

CHAPTER 2 LITERATURE REVIEW

2.1 Overview of Membrane Process

Membranes are a semi-permeable layer that provides an absolute barrier and separates pure water permeates from solution through solids retention. The permeability of a membrane depends on the nominal pore size or in the case of high-pressure membranes, which do not have defined pores, the molecular weight cut-off (MWCO) which is the smallest size of the molecules retained. The classifications of membranes from highest to lowest permeability are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). As the permeability of the membrane decreases, removal capability and operational pressure required for the membrane type increases. Figure 2.1 illustrates membrane classification according to removal capabilities and operation pressure.



A	Water
B1	Single charged ions (Na^+, Cl^-)
B2	Poly charged ions (Ca^{2+}, SO_4^{2-})
C	Macromolecules, oil and grease, suspended solids, proteins, colloids, bacteria, viruses
D	Coarse particles, microbial cells, large colloids

Figure 2.1 Membrane separation processes and corresponding particle sizes from El-Dessouky et al (2002)

Low-pressure membranes such as MF and UF are able to remove suspended solids and most bacteria and viruses (El-Dessouky et al, 2002). Low-pressure membranes generally do not require pre-treatment and constant high-quality feed-water that meets American Water Works Association (AWWA) high-pressure membrane feed-water requirements regardless of the source water quality (AWWA, 1999; Zhang et al, 2005). NF and RO are both classified as high-pressure membranes and generally require feed-water pre-treatment due to their high separation capabilities. NF retains divalent ions and is therefore applicable for water softening. RO membranes are capable of removing monovalent ions and are commonly used for brackish and salt water desalination. For IMS, such as Collins Park Water Treatment Facility in Wellington, NS, a low-pressure membrane is applied to influent as pre-treatment for high-pressure membranes such as NF and RO.

2.2 Membrane Fouling

Membrane fouling is characterized by an increased required pressure to produce an equivalent permeate flux. Schäfer et al (2006) state that a pressure increase greater than 10 to 15% is indicative of membrane fouling. High-pressure membranes are susceptible to fouling due to their stringent MWCO. Membrane fouling is caused by blockage of membrane pores or suspended or dissolved matter interactions with the membrane surface. Mitigation of membrane fouling results in increased efficiency, membrane life, cost benefits and effluent quality. Fouling is a major deterrent for use of membrane processes and mitigation of fouling is necessary for successful high-pressure membrane operation (Choi et al, 2005; Zhang et al, 2005).

There are many different types of high-pressure membrane fouling including scaling, biofouling, condensing, pore blocking, and cake or gel formation (Schäfer et al, 2006). Fouling may be mitigated by pre-treatment, membrane type, cleaning procedure and physical characteristics of the feed water such as pressure, temperature and flow rate (Schäfer et al, 2006; Yu et al, 2010). AWWA (1999) recommends guidelines for SDI, turbidity and zeta potential of high-pressure membrane feed-water to maintain successful operation of high-pressure membranes.

The SDI is commonly used as an index for design parameters at bench- and pilot-scale to predict the amount of suspended particulate fouling on a high-pressure membrane. At full-scale plants an in-line turbiditometer or particle counter is typically used to measure particulate matter. These methods are not as sensitive as SDI (Schäfer et al, 2006). The modified fouling index (MFI) is more sensitive than SDI as it takes into account both dissolved and suspended particulates and can draw a linear correlation between concentration and membrane fouling (Siobhan et al, 2002).

Zeta potential of the feed-water is an indicator of membrane fouling caused by the charge relationship between the membrane surface and foulants. To minimize membrane fouling, repulsion of the membrane surface and the foulant is important and therefore strong similiar charges are ideal. Zeta potential is indicative of the particulate surface charge, a negative surface charge will repel from negatively charged membrane surfaces which will reduce fouling. Hydrophobic interactions between the foulants and membrane are able to overcome electrostatic repulsion (Schäfer et al, 2006).

There are two major categories of membrane fouling: reversible and irreversible. Reversible fouling is a reduction in flux due to resistance caused by concentration polarization near the membrane surface (Droste, 1997). As shown in Figure 2.2a, the concentration of a solution is increased near the membrane surface due to the separation of solvents from permeate across the membrane. However, when the trans-membrane pressure (TMP) is reduced to zero the concentration polarization disperses as shown in Figure 2.2b. After an extended period of time build-up of concentration polarization may lead to adsorption of the foulants onto the membrane creating irreversible fouling (Schäfer et al, 2006).

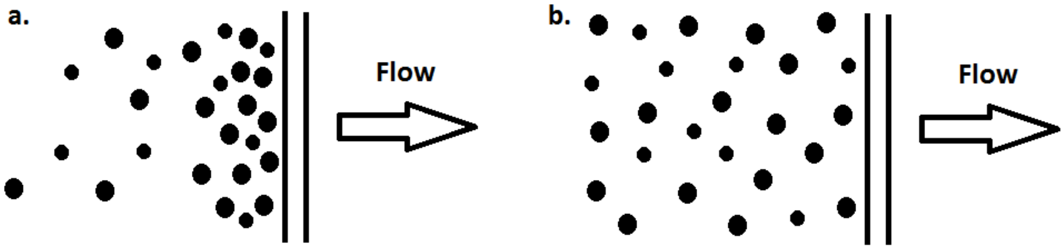


Figure 2.2 a.) Concentration polarization at high-pressure membrane surface b.) Dispersion of concentration polarization after zero-flux mode

Mitigation of concentration polarization during membrane operation can be attained with turbulence near the membrane surface through addition of air sparging or a feed-spacer; this prevents the accumulation of particulates on or near the membrane surface (Wray et al, 2013). Concentration polarization may also be mitigated by increasing cross-flow velocity, permeate pulsing or electric field (Schäfer et al, 2006). Concentration polarization is more common with larger MW organics such as protein than it is for humic acid and inorganic ions. This effect reduces the separation capabilities of the membrane and may also contribute to a decrease in permeate quality. (Schäfer et al, 2006)

Fouling mechanisms that may lead to irreversible fouling include adsorption, pore plugging or solute gel formation, leading to decreased membrane operation and efficiency (Kim et al, 2006; Yu et al, 2011). Unlike reversible fouling, irreversible fouling continues to impact the membrane operation even after the pressure is reduced, therefore mitigation of irreversible fouling requires a chemical clean and zero-flux operation (Schäfer et al, 2006). Several factors contribute to membrane fouling including operational parameters and source water quality.

2.2.1 Operational Parameters

Operational parameters such as water temperature, flux, cross-flow velocity, membrane selection and cleaning have an influence on the pressure required for membrane operation (Yu et al, 2011; Schäfer et al, 2006). Control of operational parameters is an effective way to minimize membrane fouling without increased pre-treatment.

As water temperature decreases, a greater TMP is required to produce an equivalent permeate flux. This is due to the increase in water viscosity. Flux is the amount of permeate that is produced per unit area of membrane surface and expressed in units of L/hr•m^2. For optimal membrane performance, membranes should be operated at sub-critical flux; the point where an increase in applied pressure no longer results in an equivalent incremental increase in permeate flux. Zhang et al (2005) found that the permeate flux was an important parameter to control fouling. Under like conditions the membrane was irreversibly fouled when operated above critical flux and fouling effects were reversible with backwash when operated at a sub-critical flux. An increase in flux below the critical flux did not result in a significant increase of NOM fouling (Mosqueda-Jiminez et al, 2006).

Irreversible fouling of membranes can be reduced through chemical cleaning. The type of clean and frequency are important factors. The cleaning frequency is dependent on the rate of fouling, trans-membrane pressure increase and effectiveness of cleaning in the specific membrane system. Clean in-place (CIP) is the most common cleaning procedure for high-pressure membranes and generally consists of either a caustic or acid bath depending on the nature of the foulants. Bremer et al (2005) found that CIP with variations between caustic and acidic was most effective in reduction of TMP and frequency and variation of CIP should be determined at bench-scale prior to full-scale application. Air sparge may be applied during operation and used as an intermittent or continuous turbulence clean to mitigate membrane fouling. Air sparge was found to increase permeate flux and effectively prevent particulate fouling (Cassabud et al, 2001).

The cross-flow velocity refers to the amount of feed-water flow per area in a cross-flow unit that does not pass through the membrane. The cross-flow velocity, or concentrate flow, is effective in reducing the concentration polarization that occurs near the membrane surface. Cabassud et al (2001) found cross-flow velocities increased permeate flux, removal effectiveness and prevented membrane fouling due to concentration polarization. Increased cross-flow velocities were proven more effective for removal of irreversible than reversible foulants (Choi et al, 2005). Feed spacers may be added to high-pressure membrane systems to increase the cross-flow area, which results in increased velocity and turbulence of the cross-flow.

Vrouwenvelder et al (2009) found that biofouling occurred both on the feed spacer and membrane. Biofouling occurred regardless of membrane type and permeate production and could be mitigated by adaptation of the feed spacer geometry and hydrodynamics (Vrouwenvelder et al, 2009; Schwinge et al, 2004).

Membrane fouling is affected by membrane material and subsequent surface properties, Membranes are typically constructed of cellulose acetate (CA) or polyamide (PA) materials. Schäfer et al (2006) determined the surface charge and hydrophilicity of the membrane surface to be the most important characteristics of a membrane to mitigate fouling. Kim et al (2006) found that fouling was due to both hydrophilic and hydrophobic matter and that the degree of fouling was dependent on the hydrophobicity of the membrane. Hydrophobic membranes were found to have the highest degree of fouling due to increased adsorption of organics in the MW ranges of 300 to 2000 and 20,000 to 40,000 Da onto the membrane. Vrijenhoek et al (2001) found that surface roughness was the dominant factor for degree of colloidal fouling in flat-sheet NF and RO membrane fouling. Xu et al (2006) found that membrane properties were significantly altered after initial fouling which caused increased adsorption capacity and MWCO due to membrane swelling. Surface treatment of membranes to mitigate humic adsorption including annealing, hydrolysis and oxidation, was investigated by Combe et al (1997) who determined that anionic polymer membrane coatings were most effective in reduction of humic adsorption. Membrane selection is critical for optimal high-pressure membrane performance. Membrane characteristics including composition, surface charge, permeability and surface treatments are dependent on the source water quality and operational parameters.

2.2.2 Source Water Quality

Source water quality conditions are important for successful operation of high-pressure membranes. The sensitive nature of high-pressure membranes make them susceptible to fouling due to retention of particulate matter or interaction with scalants, organics or other foulants within the feed-water. The feed-water characteristics that are strong indicators of fouling potential include turbidity, bacteria, water hardness and organic content (Choi et al, 2008).

The size of the foulants within the feed-water has an effect on the location and severity of fouling. The foulants that are larger than the membrane pore size such as colloids, organics, metal oxides and some biofoulants will create fouling on the membrane surface. Contaminants that are smaller than the pore size will distribute within or pass through the membrane. (Schäfer et al, 2006)

The type of fouling that occurs during membrane operation is dependent on the characteristics of the feed water. For hard water, scaling on the membrane occurs due to dissolved minerals within the feed-water exceeding their solubility limits (Droste, 1997). Feed-water that has high turbidity will foul due to deposition of dispersed fines or colloidal matter on the membrane. Macromolecular organic solute can lead to the formation of a cake layer or an irreversible gel layer on the membrane surface and the presence of metal hydroxides from influent waters can cause chemical reactions with the membrane surface. Adsorption of low MW substances may occur on the membrane surface and bacterial colonization is possible on hydrophobic membranes. Biofouling is excessive growth of biomasss due to a high concentration of organic foulants within the source water (Vrouwenvelder et al, 2009). Biofoulants adsorb to the membrane surface altering the surface characteristics and reduce the permeability of the membrane resulting in an operational pressure increase.

Organics, specifically the humic portion, have been recognized as contaminants for the potable water treatment process as they react with chlorine to form disinfection by-products (Singer, 1999). NOM is a biodegradable, naturally occurring substance in water that is known to be a precursor to a potentially carcinogenic DBP. The composition and characteristics of NOM vary in aromaticity, molar mass, charge, functional group and hydrophobicity (Schäfer et al, 2006). Common measurements of NOM are total and dissolved organic carbon (TOC and DOC); DOC is the portion of TOC that can pass through a low-pressure (0.45μm) membrane filter and is comprised of humic, fulvic and hydrophilic acids (Schäfer et al, 2006). Organics are a major foulant for both low- and high-pressure membranes. However, it is not clear which fraction of organics is the dominant foulant for membrane operation. Humic substances have been reported as the fraction of dissolved organics that cause severe irreversible fouling due to adsorption (Xiao et al, 2012; Combe et al, 1999). Henderson et al (2008) and Liu et al (2011) found protein to be the dominant organic fraction in membrane fouling.

Some studies have suggested that the specific fraction of organic foulants is dependent on source water characteristics. A study by Yu et al (2011) found that hydrophobic fouling was dominant with increased ionic strength as low ionic strength solution membrane foulants became more hydrophilic with increased calcium concentration. Lee et al (2004) found that high hydrophilic fractions of NOM were responsible for flux decline. Research by Contreras et al (2009) found the initial fouling mechanism in their research was organic adsorption then synergistic fouling with other fouling mechanisms became dominant.

2.3 Pre-Treatment for High-Pressure Membranes

Pre-treatment of the feed-water to reduce or alter the feed-water contaminants can mitigate membrane fouling. AWWA recommends that high-pressure membrane feed-water should have a SDI of 3-5%/min, turbidity of less than 0.2 NTU and charge of greater than -30mV recommends for successful membrane operation (AWWA, 1999). Pre-treatment reduces fouling rates and operating pressures of high-pressure membranes improving membrane efficiency and lifespan (Choi et al, 2008; Geralders et al, 2008). Pre-treatment is required in high-pressure membrane filtration to ensure stable, long-term performance of membranes (Choi et al, 2008). The two major pre-treatment types are physical and chemical. Physical pre-treatment removes solids from the feed-water, reducing the amount of contaminants in contact with the membrane. Chemical pre-treatment alters the properties of the contaminants to minimize interaction with the membrane. Chemical additives may be added to the physical processes to improve pre-treatment efficiency.

2.3.1 Physical Pre-Treatment for High-Pressure Membranes

Physical pre-treatment is the removal of particles and colloids in the water through settling, dissolved air flotation (DAF), or filtration. A decreased amount of influent solids decreases turbidity, SDI and MFI, which is beneficial for the reduction of particulate fouling in high-pressure membranes. Filtration removal methods for high-pressure membrane feed-water pre-treatment include media, biological or low-pressure membrane filtration.

2.3.1.1 Settling and Dissolved Air Flotation

Settling is a process of passive separation of solids from solution. The solution flows into a sedimentation tank or settling basin until a desired percentage of solids settle. Settling is a cost effective solids separation process that can also be very time intensive. Low density or small particles take a long time to settle out which is not feasible for most applications. Chemical additives, ballasted sand or lamella bars are occasionally added to decrease sedimentation/settling times. Farley and Morel (1986) studied sedimentation with coagulant addition and determined particle interaction had a great effect on settling rates over discrete settling times.

DAF is a complimentary process to settling which is effective for removal of low MW compounds that settle slowly. DAF is aeration of a solution causing low MW solids to attach to bubbles and rise to the surface. The solids collect on the surface can then be removed by skimming. Geralders et al (2008) found that DAF had no effect on SDI or MFI without the addition of a coagulant. With the addition of a coagulant, SDI improved but did not meet AWWA feed-water quality recommendations until filtered with a 5µm capsule filter (Geralders, 2008).

2.3.1.2 Media Filtration

Media filtration is a passive, gravity-fed process the uses granular material to remove solids from a solution. The removal capacity is a function of media porosity and depth (Droste, 1997). Granular media types that are commonly used include gravel, sand, anthracite, glass and granular activated carbon (GAC). Smaller and more uniform media types increase solids retention as the void spaces are smaller and more selective. Bonnelye et al (2004) determined that a larger effective size media top layer is required otherwise a high clogging rate resulted for media filtration, following ferric chloride coagulation. Biofiltration is a media filtration process that takes advantage of the biological growth in the media and its added removal capacity of NOM and microorganisms (Mosqueda-Jiminez et al, 2006). Biological filtration, in addition to physical separation, decreases the possibility of regrowth within the distribution system (Droste, 1997).

2.3.1.3 Low-Pressure Membrane Filtration

Membranes provide a reliable, absolute barrier that effectively removes a wide range of potable water contaminants (Mosqueda-Jimenez et al, 2006). A 0.45µm nominal pore size filter, which corresponds to a low-pressure membrane, is capable of attaining the AWWA recommendations for high-pressure membrane feed-water quality (AWWA, 1999). Low-pressure membranes are pressure-driven processes that remove colloids, microorganisms and high MW contaminants via pore size exclusion (Zhang et al, 2005). MF and UF produce high quality permeate with effective removal of particulate and microbial matter independent of feed-water quality (Zhang et al, 2005). UF is a more selective membrane than MF and therefore has increased operational pressures as shown in Figure 2.3.

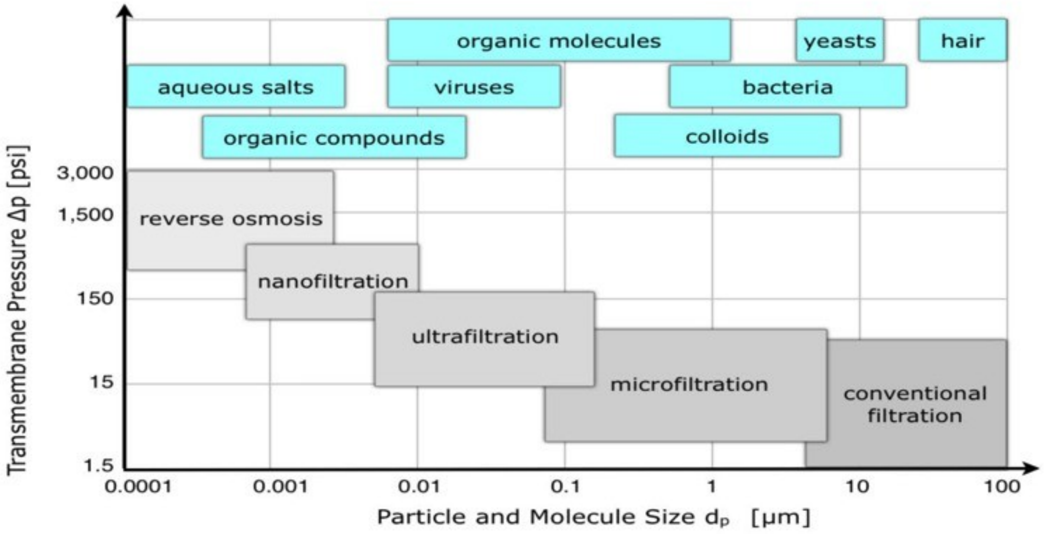


Figure 2.3 Membrane filtration removal capacities. Image taken from MBR Basics (May, 2013)

Addition of a low-pressure membrane as pre-treatment to high-pressure membrane feed-water is effective in reduction of NF trans-membrane pressure via removal of organic molecules, viruses, bacteria and colloids prior to interaction with the NF membrane (A3-USA Inc., 2013). As shown in Figure 2.3, a tight MF membrane or UF membrane permeate meets the AWWA requirements for turbidity and SDI.

UF is generally selected as the filtration for pre-treatment as it is economical, effective in removing bacteria and particles, and can achieve a SDI of 3.0%/min and turbidity of 0.2 NTU (Choi et al, 2008). UF is effective in particle removal to improve the feed water quality of high-pressure membranes by removing 25 to 50% of feed water particles under a wide pH range (Duan et al, 2002). For source waters with a high dissolved fraction of contaminants coagulation should be implemented prior to filtration to aid in dissolved material removal (AWWA, 1999).

2.3.2 Chemical Pre-Treatment for High-Pressure Membranes

Chemical pre-treatment mitigates the effects of high-pressure membrane foulants by altering their properties. Alterations of foulant properties include reduction of divalent cations, break-down of organic compounds and aggregation of aromatic compounds. Chemical pre-treatments discussed in this review include addition of anti-scalants, advanced oxidation and coagulation.

2.3.2.1 Anti-Scalants and Softening Agents

Anti-scalants and scale inhibitors are used for pre-treatment to prevent salts from exceeding their solubility limit. Membrane retention may cause salts to exceed their solubility limit resulting in precipitation of sparingly soluble salts on the influent layer of the membrane (Schäfer et al, 2006).

Anti-scalants prevent scaling by either causing the salt precipitation to form in irregular non-scaling structures or creating charge repulsion between the salt crystals (Schäfer et al, 2006). There are two main types of anti-scalants: poly phosphates and high-performance polymeric anti-scalants (AWWA, 1999). Additional treatment to moderate scaling includes water softening. This may be done with addition of lime or soda ash, or ion exchange. Water softening is effective in reducing the concentrations of Mg^{2+} and Ca^{2+} to ensure they do not become supersaturated and precipitate on the influent membrane layer. Reduction of solution pH and temperature may be sufficient to mitigate or prevent membrane scaling without water softening or addition of anti-scalants.

2.3.2.2 Advanced Oxidation

Advanced oxidation is the breakdown of large MW organics into low MW biodegradable organics through strong oxidation methods including ozonation, ultraviolet radiation and hydrogen peroxide addition. Pre-treatment of NF feed water with ozonation significantly reduced the fraction of organics with a MW greater than 1kDa which resulted in mitigation of membrane fouling and improvement in membrane cleanability (Liu et al, 2011; Linlin et al, 2011). Lamsal et al (2011) determined that the combination of ozonation and UV radiation with hydrogen peroxide addition was more effective in NOM reduction than individual advanced oxidation process. Furthermore, Liu et al (2011) found that advanced oxidation altered the fluorescence of the organic material and changed the dominant foulant from protein-like matter to humic-like matter.

2.3.2.3 Coagulants

Coagulants are chemical additives that coat particles with an adhesive layer encouraging aggregation of particles to increase the particle size and weight. By increasing the effective particle size the particles are more effectively removed by filtration and settling (Droste, 1997). The effectiveness of coagulation is dependent on coagulation conditions, water quality matrices and treatment process (Volk et al, 2000; Droste, 1997). The coagulation conditions are dependent on feed-water quality and therefore the source water of concern should be characterized to determine the most effective conditions

(Walsh et al, 2009). Aluminum and iron based coagulants are widely used for removal of NOM. A study on coagulation pre-treatment in UF systems found that the coagulant dose required is dependent on the specific water characteristics and therefore must be determined through bench and pilot-scale laboratory testing (Walsh et al, 2009). Coagulants are effective between 5 to 20°C and effectiveness of coagulation generally decreases with temperature (Droste, 1997; AWWA, 1999).

Aluminum sulphate (alum), aluminum chlorohydrate and polyaluminum chloride (PACl) are types of aluminum-based coagulants. Alum is the most common as it is effective in the removal of NOM and has few adverse effects on the distribution system and public health. Solubility and surface charge of aluminum hydrolysis products can be affected by solution chemistry specifically the presence of CO_3^{2-}, SO_4^{2-}, and H_2SiO_3 (Duan et al, 2002). As a result of these effects, the solubility of aluminum at a particular pH value will vary from that defined by theoretical equilibrium. Duan et al (2002) found that alum provided effective removal of humic substances within a wide pH range of 5 to 10.

Ferric salts such as ferric chloride and sulfate are two types of iron-based coagulants. Ferric chloride operates at an ideal pH range of 4.5 to 5.5 and is relatively insoluble thus reducing likeliness of precipitate scaling (Droste, 1997; Edzwald et al, 2011). Chinu et al (2009) found that low doses of ferric chloride prior to microfiltration are effective in reducing organic material therefore reducing the flux decline from 44% to 22%. Coagulation with ferric chloride has been found to not neutralize charge indicating that factors other than charge neutralization influence separation (Duan et al, 2002; Al-

Shamrani et al, 2002). Addition of polymers, a chemical additive, improves coagulant efficiency and can reduce the dose of coagulant required (Droste, 1997).

2.4 In-Line Coagulation for Pre-Treatment of High-Pressure Membranes

Membrane fouling is a major deterrent for application of membranes with challenged source waters. Studies to reduce membrane fouling through operational parameters and pre-treatment of feed-water have found that each application is site-specific and bench-scale analysis of the process should be performed to assess the foulants of greatest concern (Volk et al, 2000; Choi and Dempsey, 2004; Walsh et al, 2009). Low-pressure membranes are frequently used for high-pressure membrane pre-treatment but are not effective in removal of dissolved NOM (Walsh et al, 2009). The addition of a coagulant prior to low-pressure membrane filtration is effective in removal of dissolved constituent; however, more research is required to understand the effect of in-line coagulation pre-treatment.

In-line coagulation is applicable for treatment in removal of NOM from industrial, waste and potable water. In-line coagulation refers to the addition of a coagulant with turbulent mixing directly prior to a low-pressure membrane (no settling). Coagulation is very effective for water characterized with a high specific ultraviolet absorbance (SUVA) of greater than 4 (AWWA, 1999). SUVA values correspond to the fraction of NOM that are aromatic compounds (Droste, 1997). Coagulation binds with aromatic substances to increase their effective size for higher separation of dissolved matter with low-pressure filtration (Guigui et al, 2002). Coagulation increases the removal of dissolved NOM with

MF thus improving the NF feed-water quality and decreasing potential of NOM fouling such as adsorption.

Inline coagulation has been applied as a successful (Choi et al, 2004), cost effective pretreatment option or fouling control in full-scale facilities (Judd and Hillis, 2000). A bench-scale jar-test apparatus for coagulation and UF membranes were used to successfully model full-scale membrane-system plant operation (Guigui et al, 2002; Walsh et al, 2011). Coagulation conditions determined by jar-test experiments were applicable to good performance in the full-scale in-line coagulation/UF process (Guigui et al, 2002). The degree of mixing is important for reduction of NOM fouling; mechanical mixing water has been found to be more effective than pump diffusion (Kim et al, 2006). Jar-test apparatus provides bench-scale analysis of in-line coagulation with mechanical mixing that is applicable to full-scale plant operation.

Coagulation has been found to significantly increase the removal of organics with filtration (Guigui et al, 2002; Choi et al, 2004; Hillis, 2006; Kabsch-Korbutowicz et al, 2006; Walsh et al, 2009). Coagulation prior to membrane filtration was found to require a lower coagulant dose for removal of NOM than for coagulation prior to conventional media filtration (Walsh et al, 2009; Hillis, 2006). Choi and Dempsey (2004) found that under-dose coagulation conditions resulted in a cake that was less compressible and had lower hydraulic resistance. However, coagulant doses lower than the metal’s solubility limit, have been found by Hillis (2006) to cause detrimental internal fouling of low-pressure membranes due to incomplete aggregation of particles. For reduction of operational costs due to decreased hydraulic resistance and cleaning, the size of the aggregated particles must be greater than the membrane pore size (Judd and Hillis, 2000; Hillis, 2006; Kabsch-Korbutowicz et al, 2006). Guigui et al (2002) and Duan et al (2002) found low doses of coagulant were favorable as increased coagulant dose corresponded to increased cake resistance in dead-end membrane performance. Choi and Dempsey (2004) found that several types of coagulant dosing conditions including charge neutralization, sweep floc and under-dose prior to filtration are effective for removal of NOM and turbidity. Discrepancies between studies were present of whether aluminum or ferric-based coagulants were most effective. Guigui et al (2002) and Hillis (2006) found that ferric coagulants had a higher removal rate of NOM whereas Kabsch-Korbutowicz et al (2006) favored aluminum-based coagulants for NOM removal.

Consistent findings were found for relative values of pH for effective in-line coagulation. Coagulation for all coagulant types examined was found to not be effective under alkaline conditions but was effective at pH values of 6 or lower (Hillis, 2006; Kabsch-Korbutowicz et al, 2006). Guigui et al (2002) found removal of NOM via in-line coagulation with ferric chloride decreased with decreasing pH values and the highest removal of NOM occurred at a pH of 7.5. The optimal pH to reduce membrane fouling is dependent on source water characteristics as well as coagulant type. Droste (1997) recommends that to reduce membrane scaling, pH range should be within 4-6. For aluminum-based coagulants a pH of 5.5-6-3 should be implemented whereas ferric-based coagulants have an optimal pH range of 4.5-5.5.

Other studies looked into the effect of source water characteristics on the ability of coagulants to remove specific fractions of NOM. High ionic strength of source waters was found to be the dominant factor for flux decline over pH and calcium concentration (Yu et al, 2011). Yu et al (2011) also determined that at high ionic strengths the dominant foulant was the hydrophobic fraction of NOM. Gregor et al (1997) found that for low turbidity waters the addition of lime in particulate form increased NOM removal by providing sites for adsorption. The presence of cations has been found to enhance coagulation/flocculation by bridging humic polymers and increasing floc growth. (Duan et al, 2002; Fan et al, 2005)

CHAPTER 3 MATERIALS AND METHODS

3.1 Collins Park Water Treatment Plant

Collins Park Water Treatment Plant (WTP) is a small system operated by Halifax Water that supplies approximately 64 m^3/day (Halifax Regional Municipality, 2013). The plant is located in Wellington, NS on Lake Fletcher, an unprotected watershed impacted by treated wastewater, storm water, and recreational activities. As part of an unprotected watershed, Lake Fletcher is susceptible to a wide range of contaminants. The Lake Fletcher water quality analysis can be found in Table 3.1.

The water quality of Lake Fletcher is seasonally dependent and characterized by high concentrations of NOM and metals in the autumn months. Seasonal variation of organic and metals concentrations are shown in Figure 3.1 and Figure 3.2 respectively.

Table 3.1: Lake Fletcher water quality

Parameter	Units	Range	Average
pH		6.62 to 7.20	6.82
TOC	mg/L - C	3.97 to 5.67	4.49
DOC	mg/L - C	3.64 to 5.50	4.32
UV_{254}	cm^{-1}	0.145 to 0.211	0.173
SUVA	L/mg/cm	3.45 to 4.31	4.00
True color	Pt.Co	7.00 to 33.5	20.1
Turbidity	NTU	0.828 to 1.35	1.09
Aluminum	µg/L	26.5 to 74.4	37.1
Manganese	µg/L	2.27 to 89.4	34.3
Iron	µg/L	30.8 to 214	112

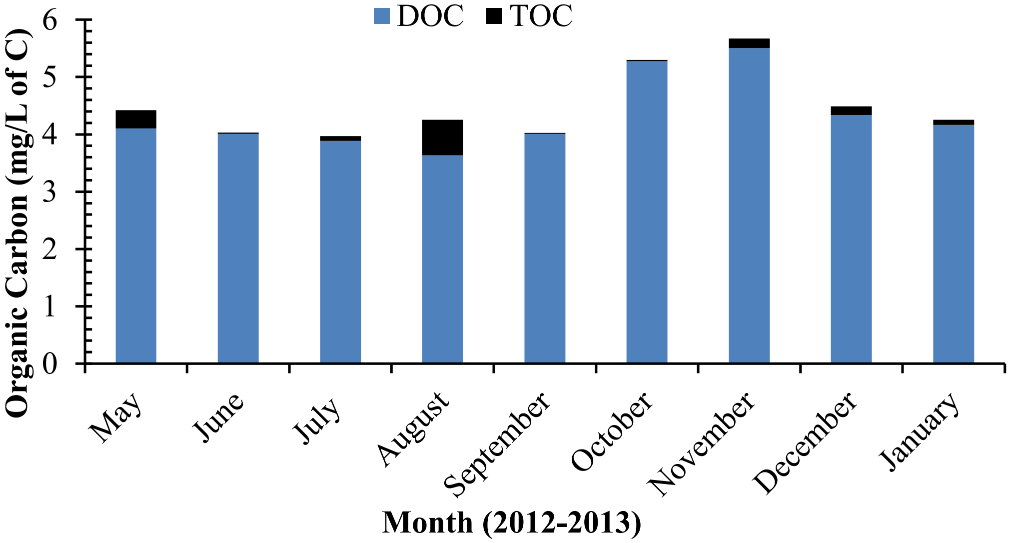


Figure 3.1 Seasonal variation of organics in Lake Fletcher

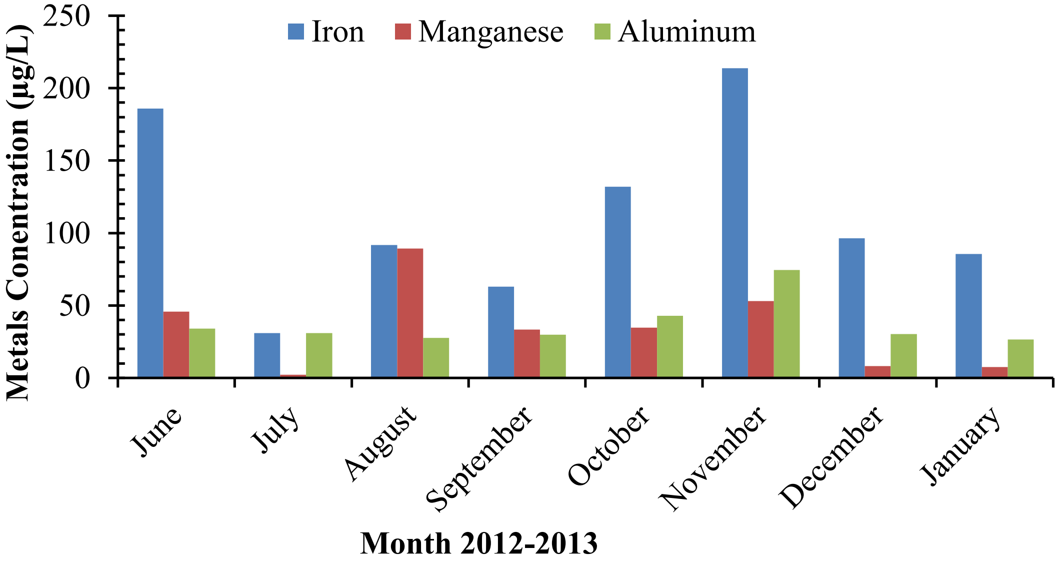


Figure 3.2 Seasonal variation of metals in Lake Fletcher

In autumn, high levels of dissolved NOM occur due to decomposition of terrestrial humics. Iron, manganese and aluminum are naturally occurring metals in lake water that may be due to erosion and weathering of rocks and minerals (GCDWQ, 2012). Sewage effluents may contribute to elevated iron concentrations in the lake (GCDWQ, 2012). Elevated NOM and metals in the NF feed-water lead to an increase in fouling of the NF membrane. Increased fouling of the NF membranes increases the TMP, operating costs and decreases the lifespan of the membrane (Choi et al, 2008).

Collins Park operates on an IMS with UF and NF. The plant schematic is shown in Figure 3.3 and consists of two major stages: filtration and disinfection. The low-pressure, dead-end ultrafiltration membranes (HYDRAcap, Hydranautics) remove suspended matter to reduce the operation pressure of the nanofiltration modules (ESPA4, Hydranautics). Due to the high fraction of dissolved NOM in Lake Fletcher, the UF membranes are not effective for NOM removal. The disinfection stage consists of primary disinfection with ultraviolet radiation for inactivation of microbiological contaminants and secondary disinfection with sodium hypochlorite to protect from biological growth within the distribution system (CDWQG, 2012).

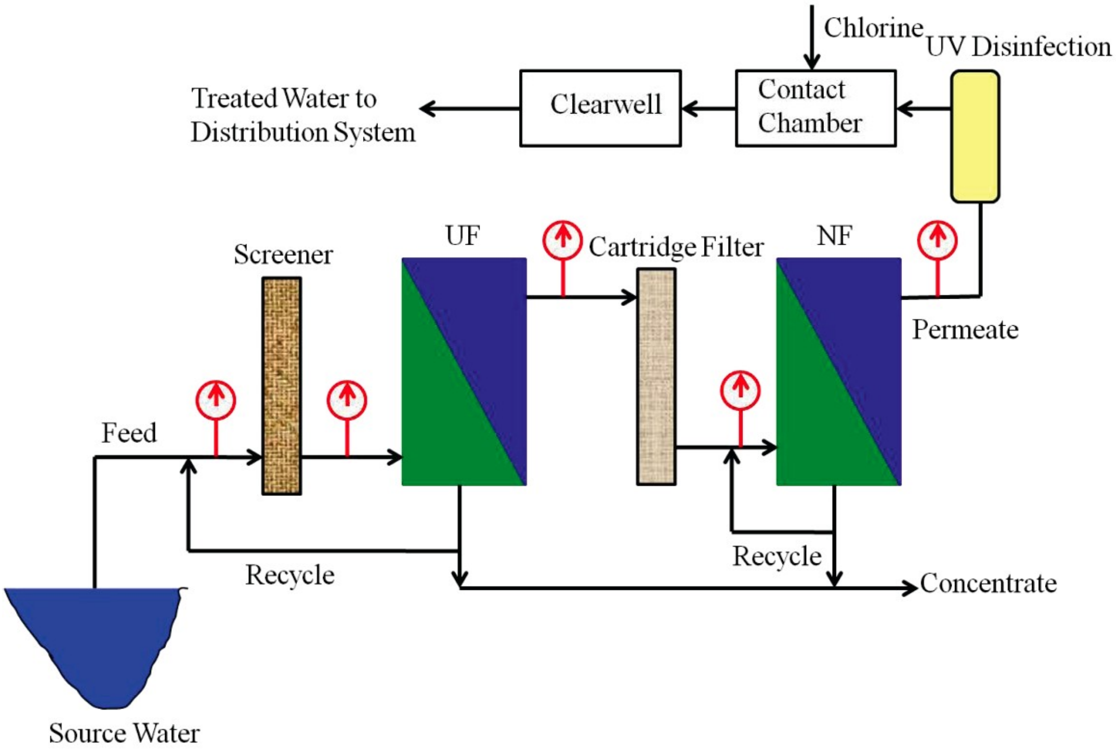


Figure 3.3: Collins Park Water Treatment Plant schematic from R. Lamsal (2012)

3.2 Bench-Scale Pre-Treatment: In-Line Coagulation

Experimental analysis was carried out with three coagulants to determine the effect of inline coagulation/MF on the trans-membrane pressure and fouling of the membrane. Dead-end MF capsules were used at bench-scale to simulate full-scale UF operation. Aluminum sulfate, polyaluminum chloride and ferric chloride were the coagulants evaluated for removal of NOM. Table 3.2 below contains the coagulant manufacturer and chemical properties. An experimental process diagram for inline coagulation/MF pre-treatment can be found below in Figure 3.4.

Table 3.2 Coagulant properties taken from manufacturer's websites

Coagulant	Abbreviation	Manufacturer	Chemical Formula
Aluminum Sulfate	Alum	General Chemical	$Al_2(SO_4)_3*14H_2O$
Polyaluminum Chloride	PACl	Kemira	$Al_2(OH)_xCl_6\text{-}x^1$
Ferric Chloride	$FeCl_3$	Fischer Scientific	$FeCl_3*6H_2O$

$^1 0<x<6$

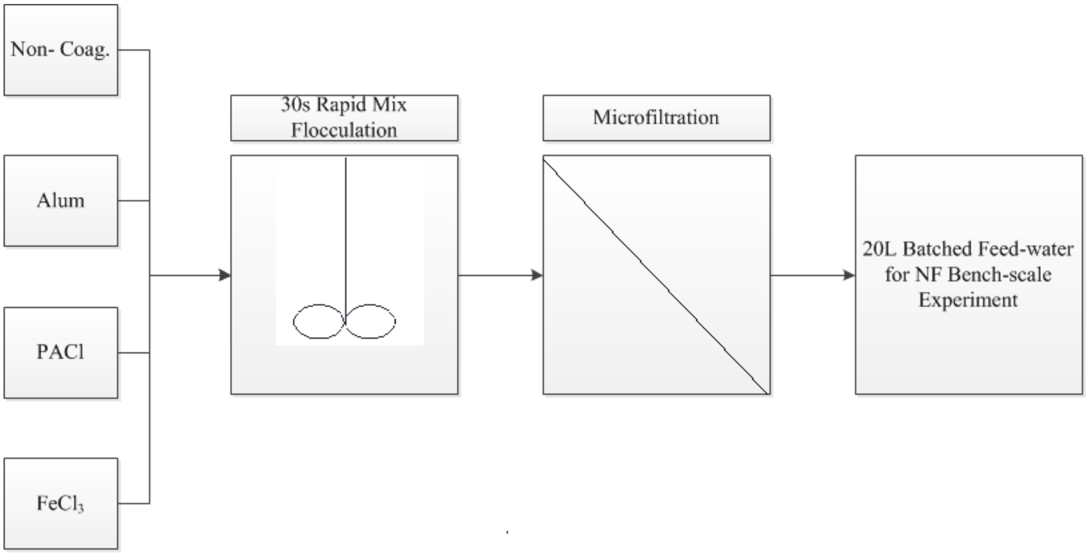


Figure 3.4 Schematic of pre-treatment prior to bench-scale NF

3.2.1 Bench-Scale Jar Tests

Jar tests were used for bench-scale determination of optimal coagulant dose and pH. A Phipps and Bird 6 x 2L jar test apparatus with rotating paddles and variable flocculation speed to control the velocity gradient was used to simulate in-line mixing of coagulants. Turbulent in-line mixing was simulated at bench-scale with rapid mix at 300rpm for 30sec (Judd and Hillis, 2000). Jar tests were performed at room temperature and pH was adjusted prior to coagulant addition. The optimal pH range for each coagulant was determined through literature and three relative pH values were assessed for each coagulant. Optimal coagulant dose and pH condition was determined using TOC and SDI as metrics. The optimal coagulant dose was determined using a modified point of diminishing returns for low-dose coagulation: when an increase in coagulant dose does not result in a significant improvement in NOM removal (Volk et al, 2000).

3.2.2 Silt Density Index

SDI (SDI-PU, Applied Membranes Inc.) was used to analyze NF feed-water suitability of the optimal coagulant dose/pH conditions for NOM removal. SDI is a measure of the effect of particulate fouling for a high-pressure membrane. American Water Works Association (1999) recommends a SDI value of 3-5%/min for successful membrane operation. Optimal SDI values for this study were between 3-3.5%/min so that pre-treatment with coagulation was an improvement on current operation conditions and within the lower range of the AWWA recommendations. The manufacturer's procedure was followed and SDI was determined using the following equation:

$$SDI_T = \frac{\left[1 - \frac{t_i}{t_f}\right] \times 100}{T}$$

T: length of time, 15min is most common, but 5 and 10min may also be used
t_i: length of time it takes to filter 500mL from start
t_f: length of time it takes to filter 500mL from time T

3.3 Bench-Scale Membrane Filtration System

Bench-scale analysis of high-pressure membrane fouling was assessed using a bench-scale cross-flow filtration unit (Sepa CF II membrane cell, GE Osmonics). Both feed and permeate spacers were employed for improved hydrodynamic conditions including cross-flow velocity. Bench-scale flat sheet DK-NF thin film membranes from GE Osmonics were used for experimental analysis. Flat sheet membrane specifications are listed in Table 3.3.

Table 3.3 Flat sheet NF membrane specifications taken from GE

Parameter	Designation
Manufacturer	GE Osmonics
Polymer	Thin Film
Molecular Weight Cut-off	150-300
Rejection Size	98% $MgSO_4$
pH Range at 25°C	2-10
Typical Flux/psi	22/100 (GFD/psi)

The membrane was operated in constant flux mode with variable pressure. Bench-scale NF flux was equivalent to Collins Park (full-scale) water treatment facility flux at 20°C: a bench-scale permeate flow rate of 6mL/min. The total volume of NF permeate produced over the 200hrs runtime was 72.0L and this volume was used to calculate mass balances for each trial. The feed-water tank consisted of Lake Fletcher water that has undergone in-line coagulation followed by 0.45µm filtration (POLYcap, Whatman GW). The feed-water was pumped (Hydracell Pump, Lincoln Motors) from the feed tank through a cold water bath (Neslab RTE 17, Thermo Scientific) to ensure a constant feed-tank temperature of 20°C ± 2°C. The NF membrane system was operated in recycle mode where the concentrate and permeate flows were returned to the feed-tank. The feed, concentrate and permeate were monitored throughout the 200hr experiment to ensure that water quality, flux, cross-flow velocity and temperature remained constant. To maintain constant NOM and metals concentrations in the feed-tank during the 200hrs run time, a peristaltic pump circulated the feed-tank to minimize settling.

3.4 Analytical Methods

3.4.1 General Water Quality Parameters

All methods, unless otherwise stated, followed the equipment manufacturer's procedures or the procedures set forth by *Standard Methods for the Examination of Water and Wastewater (APHA, 2012).* Total and dissolved organic carbon was measured with a Shimadzu TOC-VCSH Total Organic Carbon Analyzer (MDL=0.1mg/L of C, RDL=0.3mg/L of C). True color and UV_{254} were measured using the Hach DR 5000 Spectrophotometer. Conductivity and zeta potential were measured with the Malvern ZetaSizer Nano ZS. pH was measured with an Accumet Excel probe (XL50) that was calibrated prior to use. Concentrations of aluminum, manganese and iron were measured with Inductively Coupled Plasma-Mass Spectrometry (ICP-MS).

3.4.2 NOM Characterization

Natural Organic Matter (NOM) characterization was used to determine if coagulant type was a factor in removal of certain organic fractions for NF membrane fouling. The NOM characterization method that was implemented was High Performance Size Exclusion Chromatography (HP-SEC). HP-SEC provides analysis on the MW distribution of a solution through size exclusion. Samples are pH adjusted between 3 and 7 and filtered by a 0.45µm membrane to meet procedure specifications. Samples are then analyzed with a Perkin Elmer Series 200 Autosampler and Perkin UV/Vis detector at 254nm. To analyze removal of specific fractions of NOM, MW ranges were designated in increments of 500 Da. HP-SEC peaks were integrated and classified into five MW ranges: <500, 500 to

1000, 1000 to 1500, 1500 to 5000, and 5000+ Da. The average MW of the peak determined the MW range designation.

3.4.3 Membrane Analysis

SEM (Hitachi S-4700 FEG SEM) was performed to obtain detailed surface imaging of the virgin and fouled membranes. Prior to analysis, membranes were air-dried for five or more days and then coated (Polaron SC502 Sputter Coater) with a gold-palladium conductive layer to enhance resonance imagery. Membrane surface was analyzed with constant current of 20μA and 15kV with varying magnification. Energy Dispersive X-Rays (EDS) (Oxford Inca EDS) and electron backscatter diffraction (HKL) were used for compositional analysis of the membrane surface and membrane foulants.

3.4.4 Statistical Analysis

Statistical Analysis was performed to determine if there was a statistically significant difference of means of the effect of pre-treatment type on NF feed-water and permeate quality. Tukey-Kramer significance test at 95% significance was applied to the data sets that varied in sample size and were non-parametric. The Tukey-Kramer interval for μ_i - μ_j is:

$$q_{\propto,C,\nu}\sqrt{\left(\frac{MSE}{2}\right)\left(\frac{1}{n_i}+\frac{1}{n_j}\right)}$$

$q_{\alpha, C, \nu}$: Critical q value dependent on significance

C: Number means compared, for this experiment there are four (1 baseline, 3 coagulants)
ν: Degrees of freedom, based on pooled deviation
MSE: Mean squared error
n_i: Number of samples in the i^{th} sample set
n_j: Number of samples in the j^{th} sample set

3.5 Experimental Set-Up

The experiments followed a modified 3^3 factorial design: three coagulants, three pH values, and six or more coagulant dosages. The factorial design is shown in Table 3.4.

Table 3.4 Factorial design

Coagulant	pH	Doses (mg/L of metal)
Aluminum Sulfate	5.2, 5.5, 5.8	0.20, 0.40, 0.60, 0.70, 0.80, 0.90, 1.10, 1.30
Polyaluminum Chloride	5.7, 6.0, 6.3	0.15, 0.35, 0.55, 0.75, 0.95, 1.05, 1.15, 1.25, 1.45, 1.65
Ferric Chloride	4.7, 5.0, 5.3	0.10, 0.15, 0.25, 0.50, 0.75, 1.00

Relevant water quality parameters included TOC, UV_{254}, true color, HP-SEC, and metals concentration including aluminum, manganese and iron, and will be referred to as 'general water quality' from this point. General water quality parameters were measured for each sampling event of Lake Fletcher water and for each jar test. Jar tests for the optimal coagulation conditions and for baseline conditions were also assessed for SDI, conductivity and zeta potential.

For the bench-scale NF experiment both physical operational parameters and general water quality of the permeate, feed-water and concentrate were monitored bi-hourly. The monitored operational parameters included: feed-tank temperature, permeate flow, concentrate flow, and TMP.

CHAPTER 4 RESULTS AND DISCUSSION

4.1 Need for Pre-Treatment under Baseline Conditions

4.1.1 Baseline Conditions

The effects of baseline conditions on the NF feed-water quality and membrane fouling of Collins Park Water Treatment Plant were assessed. Baseline conditions were reproduced at bench-scale with 0.45μm filtration of Lake Fletcher water prior to NF. NF feed-water and permeate quality for the bench-scale trial is shown in Table 4.1.

Table 4.1 NF feed-water quality at baseline conditions

Parameter	Permeate	Feed
TOC (mg/L of C)	0.379 ± 0.0631	3.81 ± 0.226
UV_{254} (cm^{-1})	0.002 ± 0.000464	0.116 ± 0.00460
SUVA (L/mg/cm)	0.528	3.04
SDI (%/min)	---	4.40
Zeta Potential (mV)	---	-21.2
Conductivity (mS/cm)	---	0.165
Aluminum (μg/L)	2.79 ± 1.72	20.6 ± 2.24
Manganese (μg/L)	0.935 ± 0.110	3.53 ± 0.189
Iron (μg/L)	1.78 ± 2.24	11.9 ± 6.67

There was a large variance in the concentration of metals. This indicated that the rate of settling of aluminum and iron in particular were able to overcome the mixing of the peristaltic pump. As a result there was a decrease in metals concentration throughout the operation of the bench-scale NF membrane. The feed-water TOC and UV_{254} concentrations were maintained throughout the trial. The permeate TOC and UV_{254} concentrations were consistent indicating that the quality of the NF membrane was not compromised and the membrane permeability was not variable. The NF feed-water

SUVA value of 3.04 L/mg/cm indicates that only a portion of the humic matter was removed.

The feed-water for the NF membrane at the current plant operation conditions meets the AWWA (1999) recommended guidelines of a SDI index with 3-5%/min with a value of 4.4%/min and zeta potential of >-30mV with -21.2mV. The MF membrane removes suspended matter from the feed-water, but a large majority of the NOM is dissolved and able to pass through the MF pores. The MF membrane does not attain sufficient removal of aluminum and natural organic matter. To express the amount of NOM retained by both the MF and NF membrane over the 200hrs run time, a NOM mass balance of the system was constructed. The NOM mass balance in Figure 4.1 shows the MF without coagulation only removed 3.5% of NOM. This resulted in the retention of 266mg (87.1%) of NOM by the NF membrane.

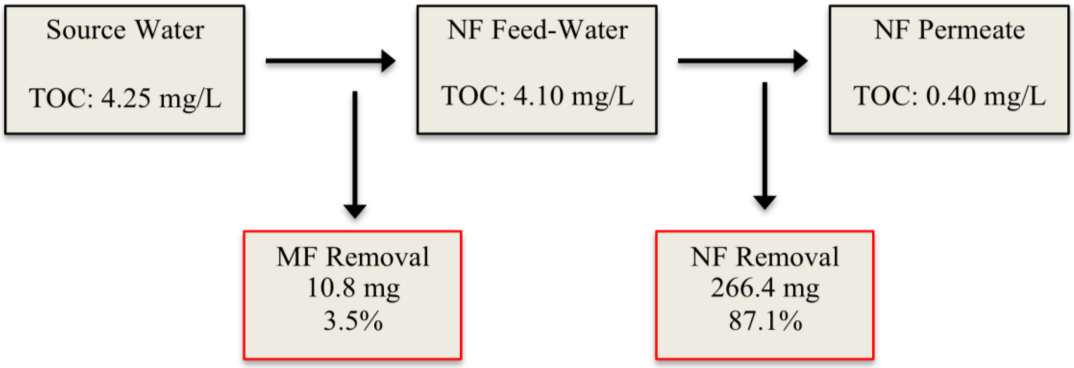


Figure 4.1 Analysis of NOM removal with MF pre-treatment

HP-SEC analysis gave additional detailed information on the fraction of NOM that were removed by the MF and NF membranes. HP-SEC Analysis shown in Figure 4.2 indicated that the MF pre-treatment removed 53 % and 84% of MW ranges 1500-5000 and 5000+ Da respectively, and minimal removal of the lower MW range of 0-1500 Da. The majority of NOM with MWs less than 5000Da were retained by the NF membrane as indicated below by the reduction of NOM from the NF feed-water to permeate.

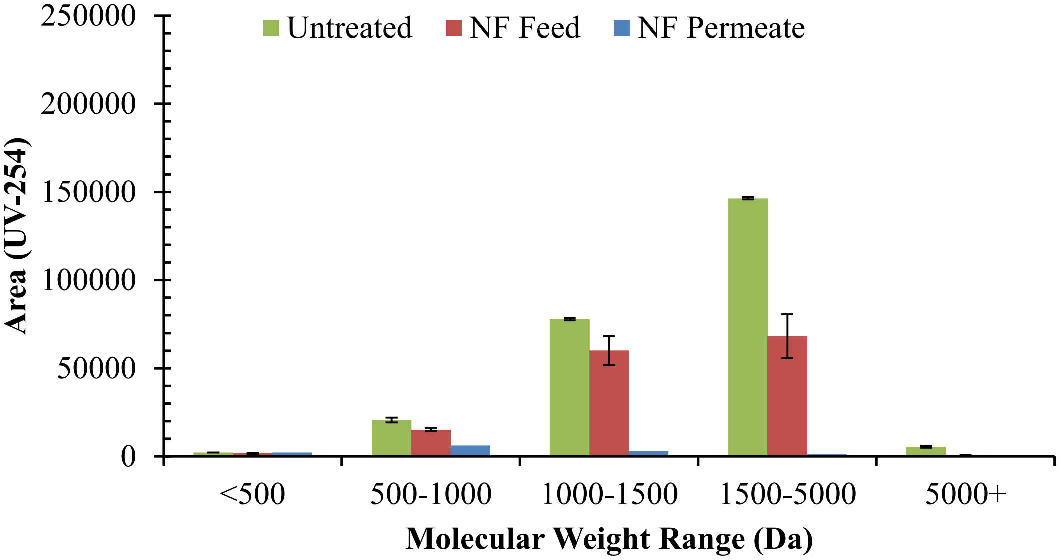


Figure 4.2 HP-SEC of NF bench-scale organic fraction removal with MF pre-treatment (error bars represent standard deviation)

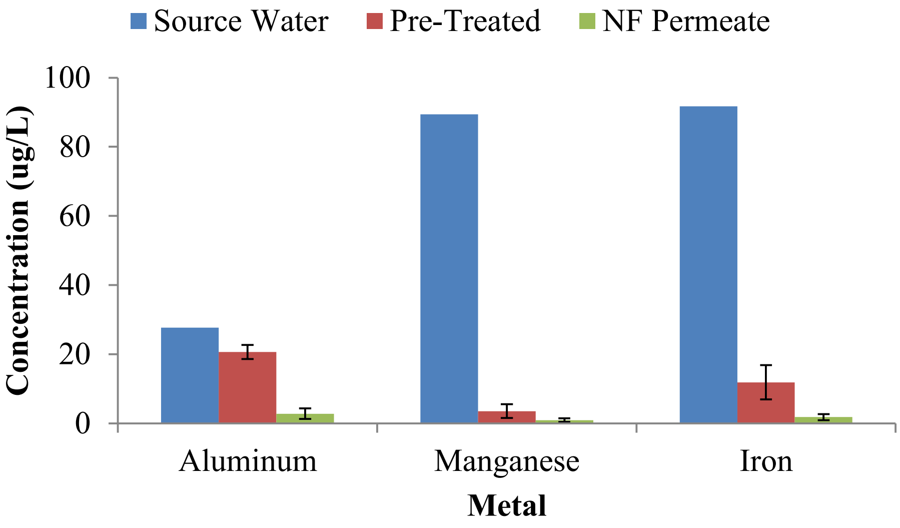


Figure 4.3 Analysis of metals concentration with MF pre-treatment (error bars represent standard deviation)

Reduction of manganese and iron were obtained with MF shown in Figure 4.3. The removal of aluminum, manganese and iron with MF pre-treatment were 25.4%, 96% and 87% respectively. Additional removal of metals may have occurred due to settling in the NF feed-water tank.

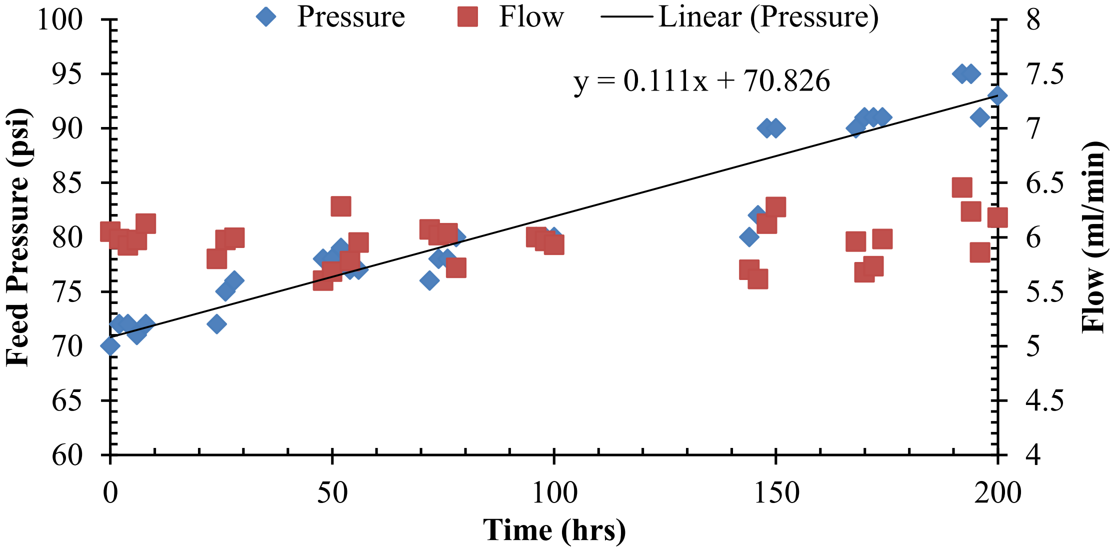


Figure 4.4 TMP increase over 200hrs operation of baseline conditions

The TMP increase was linear with a slope of 0.111psi/hrs and initial TMP of 70.8psi. There were two unusual observations at 144hrs and 146hrs with residuals of -6.8 and -5.0 psi respectively. This likely corresponded to decreased permeate flows of 5.7 mL/min at time 144hrs and 5.62mL/min at 146 hrs. The permeate flow rate increased to 6.12mL/min at 148hrs and required a TMP of 90psi. The average TMP for the 200hrs runtime was 81.3psi.

4.1.2 Membrane Analysis

Scanning electron microscopy was implemented to obtain surface images of the fouled membrane surface. Figure 4.5 illustrates a virgin flat-sheet NF membrane and a fouled NF membrane with deposition of matter on the membrane surface in Figures 4.5a and b respectively.

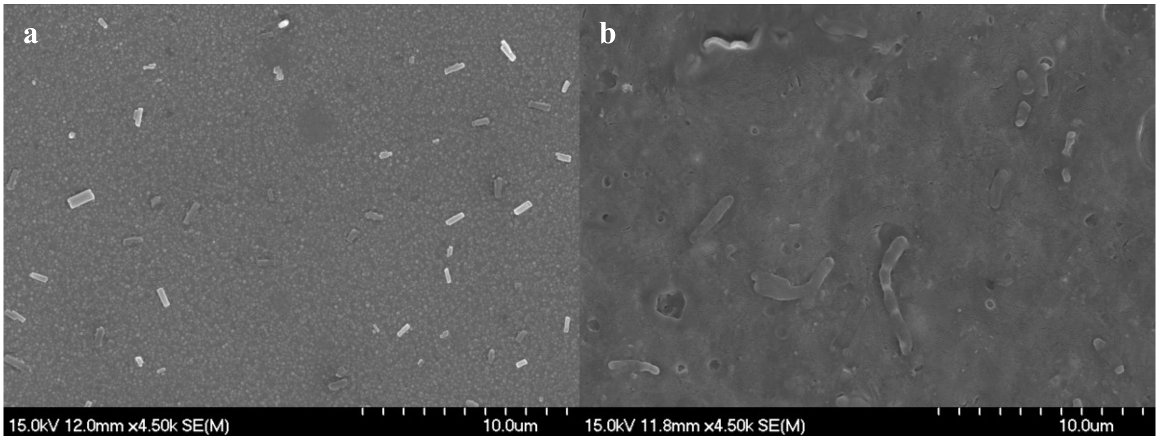


Figure 4.5 SEM images depicting **a.** virgin NF membrane and **b.** NF membrane fouled with deposition of matter post MF pre-treatment

In Figure 4.5a, the virgin membrane pores and fibers are visible. In Figure 4.5b the membrane was fouled over the 200hrs NF bench-scale run time following pre-treatment with MF. Deposition of matter and bacteria covered the membrane pores and fibers, which resulted in clogging or blockage of the membrane pores and increased TMP. EDS analysis indicated that the composition of the foulant layer was primarily composed of NOM with elemental analysis showing high levels of carbon, oxygen and nitrogen.

Inorganic matter was also shown in the SEM images. Figure 4.6 showed a large deposition of inorganic matter found on the fouled NF membrane following MF pre-treatment. The collective size of deposited inorganic matter found on the fouled membrane varied from <25 μm^2 to approximately 15 000 μm^2. EDS analysis identified high levels of iron and silica in several samples of the fouled membrane with trace amounts of sodium, chlorine, copper, sulfur, chromium, zinc, lead and aluminum. The inorganic matter was presumed to be due to impact of contaminants on the unprotected watershed.

Figure 4.7, depicts the variation in surface topography as a result of membrane fouling. The membrane surface appeared smoother than the virgin membrane due to a cake-layer formation on the membrane surface. There are several valleys and peaks in the foulant layer that contribute to localized increased fouling of the NF membrane as foulants within the concentrate cross-flow were retained.

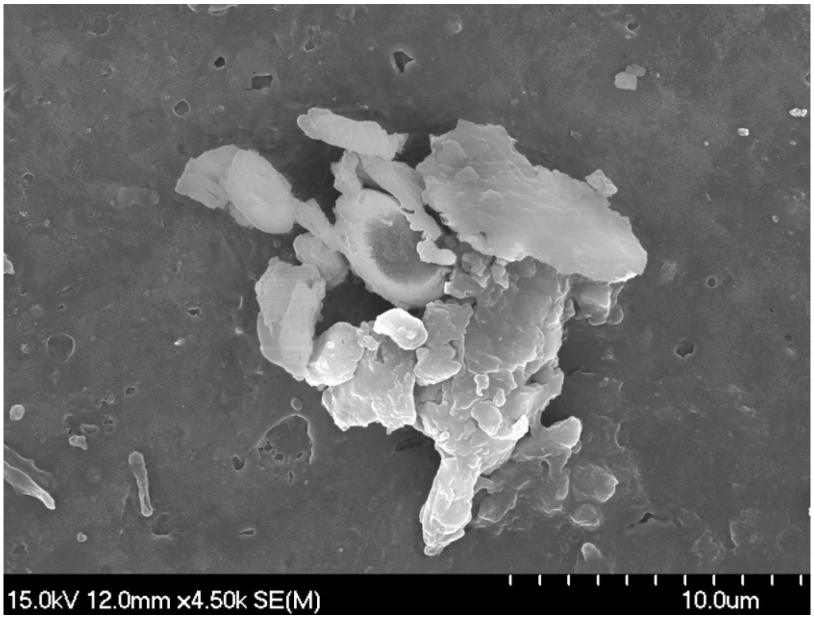


Figure 4.6 SEM image depicting deposition of inorganic material on a fouled NF membrane surface with MF pre-treatment

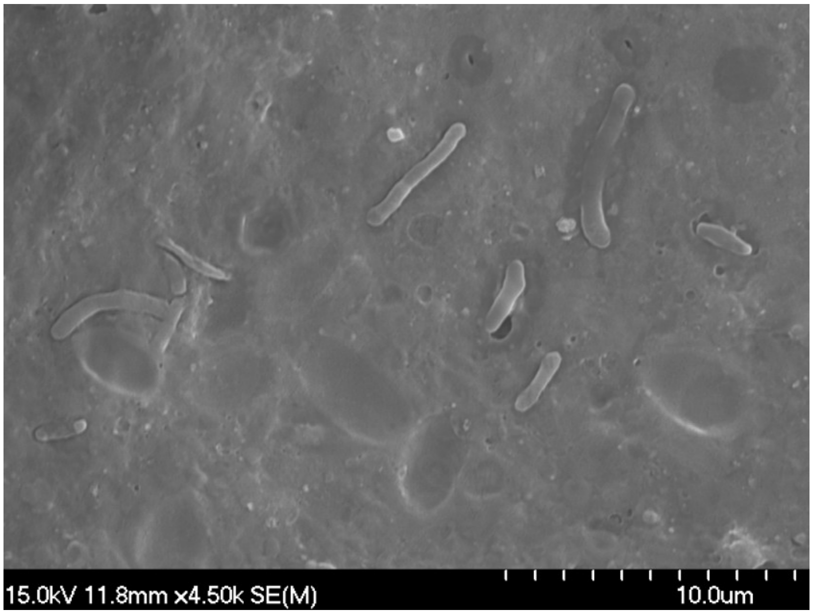


Figure 4.7 SEM image depicting deposition of material on a fouled NF membrane surface with MF pre-treatment resulting in differential surface topography

4.1.3 Summary of Baseline Conditions

The TMP under base-line conditions, increased from 70 to 95 psi over the 200hrs run time of the bench-scale NF membrane. The severe increase in required TMP indicated that the NF membrane became fouled under baseline conditions. Baseline conditions met AWWA (1999) feed-water quality guidelines for SDI which indicated SDI is not an appropriate parameter for NF feed water quality for feed-waters containing NOM (Glucina et al, 2007 and Geraldes et al, 2008). Other studies have found that MF was adequate in removing suspended solids but not effective for NF feed-water pre-treatment for waters with elevated NOM concentrations (Hong & Elimelech, 1997; Fan et al, 2001; Zularisam et al, 2006; Kim et al, 2007).

HP-SEC analysis indicated MF removed higher MW fractions as identified by the 79.9% and 53.5% removal of organic compounds greater than 5000 and 1500-5000Da respectively. This is consistent with findings from Fan et al (2001) and Lee et al (2004) that MF was effective in removal of high MW NOM. Kim et al (2007) found that fouling due to NOM caused rapid TMP increase due to adsorption of NOM onto the NF membrane. Membrane fouling resulted in a smoother appearance of membrane surface by SEM analysis similar to findings of Xu et al (2006). EDS of membrane fouling indicated inorganics substances were found on the fouled NF membranes; the inorganics had similar composition as inorganic foulants identified by a study with Xu et al (2006): silica, iron, copper, zinc and calcium.

The large 3.5% organics removal and TMP rate and SUVA value of 0.111psi/hrs and 3.04L/mg/cm indicated that additional pre-treatment would be required for additional removal of organics from the NF feed-water. Addition of coagulants prior to MF has been found to improve MF effectiveness of NOM removal (Fan et al, 2001; Zularisam et al, 2006; Glucina et al, 2007).

4.2 Determining Optimal Coagulant Dose and pH

To determine the optimal coagulation conditions for alum, PACl and $FeCl_3$, jar tests were performed at variable coagulant dose and pH. Lake Fletcher water with a TOC of 4.10 mg/L and DOC of 3.92 mg/L from July, 2012 was used to determine optimal coagulation conditions excluding additional analysis of PACl doses from 0.15 to 0.95 mg/L of Al.

4.2.1 Aluminum Sulphate Coagulation/MF Pre-Treatment

Jar tests were performed to determine the optimal coagulant conditions for in-line low-dose coagulation of alum. Alum conditions were assessed within a dose range of 0 to 1.3 mg/L of aluminum and at pH values of 5.2, 5.5 and 5.8. The results of the alum jar tests with TOC as a metric are shown in Figure 4.8.

Three optimal coagulant conditions for alum were selected: 0.6 mg/L of Al at pH 5.5, 0.7 mg/L of Al at pH 5.5, and 0.8 mg/L of Al at pH 5.2. The three optimal conditions were then assessed with SDI to ensure an improvement on baseline conditions. The SDI results for the three optimal coagulation conditions can be found in Table 4.2.

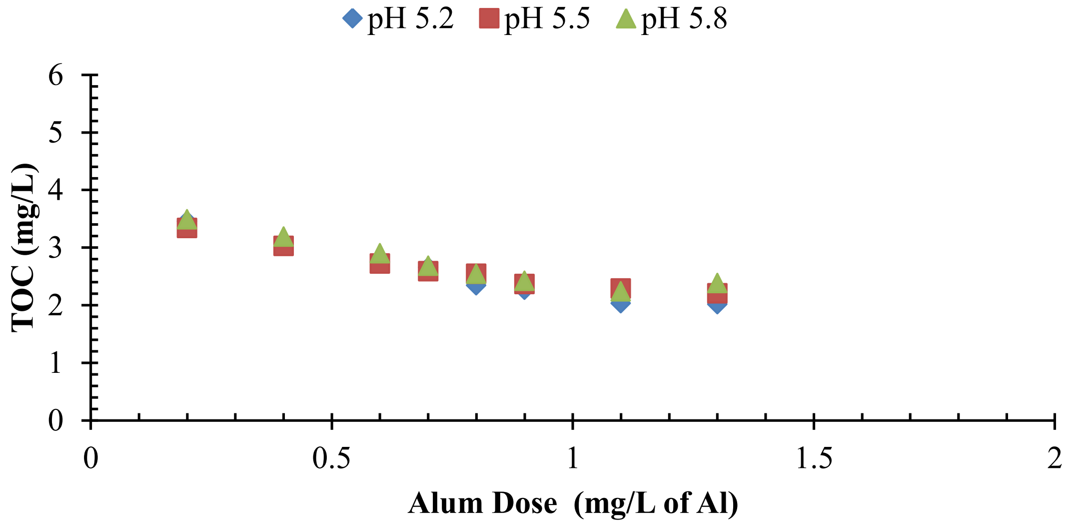


Figure 4.8 Selection of optimal aluminum sulfate dose/pH via TOC removal

Table 4.2 SDI analysis of optimal alum coagulation/MF pre-treatment

Coagulation Conditions	SDI Value (%/min)
0.6 mg/L of Al @pH 5.5	3.02
0.7 mg/L of Al @pH 5.5	2.49
0.8 mg/L of Al @pH 5.2	1.75

Table 4.3 NF feed-water quality 0.6mg/L of alum/MF at pH 5.5

Parameter	Value
TOC (mg/L of C)	2.72
UV_{254} (cm^{-1})	0.059
SUVA (L/mg/cm)	2.17
SDI (%/min)	3.02
Zeta Potential (mV)	-1.55
Conductivity (mS/cm)	0.195
Aluminum (µg/L)	101
Manganese (µg/L)	9.07
Iron (µg/L)	7.13

A dose of 0.6 mg/L of aluminum and a pH of 5.5 was selected as the optimal coagulation conditions for coagulation with alum because it was a significant improvement on baseline conditions SDI and was within the recommended feed-water SDI by AWWA of 3-5%/min. Optimal coagulation conditions resulted in good removal of humic matter as indicated by the SUVA value of 2.17 L/mg/cm. Optimal coagulation conditions for alum attained the feed-water quality shown in Table 4.3 for bench-scale NF testing.

The addition of alum at optimal coagulation conditions reduced the concentration of TOC from 4.10 to 2.72mg/L (31.2%) and resulted in an increased NF feed-water concentration of aluminum from 37.1 to 101µg/L. The SDI value was also decreased to 3.02%/min which is a large improvement on the baseline SDI of 4.40%/min. The zeta potential of the NF feed-water increased to -1.55 mV, which indicates near charge neutralization of NOM occurred. Charge neutralization indicated that the flocs would not be as strongly repelled by the negative membrane surface, as negatively charged NOM. Charge neutralization was also representative of stable floc formation.

4.2.2 Polyaluminum Chloride Coagulation/MF Pre-Treatment

Polyaluminum chloride conditions were assessed with a dose of 0 to 1.65 mg/L of aluminum at pH values of 5.7, 6.0 and 6.3. The results of the alum jar tests with TOC as a metric are shown in Figure 4.9. The PACl coagulation conditions were examined with Lake Fletcher water from two sampling dates with dissimilar NOM content. To account for unlike source water NOM concentrations, the % removal of TOC was assessed to determine the optimal coagulation conditions.

The three optimal PACl coagulant conditions were: 1.15 mg/L of Al at pH 5.7, 1.25 mg/L of Al at pH 5.7, and 1.25 mg/L of Al at pH 6.0. The SDI analysis of the three optimal coagulation conditions determined the suitability as NF membrane feed-water is found in Table 4.4.

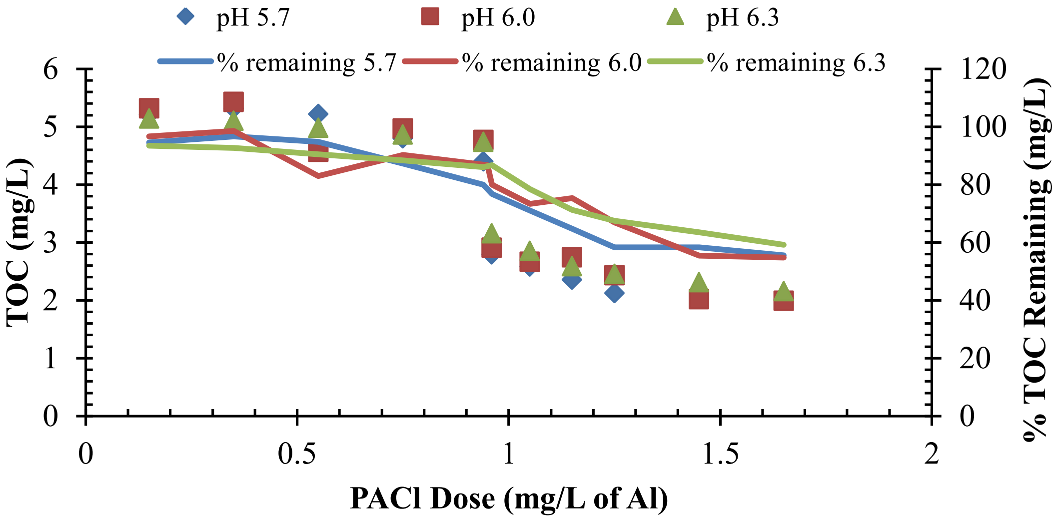


Figure 4.9 Selection of optimal polyaluminum chloride dose/pH via TOC removal

Table 4.4 SDI analysis of optimal PACl coagulation/MF pre-treatment

Coagulation Conditions	SDI Value (%/min)
1.15 mg/L of Al @pH 5.7	3.46
1.25 mg/L of Al @pH 6.0	3.04
1.25 mg/L of Al @pH 5.7	2.91

Optimal coagulation condition of 1.15 mg/L of Al and pH of 5.7 were determined for in-line coagulation with PACl/MF for Lake Fletcher with a SDI value of 3.46%/min. At 1.15mg/L of Al the pre-treatment attained sufficient reduction of SDI which was an improvement from the SDI of 4.40%/min at baseline conditions. Very good removal o humic matter was attained with the addition of PACl prior to MF as indicated by the SUVA value of 2.02 L/mg/cm. The water quality of the fore-mentioned conditions may be found in Table 4.5.

Table 4.5 NF feed-water quality 1.15mg/L of PACl/MF at pH 5.7

Parameter	Value
TOC (mg/L of C)	2.35
UV_{254} (cm^{-1})	0.0475
SUVA L/mg/cm)	2.02
SDI (%/min)	3.46
Zeta Potential (mV)	-1.95
Conductivity (mS/cm)	0.171
Aluminum (µg/L)	94.8
Manganese (µg/L)	0.332
Iron (µg/L)	1.76

Pre-treatment with polyaluminum chloride addition prior to MF resulted in increased feed-water quality by reducing TOC from 4.10 to 2.35 mg/L (40.4%) and SDI by 0.94%/min. PACl/MF resulted in a significant zeta potential increase of the feed-water from -21.2 to -1.945mV indicating charge neutralization occurred. Addition of polyaluminum chloride resulted in an increase in aluminum concentration from 20 to 95µg/L, indicating aluminum-based coagulation increases the concentration of dissolved aluminum to the NF feed-water.

4.2.3 Ferric Chloride Coagulation/MF Pre-Treatment

Coagulation conditions of ferric chloride were assessed with a dose of 0 to 1.0 mg/L of iron at pH of 4.7, 5.0 and 5.3. TOC removals with ferric chloride coagulation under the above conditions are shown in Figure 4.10.

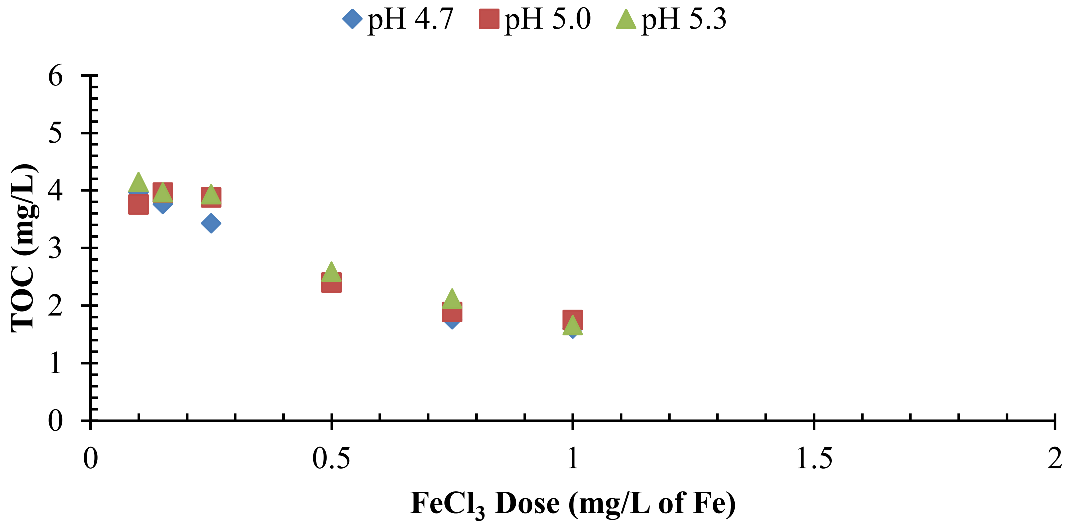


Figure 4.10 Selection of optimal ferric chloride dose/pH via TOC removal

The three optimal coagulation conditions for pre-treatment with $FeCl_3$ coagulation/MF were determined to be: 0.5 mg/L of Fe at pH 5.0, 0.75 mg/L of Fe at pH 5.0, and 0.75 mg/L of Fe at pH 4.7 as the slope decreased as an increase in FeCl3 did not correspond to a significant increase of NOM removal. The three optimal ferric chloride coagulation/MF SDI analysis results are below in Table 4.6.

Table 4.6 SDI analysis of optimal $FeCl_3$ coagulation/MF pre-treatment

Coagulation Conditions	SDI Value (%/min)
0.5 mg/L of Fe @pH 5.0	3.39
0.75 mg/L of Fe @pH 5.0	3.05
0.75 mg/L of Fe @pH 4.7	2.74

From SDI analysis, a coagulation condition of 0.5 mg/L of Fe at a pH of 5.0 with a SDI value of 3.39%/min was selected as optimal as it was a significant reduction on current operation conditions SDI by addition of only 0.5mg/L of Fe. Very good removal of humic matter was attained with the addition of $FeCl_3$ prior to MF as indicated by the

SUVA value of 2.06 L/mg/cm. The water-quality of the optimal $FeCl_3$ condition is below in Table 4.7.

Table 4.7 NF feed-water quality 0.5mg/L of $FeCl_3$/MF at pH 5.0

Parameter	Value
TOC (mg/L of C)	2.40
UV_{254} (cm^{-1})	0.0495
SUVA (L/mg/cm)	2.06
SDI (%/min)	3.39
Zeta Potential (mV)	-4.60
Conductivity (mS/cm)	0.191
Aluminum (µg/L)	7.52
Manganese (µg/L)	43.3
Iron (µg/L)	74.1

Analysis of feed-water quality post $FeCl_3$/MF showed a great improvement on current operation feed-water quality. There was significant NOM removal as indicated by a significant reduction of TOC from 4.10 to 2.40 mg/L (39.3%). Addition of an iron-based coagulant resulted in increased iron concentrations from 12 to 74µg/L. The zeta potential of the $FeCl_3$/MF pre-treatment was -4.6mV indicating that charge neutralization did not occur and coagulation conditions were under-dosed.

4.2.4 Comparison of Coagulants

Addition of in-line coagulation prior to MF resulted in increased removal of NOM for NF feed-water. The optimal coagulation conditions for the three coagulants are in Table 4.8.

Table 4.8 Pre-treatment coagulation conditions

Pre-Treatment Type	Coagulant Dose	pH
Non-coagulated/MF	--	6.8
Aluminum sulfate/MF	0.6 mg/L of Al	5.5
Polyaluminum chloride/MF	1.15 mg/L of Al	5.7
Ferric chloride/MF	0.5 mg/L of Fe	5.0

Ferric chloride was the coagulant that required the smallest dose, 0.5mg/L to obtain improved removal of NOM and SDI reduction from NF feed-water. Alum also required a low dose of 0.6mg/L while PACl required 1.15mg/L for equivalent removal of NOM and particulate matter. This was consistent with findings that ferric chloride required a lower dosage than aluminum-based coagulants for equivalent NOM removal (Hillis, 2006; Guigui et al, 2002). Guigui et al (2002) and Tabatabai et al (2009) both found $FeCl_3$ was effective at 0.5-1.0mg/L at pH 5-5.5 for reduction of NOM and SDI. However, Tabatabai et al (2009) found that at 0.5mg/L and below, $FeCl_3$ formed small flocs that increased cake resistance. Choi & Dempsey (2004) and Tabatabai et al (2009) found similar coagulation conditions for PACl and alum, respectively.

Charge neutralization and under-dose coagulation conditions for both aluminum- and iron-based coagulants respectively, were effective in removal of NOM as indicated by Figure 4.11. These results were consistent with findings from Choi and Dempsey (2004). Coagulant addition resulted in about 30% NOM removal for all coagulant types. PACl and $FeCl_3$ were most effective in NOM removal with 37% TOC reduction.

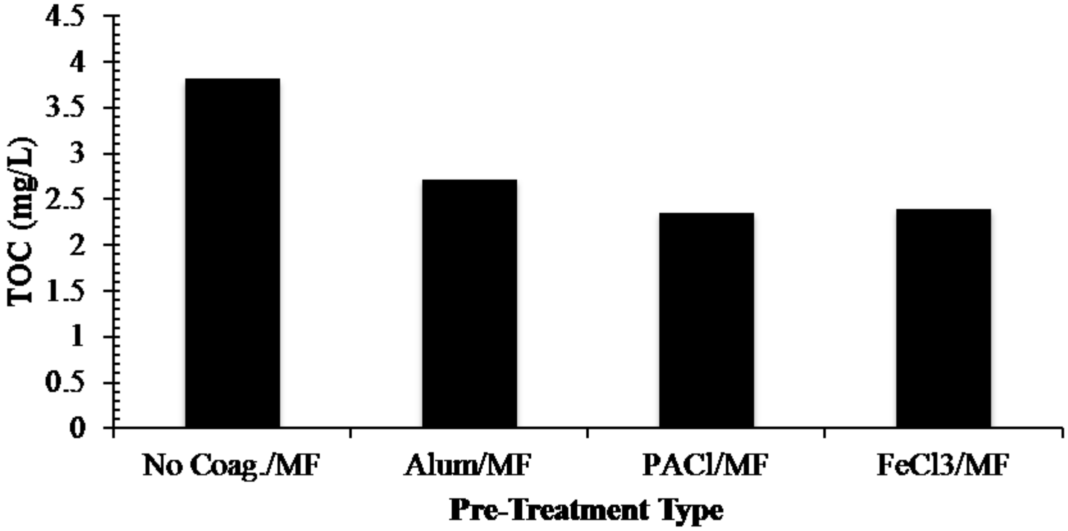


Figure 4.11 Analysis of pre-treatment NOM removal

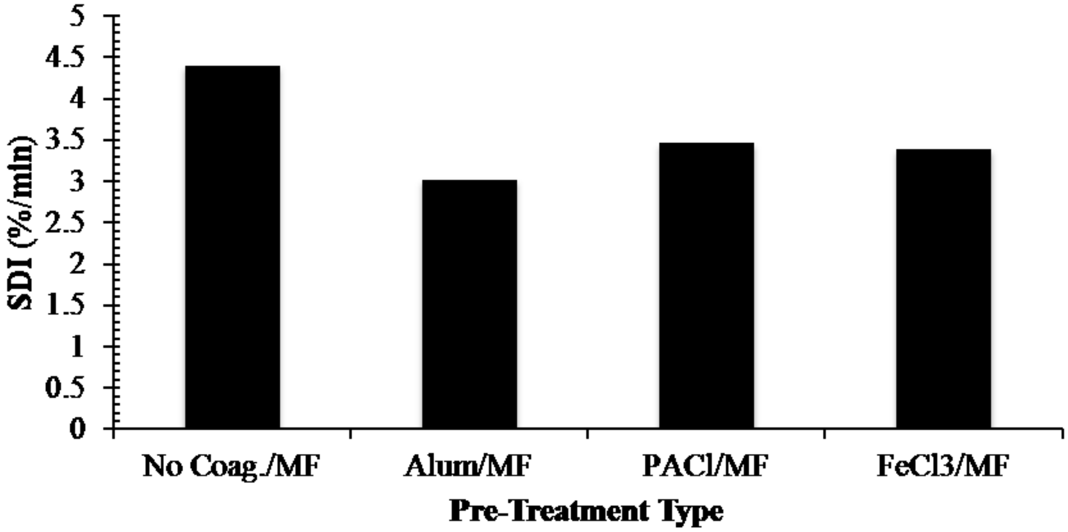


Figure 4.12 Analysis of pre-treatment particulate removal

The reduction of feed-water NOM with pre-treatment contributed to a reduction of NF feed-water SDI. Pre-treatment with coagulation was capable of reducing the SDI by greater than 20%. Reduction of TOC did not have a correlation with SDI reduction as

SDI is a measure of particulates and organic fouling mechanisms are not accounted for (Sutzkover-Gutman et al, 2002). The SUVA values indicated that the humic fraction was reduced with the addition of all three coagulant types. Alum was most effective in particulate removal as indicated by the 31% reduction in SDI.

Analysis of the effect of coagulant addition on relevant metals concentrations from baseline conditions was observed (Figure 4.13). The addition of metal-based coagulants increased the metals concentrations of the NF feed-waters. The addition of alum and PACl increased the concentration of aluminum by 80.3 and 74.2µg/L respectively. Addition of $FeCl_3$ resulted in an increase of 62.2µg/L of iron in the NF feed-water. Tabatabai et al (2009) found that increasing the pH from 5.5 to 6.2 for aluminum-based coagulants significantly reduced the aluminum residual. However, Choi & Dempsey (2004) found that there was a low aluminum residual at conditions of 0.59mg/L of Al at a pH of 5.5. Increased metals concentrations have been found to interact with humic matter and increase UF membrane fouling (Hao et al, 2011).

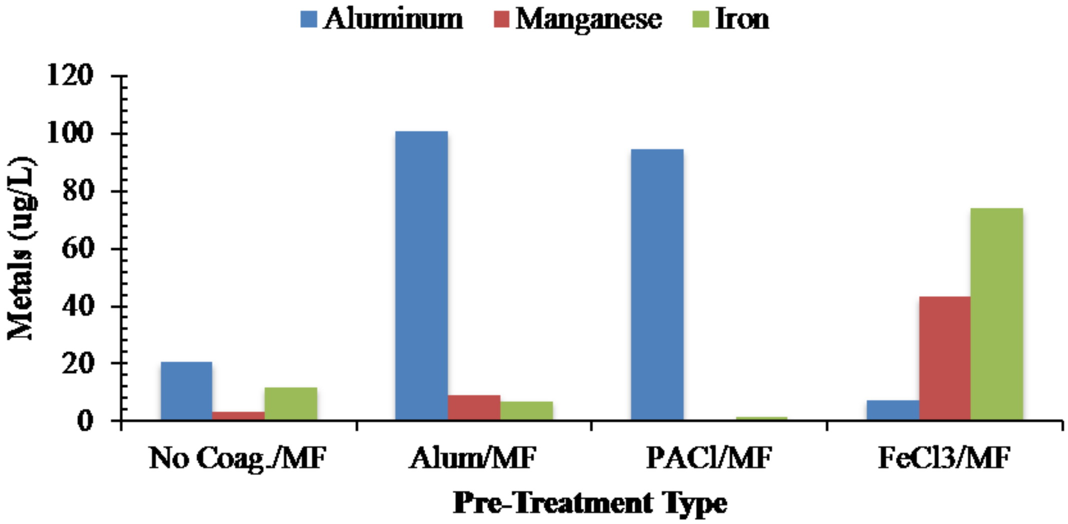


Figure 4.13 Analysis of pre-treatment metals removal

4.3 Bench-Scale Analysis of In-Line Coagulation/MF as Pre-Treatment

Bench-scale trials to simulate NF membrane fouling were performed to assess the impact of in-line coagulant addition prior to MF for three coagulants. Each trial was performed with Lake Fletcher water from unique dates that varied in quality from each other and from Section 4.2.

4.3.1 Aluminum Sulphate

Alum was dosed at pre-determined optimal coagulation conditions of 0.6 mg/L at pH of 5.5. The water was then microfiltered, batched and applied as feed-water for bench-scale NF. The water quality of the permeate and feed-water of the NF system from the alum/MF trial are in Table 4.9. The following parameters were held relatively constant throughout the 200hrs bench-scale NF operation.

Table 4.9 NF bench-scale water quality post alum/MF

Parameter	Permeate	Feed
TOC (mg/L of C)	0.284 ± 0.127	2.91 ± 0.283
UV_{254} (cm^{-1})	0.0022 ± 0.0007	0.080 ± 0.0080
Aluminum (µg/L)	17.7 ± 26.8	52.7 ± 38.6
Manganese (µg/L)	7.00 ± 5.70	28.5 ± 7.28
Iron (µg/L)	2.01 ± 10.9	20.4 ± 50.2

The feed-water possessed relatively low concentrations of organics and metals as indicated by Table 4.9. The concentration of organics was significantly reduced by 46.3% within the pre-treatment stage as shown in the NOM mass balance shown below in Figure 4.14. This NOM reduction via pre-treatment increased the quality of the feed-water resulting in retention of 149mg (46.1%) of NOM within the NF membrane.

Alum/MF pre-treatment was capable of reducing both low and high MW ranges (Figure 4.15). NOM sizes of 5000Da and greater were completely removed with pre-treatment. A 67.7% reduction of the 1500-5000Da range was also accomplished. Low removal of NOM less than 1500Da was obtained with alum/MF. The NF removal had high retention of NOM between 1000 and 5000Da but not NOM less than 1000Da.

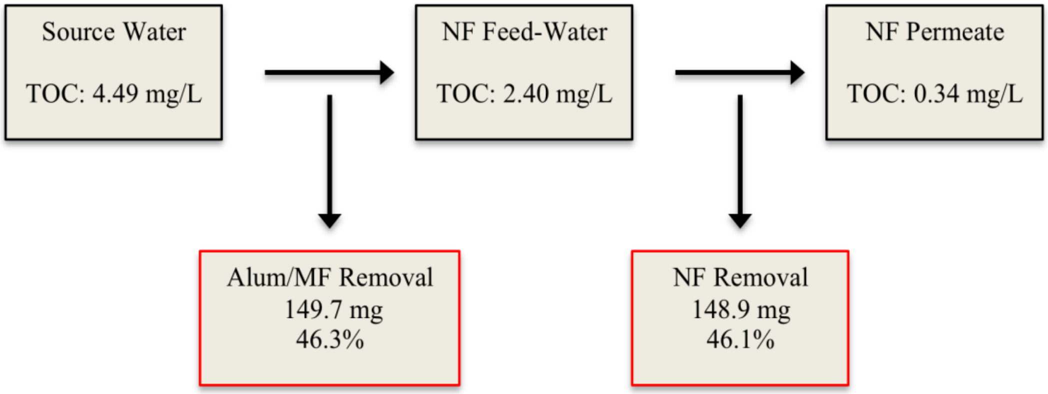


Figure 4.14 Analysis of NOM removal with alum/MF pre-treatment

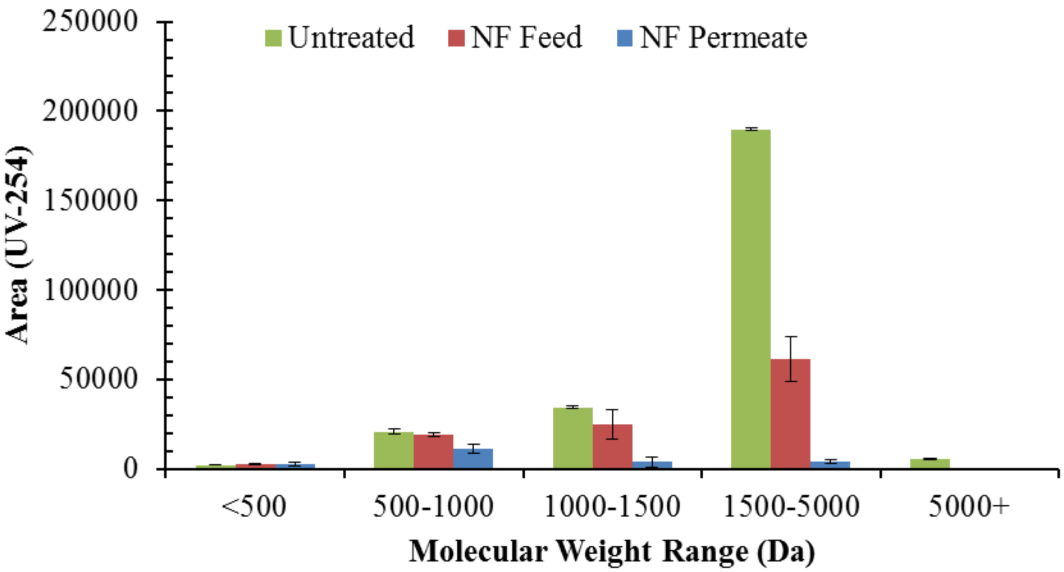


Figure 4.15 HP-SEC of NF bench-scale organic fraction removal with alum/MF pre-treatment (error bars represent standard deviation)

The concentration of metals in the NF feed-water was monitored to assess whether the addition of a metal-based coagulant had a significant effect of the metals concentration entering the bench-scale system. As shown in Figure 4.16, the addition of alum resulted in an increase of aluminum concentration from the source to the pre-treated water. There was also an increase in manganese concentration.

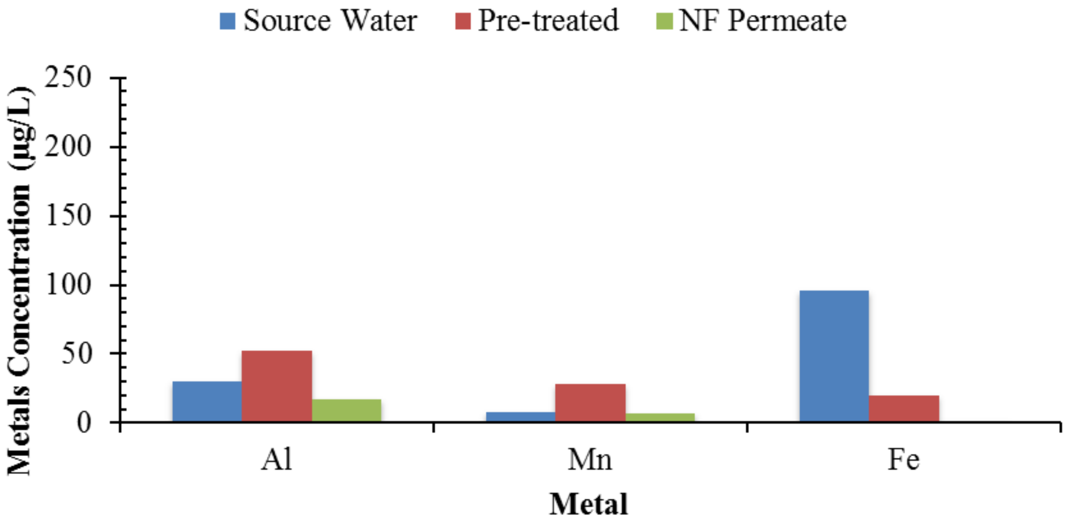


Figure 4.16 Analysis of metals concentration with alum/MF pre-treatment

The TMP did not linearly increase over the 200hrs run-time for pre-treatment with alum/MF (Figure 4.17). The TMP rose drastically within the first 50 hours of operation before leveling off and then spiking once again at the 150hrs mark. The sharp increases in TMP may have been due to severe reduction of the cross-flow velocity. The cross-flow velocity was very difficult to maintain at steady flow throughout the alum/MF trial. The alum/MF pre-treatment trial was not successful in reduction of TMP as the TMP increased by nearly 100% and had the same TMP at 200hrs as the trial under baseline conditions. When the value of the cross-flow velocity approached zero, the NF membrane operated in dead-end filtration mode and resulted in increased cake resistance and fouling rates. The TMP for the bench-scale NF trial with alum/MF pre-treatment increased at a rate of 0.170psi/hrs and averaged 69.7psi over the 200hrs NF operation.

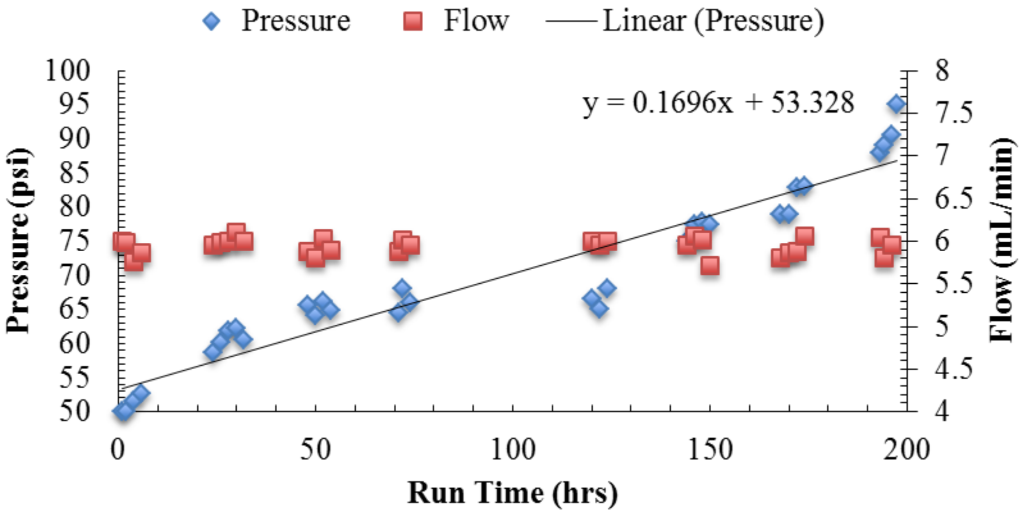


Figure 4.17 TMP increase over 200hrs operation with alum/MF pre-treatment

4.3.2 Polyaluminum Chloride

PACl/MF was assessed for NF feed-water pre-treatment under coagulation conditions of 1.15mg/L of Al at pH 5.7. The PACl/MF trial was performed with Lake Fletcher water sampled in November 2012, when Lake Fletcher NOM concentrations were most elevated. Permeate and feed-water quality for the 200hrs bench-scale NF trial is shown in Table 4.10. The concentrations of NOM were held relatively constant throughout the trial, however the metals were able to overcome feed tank mixing and settle out during the 200hrs run time as indicated by the large variances in feed-water metals concentrations.

Pre-treatment with PACl/MF effectively reduced the concentrations of influent NOM to the bench-scale NF system (Figure 4.18). Following PACl coagulation the MF membrane retained 121mg (29.7%) of NOM that resulted in the NF membrane retention of 269mg (65.9%) of NOM. The NF bench-scale system attained very good NOM removal with a permeate TOC concentration of 0.25mg/L, below the equipment RDL of 0.3mg/L.

Table 4.10 NF bench-scale water quality post PACl/MF

Parameter	Permeate	Feed
TOC (mg/L of C)	0.252 ± 0.039	3.99 ± 0.218
UV_{254} (cm^{-1})	0.0019 ± 0.0008	0.130 ± 0.0091
Aluminum (µg/L)	11.2 ± 9.25	64.1 ± 41.3
Manganese (µg/L)	1.20 ± 0.761	5.48 ± 3.14
Iron (µg/L)	22.1 ± 21.3	34.6 ± 24.2

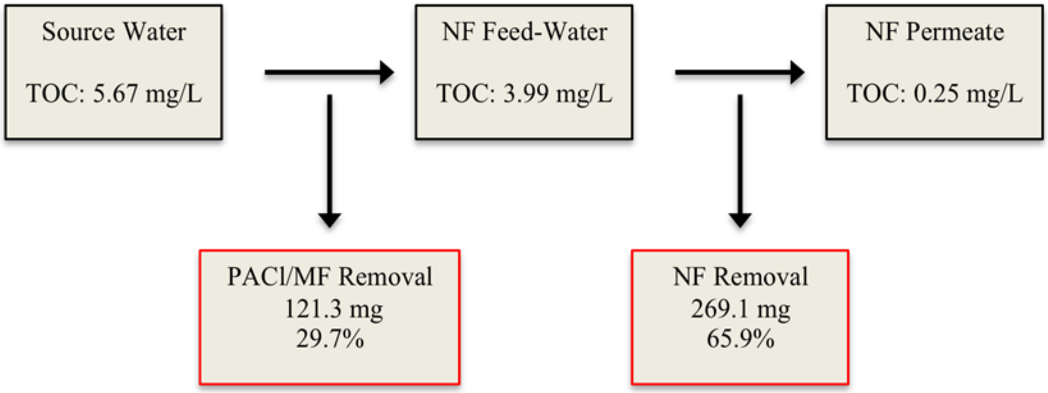


Figure 4.18 Analysis of NOM removal with PACl/MF pre-treatment

HP-SEC analysis indicated that high MW NOM was effectively removed by pre-treatment (Figure 4.19). The removal of NOM with PACl/MF pre-treatment was 42.7% and 94.8% for MW ranges 1500-5000Da and greater than 5000Da respectively. The NF membrane retained NOM with MW greater than 1000Da and achieved 63.2% removal of NOM between 500 and 1000Da.

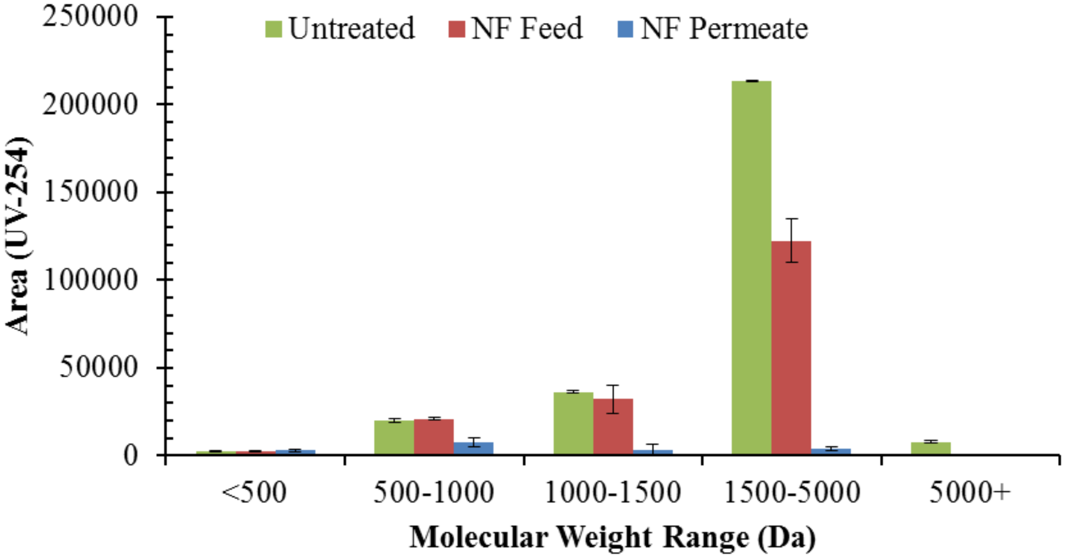


Figure 4.19 HP-SEC of NF bench-scale organic fraction removal with PACl/MF pre-treatment (error bars represent standard deviation)

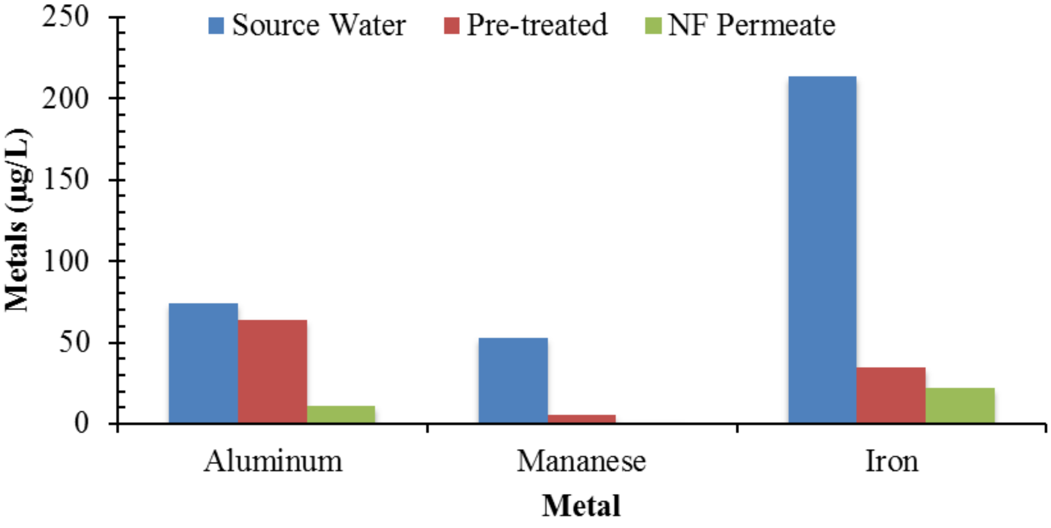


Figure 4.20 Analysis of metals concentration with PACl/MF pre-treatment

Pre-treatment effectively reduced the concentrations of manganese from 53.1 to 5.48μg/L and iron from 214 to 34.6μg/L. Pre-treatment had little effect on aluminum concentration. Minimal manganese was retained with the NF membrane although retention of aluminum and iron were evident (Figure 4.20).

The reduction of NOM with PACl/MF pre-treatment did not result in as great of a TMP increase as baseline conditions over the 200hrs run time of the bench-scale NF membrane. The initial TMP of 60 psi was maintained for nearly 150hrs of operation, indicating minimal fouling occurred until this point. The sudden increase in TMP at 150hrs may be concurrent with partial or full blockage of membrane pores. The TMP for the NF bench-scale set-up with PACl/MF feed-water decreased slightly at a rate of 0.0734psi/hrs and averaged 66.0psi.

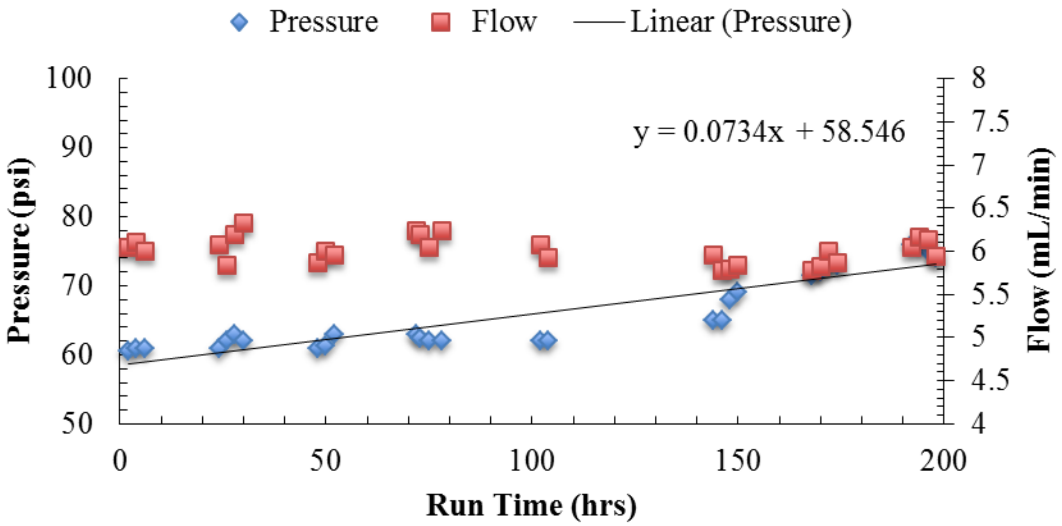


Figure 4.21 TMP increase over 200hrs operation with PACl/MF pre-treatment

4.3.3 Ferric Chloride

Optimal coagulant conditions for $FeCl_3$/MF pre-treatment were determined to be 0.5mg/L of Fe at pH 5.00. This trial was performed in October 2012 when Lake Fletcher TOC levels were 5.30mg/L. The NF permeate and feed-water quality may be found in Table 4.11.

Table 4.11 NF bench-scale water quality post $FeCl_3$/MF

Parameter	Permeate	Feed
TOC (mg/L of C)	0.271 ± 0.126	2.32 ± 0.175
UV_{254} (cm^{-1})	0.0030 ± 0.0011	0.0477 ± 0.0026
Aluminum (µg/L)	2.41 ± 2.34	10.9 ± 6.10
Manganese (µg/L)	18.6 ± 2.92	83.8 ± 3.12
Iron (µg/L)	3.25 ± 5.99	33.7 ± 62.9

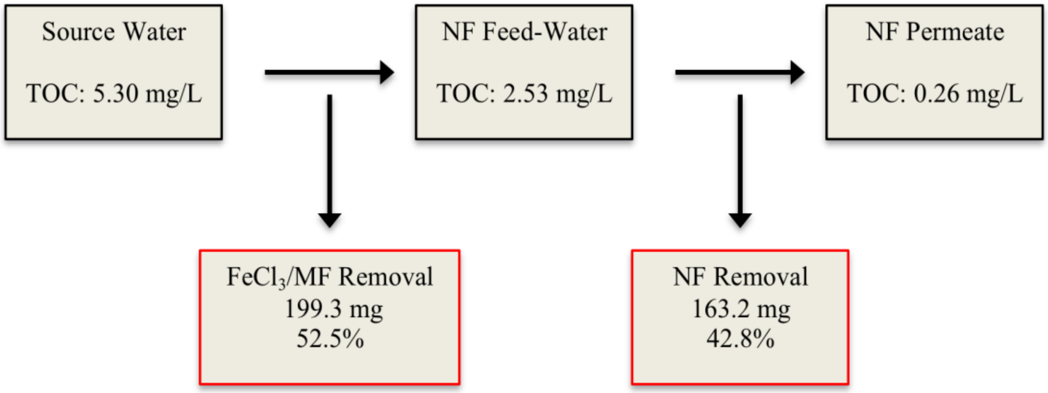


Figure 4.22 Analysis of NOM removal with $FeCl_3$/MF pre-treatment

$FeCl_3$/MF was very effective in removal of NOM. Figure 4.22 shows that 199mg (52.5%) of NOM was removed with pre-treatment, which greatly reduced the NOM retained by the NF membrane to only 163mg (43.8%). $FeCl_3$/MF resulted in a larger amount of NOM removal within the MF membrane than the NF membrane.

HP-SEC analysis found that near complete removal of high MW NOM could be obtained with $FeCl_3$/MF as indicated by the 92.1% and 100% removal of MW ranged 1500-5000Da and greater than 5000Da, respectively (Figure 4.23). The range of MW NOM foulant for the NF membrane was 1000-1500Da with 82.1% retained by the NF membrane.

The addition on $FeCl_3$ did not result in an increased iron concentration (Figure 4.24). An unexpected increase in manganese concentration with pre-treatment resulted in a high retention of manganese with NF during the 200hrs NF run time. A very large range of iron concentrations existed within the feed tank, which indicated that settling forces of iron was able to overcome the mixing force.

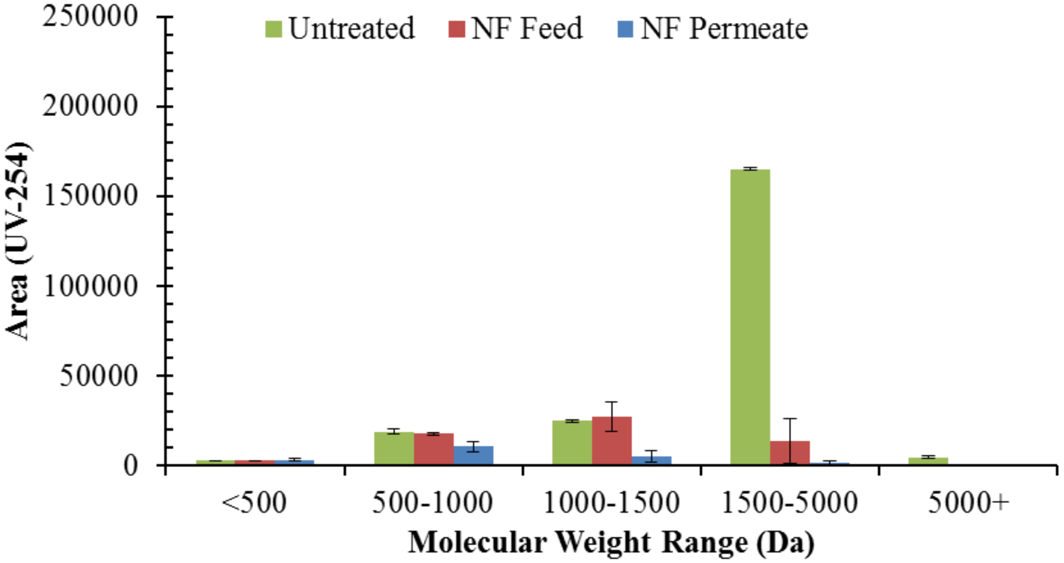


Figure 4.23 HP-SEC of NF bench-scale organic fraction removal with $FeCl_3$/MF pre-treatment (error bars represent standard deviation)

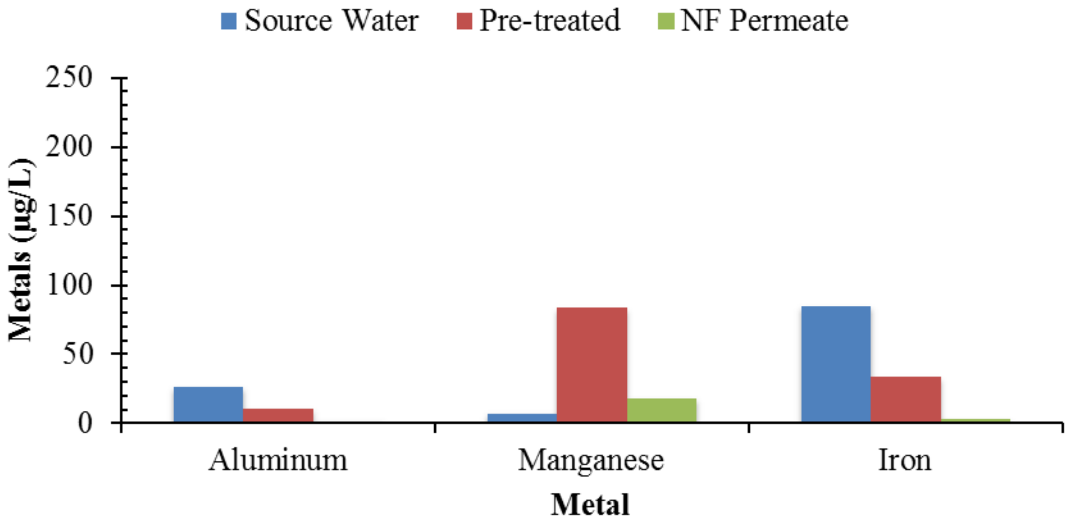


Figure 4.24 Analysis of metals concentration with $FeCl_3$/MF pre-treatment

NF feed-water pre-treatment with $FeCl_3$/MF pre-treatment led to decreased TMP increase over the 200hrs run time of the bench-scale NF membrane compared to baseline conditions. The initial TMP was 60 psi and remained relatively constant over the 200hrs run-time. The divergence from the linear increase in TMP is consistent with variation of the feed-tank water temperature that occurred between 120 and 170hrs. The TMP for the NF bench-scale set-up with $FeCl_3$/MF feed-water increased at a rate of 0.0422psi/hrs and averaged 63.0psi.

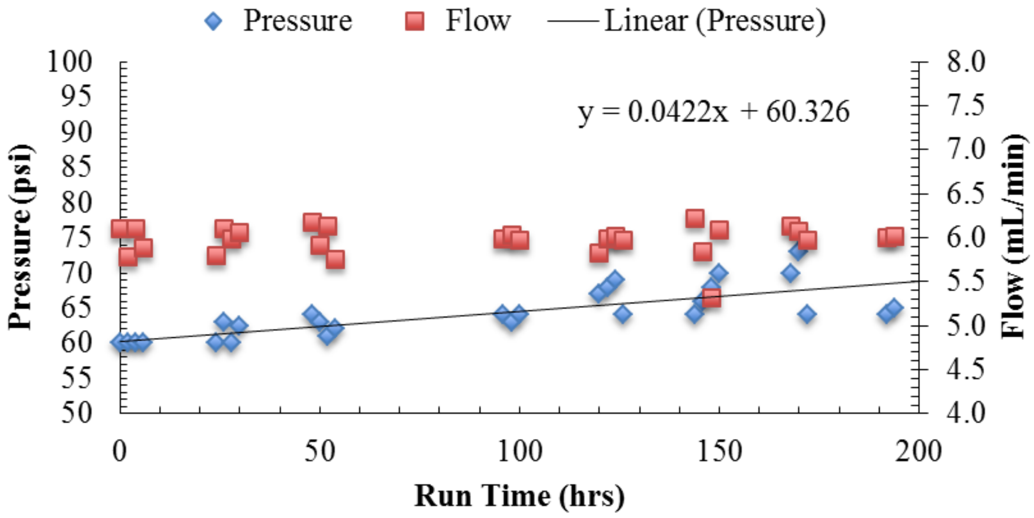


Figure 4.25 TMP increase over 200hrs operation with $FeCl_3$/MF pre-treatment

4.3.4 Membrane Analysis

Membrane analysis was performed with SEM to obtain surface morphology images for qualitative analysis of the NF membrane foulant surface. SEM imaging identified three likely types of dominant fouling: NOM, inorganics and bacteria. The semi-uniform cake layer, rod-shaped matter and irregularly shaped particulates were presumed to be NOM, bacteria and inorganics respectively. Cracks within the cake-layer were assumed to be a result of membrane drying and not membrane tears.

SEM analysis of the fouled NF membrane from the Alum/MF trial is shown below in Figure 4.26. The TMP increase from 50 to 95psi indicated that severe fouling occurred during the alum/MF trial. The SEM image indicates that the majority of the fouling that occurred was NOM fouling due to the retention of organic matter within the feed-water.

Evidence of bacteria within the cake layer was evident. The deep cracks from membrane drying were indicative of a thick foulant layer that corresponds to a large TMP increase. The surface topography appears to be relatively smooth and uniform with evidence of inorganics deposition.

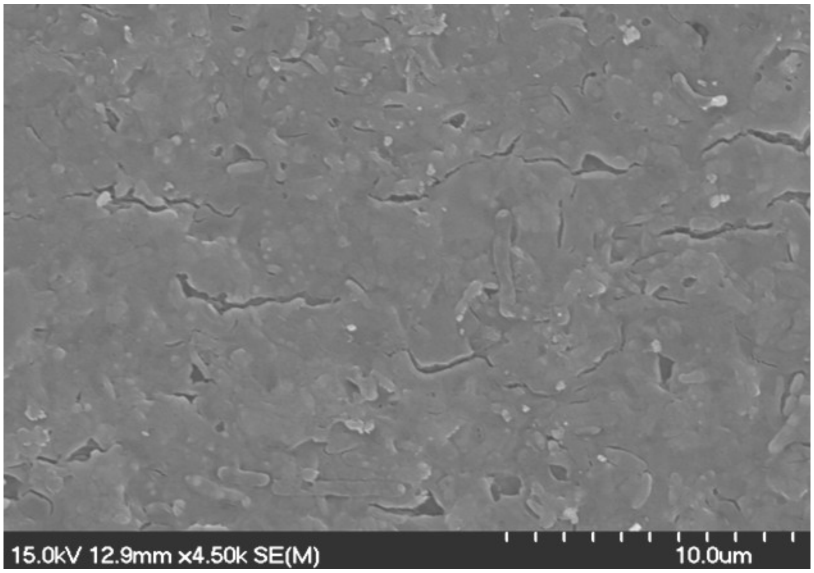


Figure 4.26 SEM imaging of fouled NF membrane post alum/MF pre-treatment

The SEM analysis of the fouled NF membrane from the PACl/MF trial is shown below in Figure 4.27. The foulant layer consisted of a very large quantity of bacteria, which resulted in a very rough surface topography. A rough surface topography may correspond to the TMP increase in the final hours of bench-scale NF operation as contaminants are collected within the foulant layer valleys. The deposition of bacteria likely did not result in TMP increase as the relatively large size of bacteria would result in a porous substructure that water can pass through. High levels of bacteria, NOM and metals characterized this trial and are likely a result of seasonal variation. Retention of NOM by the NF membrane was also evident with a cake layer covering the membrane pores and fibres. The thickness of the foulant layer appears to vary with location and relative thickness is difficult to determine due to the large amount of bacteria.

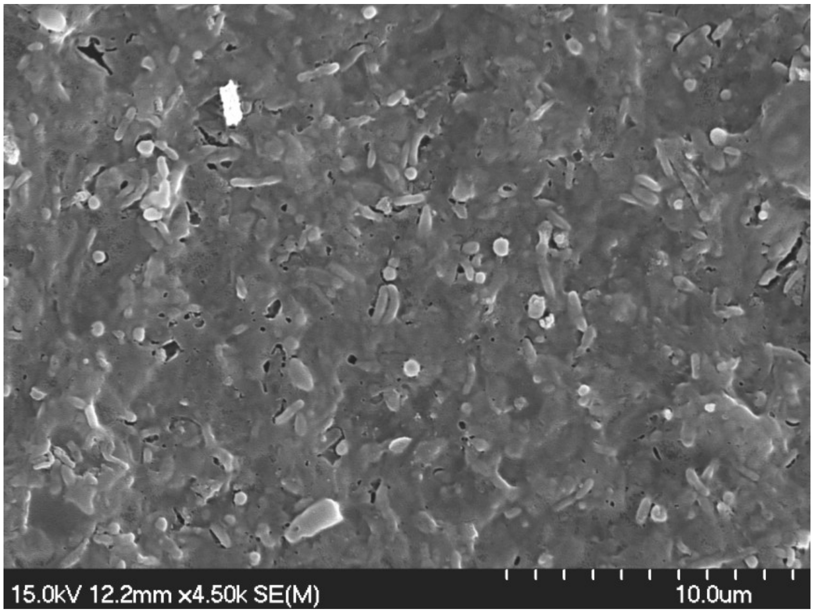


Figure 4.27 SEM imaging of fouled NF membrane post PACl/MF pre-treatment

SEM imaging of the fouled NF membrane from the $FeCl_3$/MF trial is below in Figure 4.28. Relatively few bacteria are present and the major foulant constituent appears to be NOM. The small, shallow cracks due to drying indicate that the foulant layer is relatively thin; this is also consistent with the low TMP increase throughout the 200hrs bench-scale run time.

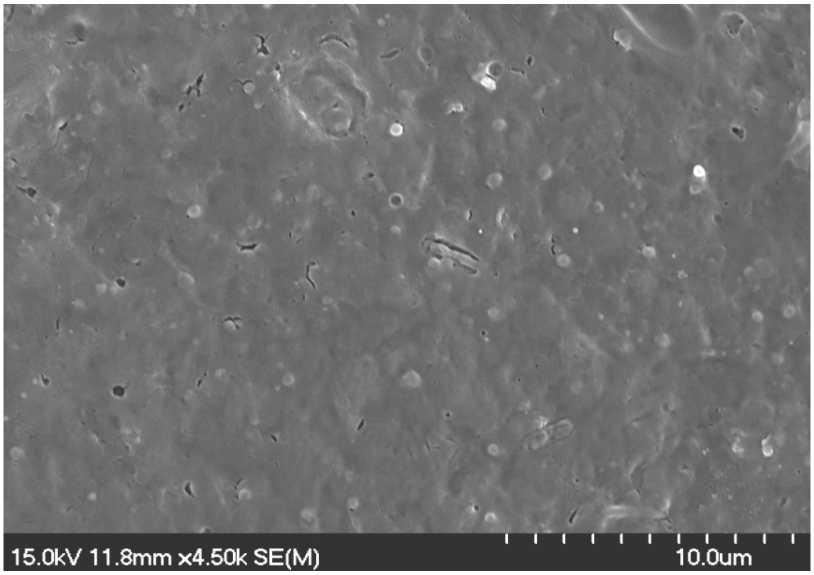


Figure 4.28 SEM imaging of fouled NF membrane post $FeCl_3$/MF pre-treatment

Membrane analysis indicated that the $FeCl_3$/MF trial had a thin foulant layer with little bacterial content, especially compared to the PACl/MF trial. The PACl trial had the most bacteria collected within the foulant layer that did not appear to have a direct effect on the TMP. Alum had the highest TMP increase which likely corresponded to the thick NOM cake layer. Tabatabai et al (2009) found that the addition of low-dose coagulants substantially decreased the TMP during NF operation.

4.3.5 Comparison of Pre-Treatment Type and Bench-Scale NF Operation

All three of the coagulation conditions showed improved removal rates of NOM from the NF feed-water. The mass balance of NOM removal from the MF and NF systems for each trial is shown in Figure 4.29. A standardized mass balance of NOM removal within the MF/MF system is shown in Figure 4.30 to account for seasonal variation of Lake Fletched NOM content. The seasonal variation in feed-water quality is evident all four trials had varying concentrations of NOM and metals. $FeCl_3$/MF showed superior pre-treatment NOM removal although PACl/MF obtained the greatest NOM removal for the entire MF/NF system. Alum/MF had similar NOM removal as $FeCl_3$/MF pre-treatment, but was not as effective in NF removal.

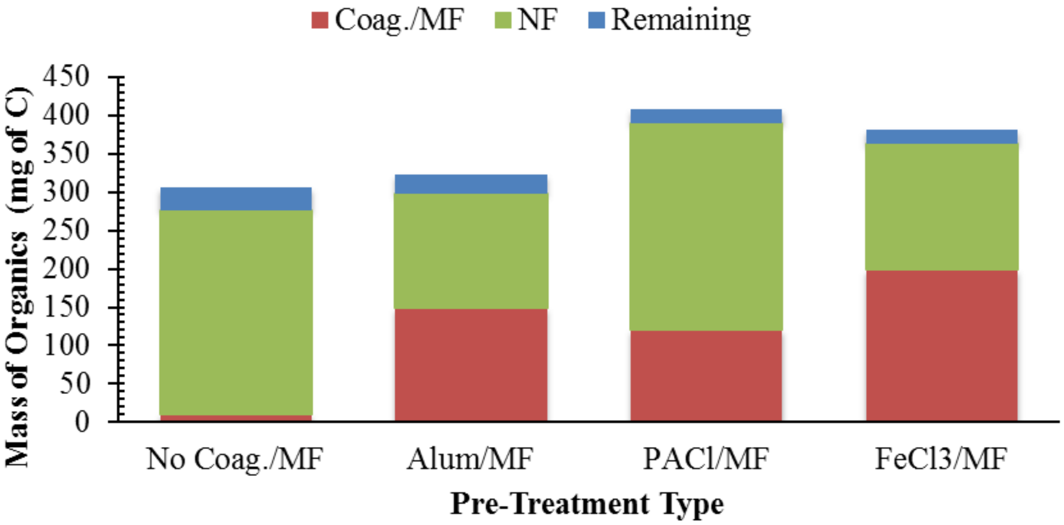


Figure 4.29 Mass balance of NOM removal with pre-treatment type

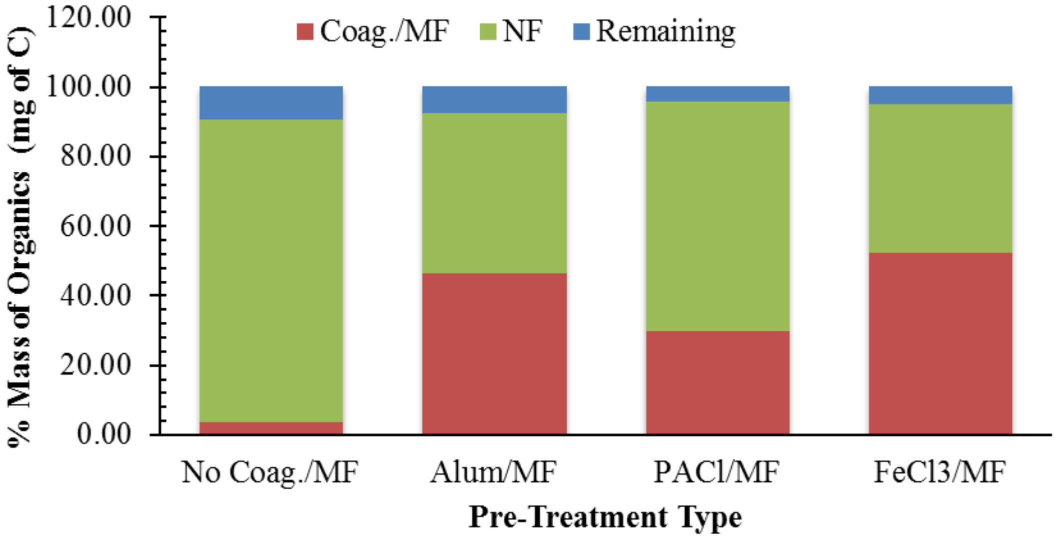


Figure 4.30 Standardized mass balance of NOM removal

The average TOC concentration of the PACl/MF permeate was 3.99mg/L and was not a significant improvement on Non-Coag./MF feed-water with average concentration of 3.81mg/L ($\alpha = 0.05$). Pre-treatment with $FeCl_3$/MF and Alum/MF significantly improved TOC reduction with TOC concentrations of 2.24mg/L and 2.92mg/L, respectively. PACl/MF had a decreased percent NOM removal from the preliminary trials which may indicate that an increased coagulant dose was required at decreased water qualities compared to $FeCl_3$ and Alum (Volk et al, 2000)

NOM removal effectiveness within the MF/NF system did not appear to be dependent on NF feed-water quality. PACl/MF significantly had the lowest TOC concentrations in the NF permeate with 0.252mg/L. This may be due varying charge densities. Yoon et al (2005) found that charge density was the most important factor in flux decline and NOM retention. The Alum/MF NF permeate (TOC = 0.284mg/L) was a significant improvement on baseline conditions (TOC = 0.379mg/L) but did not differ statistically from the TOC concentrations of $FeCl_3$/MF NF permeate (TOC = 0.341mg/L). $FeCl_3$/MF NF permeate TOC concentration did not statistically differ from baseline conditions.

The removal of certain fractions of NOM from the source water to the NF feed and permeate are shown in Table 4.12 and Table 4.13 respectively. The negative values that are present in some of the smaller MW ranges are representative of NOM breakdown due to turbulence in within either the MF or NF system.

Pre-treatment NOM removal occurred mostly in the larger MW ranges: 1500Da or greater, humic matter (Gorenfio et al, 2002). FeCl3/MF and Alum/MF obtained 100% removal of NOM greater than 5000Da and had superior removal of NOM within 1500 and 5000Da. The PACl/MF had higher removal of NOM with MW greater that 5000Da, but had lower removal of NOM with MW less than 5000Da than baseline conditions. FeCl3/MF had superior removal of NOM greater than 1500Da for all pre-treatment types; this is consistent with findings from Volk et al (2002).

Table 4.12 Percent removal of NOM MW fractions with pre-treatment

MW Range (Da)	MF	Alum/MF	PACl/MF	$FeCl_3$/MF
<500	19.7	-18.6	5.65	1.08
500-1000	26.6	7.69	-5.16	6.69
1000-1500	22.9	28.4	11.7	-8.93
1500-5000	53.4	67.7	42.7	91.9
5000+	84	100	94.9	100

NF had poor removal of NOM within the NOM MW range of 500-1000Da with % removal ranging from 44.5 to 70.1%. The membrane manufacturer, membrane specifications indicate a MWCO of 300Da and the results in Table 4.13 are not in agreement. Presence of metal ions has been found to reduce NF membrane retention of NOM (Liikanen et al, 2004). Cho et al (2000) found that NF membrane MWCO was dependent on feed-water NOM characteristics.

Table 4.13 Percent removal of NOM MW fractions with NF

MW Range (Da)	MF	Alum/MF	PACl/MF	$FeCl_3$/MF
<500	-2.28	-17.2	-14.8	-22.5
500-1000	70.1	46.0	61.3	44.5
1000-1500	96.0	89.1	90.6	80.4
1500-5000	99.1	97.8	98.2	99.2
5000+	100	100	100	100

Concerns associated with adding a metal-based coagulant were that the coagulant would not fully precipitate and would result in an increased metals concentration. The addition of PACl resulted in a significantly greater aluminum concentration following MF of 64.1µg/L compared to non-coagulated, alum and $FeCl_3$ coagulant conditions which had aluminum concentrations of 20.6, 52.7, and 12.9µg/L respectively. Due to the large variation in feed-water quality the aluminum concentration of alum/MF did not significantly differ from baseline conditions although it was significantly higher than $FeCl_3$/MF conditions. There was no statistical difference of iron concentrations with $FeCl_3$/MF pre-treatment within the feed water with concentrations of iron ranging from 15.2 to 34.6µg/L.

The addition of metal-based coagulants did not have a significant effect on NF permeate concentrations of aluminum or iron. All monitored metals met the Guidelines for Canadian Drinking Quality (2012). Aluminum has an operational guidance value of 100µg/L and the NF permeate of baseline, Alum/MF, PACl/MF, and $FeCl_3$/MF were below the suggested value with average concentrations of 2.79, 17.7, 11.2 and 1.90µg/L (GCDWQ, 2012).

The aesthetic objective for iron concentration is 300µg/L and NF permeates of baseline, Alum/MF, PACl/MF and $FeCl_3$/MF were well below this objective with respective iron concentrations of 1.78, 2.01, 22.1 and 0µg/L (GCDWQ, 2012). Manganese concentrations were relevantly similar and did not exceed 30µg/L for any NF feed-waters or 10µg/L for all NF permeates. This is within the Guidelines for Canadian Drinking Water Quality (2012) that recommends an aesthetic objective of 50µg/L.

The amount of metals and NOM retained as well as physical operational conditions of the bench-scale NF membrane impacted the required feed pressure for NF filtration. Figure 4.31 depicts the required pressure throughout the 200hrs run time for each pre-treatment condition. All trials with coagulant addition except Alum/MF resulted in a lower TMP rate and all coagulated trials significantly reduced the average TMP on baseline conditions. The TMP rates were 0.111, 0.170, 0.0734 and 0.0422psi/hrs for baseline conditions, alum/MF, PACl/MF and $FeCl_3$/MF respectively. This corresponds to the removal of humic matter with PACl/MF and $FeCl_3$/MF pre-treatment. The highest average TMP in decreasing order are baseline, Alum/MF, PACl/MF and $FeCl_3$/MF with respective average TMP of 81.3, 69.7, 66.0 and 63.2psi. $FeCl_3$/MF was significantly lower that Alum/MF, but did not differ significantly from PACl/MF conditions. Although the average TMP was a good indicator of membrane fouling, comparison on the TMPs between the four trials is not a good comparison of pre-treatment types as the source water quality varied with each trial.

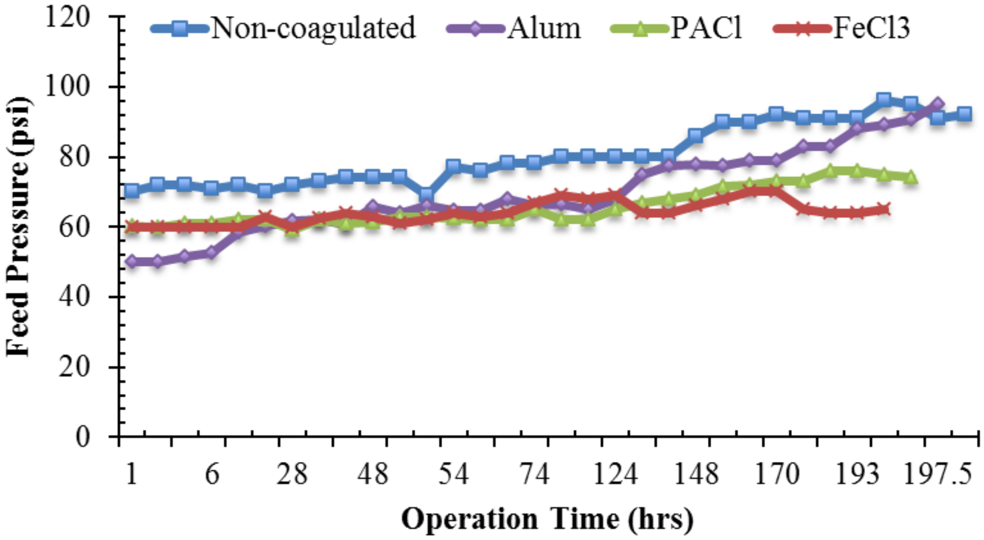


Figure 4.31 Required TMP for NF during 200hrs of operation

CHAPTER 5 RECOMMENDATIONS

This study was found that $FeCl_3$/MF was an effective pre-treatment for Lake Fletcher for one sample of source water. Multiple trials for each pre-treatment type with varying water quality should be performed to determine the effect of each coagulant under varied conditions. Also multiple trials would ensure statistical analysis could be performed.

Further analysis should analyze the effect of coagulant addition on the low-pressure membrane. Low levels of coagulant may result in the concentration of metals below their saturation index and cause detrimental fouling to the low-pressure membrane thus hindering a component of the IMS treatment process. Improved methods for coagulation condition optimization should be investigated in subsequent trials.

Identification of NOM foulant fractions for both low- and high-pressure membranes would be beneficial. Fluorescence excitation emission matrix and adenine triphosphate analysis are technologies that would provide additional information on NOM foulants.

CHAPTER 6 CONCLUSION

This study investigated NF membrane fouling in an IMS due to seasonal variation of NOM in Lake Fletcher. The effectiveness of low-dose in-line coagulation addition prior to low-pressure membrane filtration for NF feed-water pre-treatment was assessed for reduction of NF membrane fouling. Current literature has voids on whether the type of in-line coagulant has an effect on NF membrane fouling. This study sought to determine three things:

1.) Is there a need for NF feed-water pre-treatment with source water from Lake Fletcher?
2.) Is in-line coagulation an effective pre-treatment for IMS treatment facilities?
3.) What effect does the coagulant type have on NF fouling?

Jar tests were performed to identify optimal coagulant conditions and bench-scale NF operation for the four feed-water conditions were run to compare the effect of pre-treatment type on NF fouling.

6.1 Need for NF Feed-Water Pre-Treatment under Baseline Conditions

Analysis of bench-scale NF operation at baseline conditions indicated that there was significant NF membrane fouling. This was indicated by a 25psi TMP increase over the 200hrs runtime and retention of 87.1% of NOM on the NF membrane. The low concentration of metals did not appear to have an effect on NF membrane fouling. The SUVA value of 3.04L/mg/cm indicated humic matter was not removed with MF pre-treatment. Membrane autopsies performed with SEM indicated that an organic cake-layer was responsible for pore-blockage that led to increased resistance and then membrane fouling. These factors indicated that pre-treatment for removal of NOM was required for improved NF membrane performance and decreased NF membrane fouling.

6.2 Effect of In-Line Coagulation for NF Feed-Water Pre-Treatment

In-line coagulation was effective in reduction of NF membrane fouling due to NOM. This average TMP was reduced from 80psi at baseline conditions to under 70psi with coagulation/MF pre-treatment. The reduction of TMP can be attributed to the reduced SDI and concentration of NOM in the NF feed-water for the coagulated trials. The SDI was reduced from 4.40%/min under baseline conditions to below 3.50%/min for all trials with coagulation. The removal of NOM increased from 3.51% removal with MF to over 30% with coagulation/MF. Coagulation addition resulted in the removal of humic matter within the NF feed-water. The addition of metal-based coagulants resulted in increased aluminum concentrations in the NF feed-water for alum/MF and PACl/MF and increased iron and manganese with $FeCl_3$/MF. The addition of coagulant reduced the NF influent NOM and particulate matter, and increased the concentration of dissolved metals that resulted in decreased NF membrane fouling indicated by decreased average TMP.

6.3 Effect of Coagulant Type on NF Fouling

The reduction of NF membrane fouling was found to differ with pre-treatment. $FeCl_3$/MF pre-treatment was more effective in reduction of average TMP than alum/MF and PACl/MF. At a Fe dose of 0.5mg/L and pH 5.0, ferric chloride removed a larger fraction of organics and did not significantly increase the iron concentration of the NF feed-water.

The addition of coagulants prior to MF decreased the TMP increase for all coagulatnt types except alum. The average TMP of the baseline, alum/MF, PACl/MF, and $FeCl_3$/MF were 81.3psi, 69.7psi, 66.0psi, and 63.2psi, respectively.

The reduction of TMP was due to reduction of NOM, metals and SDI in the NF feed-water. $FeCl_3$/MF and PACl/MF had the highest reduction of TOC with the same source water however $FeCl_3$/MF had significantly better removal of NOM between 1500 and 5000Da. Also, $FeCl_3$/MF was able to attain similar removal during decreased water quality during the bench-scale NF trial whereas the PACl/MF had significantly reduced NOM removal than it had in the determination of optimal coagulant conditions. The addition of $FeCl_3$/MF did not significantly increase the concentration of iron in the NF feed-water from baseline conditions.

$FeCl_3$/MF was determined to be the most effective NF pre-treatment. $FeCl_3$/MF effectively improved NF feed-water quality at a low-dose and did not result in severe membrane fouling, indicated by increased TMP. $FeCl_3$ differentiated from the other coagulants as $FeCl_3$ is an iron-based coagulant, and the mechanism of coagulation was under-dose. Alum and PACl are both alumiunum-based coagulants that coagulated with charge neutralization as a coagulation mechanism.

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APPENDIX

Trans-Membrane Pressure
One-way ANOVA: raw, alum, pacl, ferric

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Source   DF       SS      MS      F      P
Factor    3   5518.7  1839.6  27.85  0.000
Error   110   7266.0    66.1
Total   113  12784.8

S = 8.127   R-Sq = 43.17%   R-Sq(adj) = 41.62%


                            Individual 95% CIs For Mean Based on
                            Pooled StDev
Level    N    Mean   StDev  -----+---------+---------+---------+----
raw     32  81.250   7.800                             (---*---)
alum    31  69.700  12.240            (----*---)
pacl    28  65.954   5.485       (---*----)
ferric  23  63.196   1.820  (----*----)
                            -----+---------+---------+---------+----
                              63.0      70.0      77.0      84.0

Pooled StDev = 8.127


Grouping Information Using Tukey Method

         N    Mean  Grouping
raw     32  81.250  A
alum    31  69.700    B
pacl    28  65.954    B C
ferric  23  63.196      C

Means that do not share a letter are significantly different.


Tukey 95% Simultaneous Confidence Intervals
All Pairwise Comparisons

Individual confidence level = 98.97%


raw subtracted from:

          Lower   Center    Upper  ----+---------+---------+---------+-----
alum    -16.894  -11.550   -6.206           (----*-----)
pacl    -20.784  -15.296   -9.809       (-----*----)
ferric  -23.851  -18.054  -12.257  (-----*-----)
                                   ----+---------+---------+---------+-----
                                     -20       -10         0        10

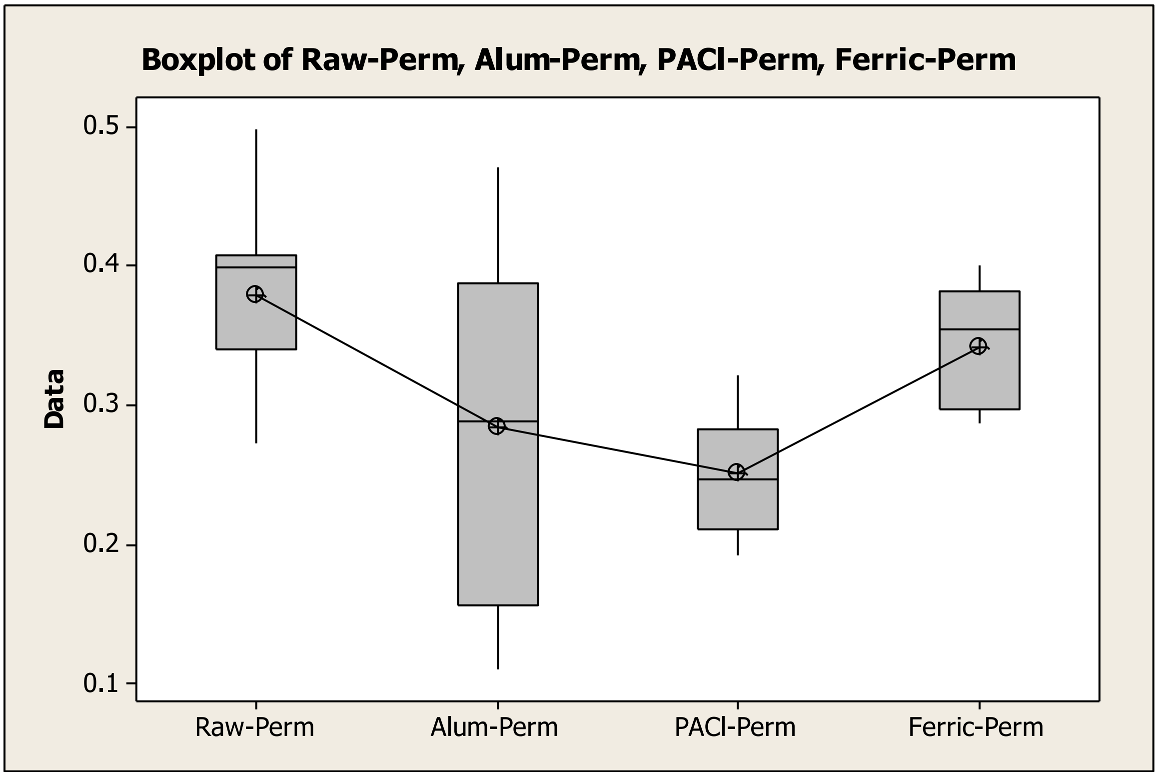

alum subtracted from:

          Lower  Center   Upper  ----+---------+---------+---------+-----
pacl     -9.275  -3.746   1.782                 (----*-----)
ferric  -12.340  -6.504  -0.668              (----*-----)
                                 ----+---------+---------+---------+-----
                                   -20       -10         0        10
```

```
pacl subtracted from:

         Lower  Center  Upper  ----+---------+---------+---------+-----
ferric  -8.726  -2.758  3.210                (-----*-----)
                               ----+---------+---------+---------+-----
                                 -20       -10         0        10
```

TOC PERM



Results for: Worksheet 2

One-way ANOVA: Raw-Perm, Alum-Perm, PACl-Perm, Ferric-Perm

```
Source  DF       SS       MS     F      P
Factor   3  0.12256  0.04085  6.99  0.001
Error   44  0.25707  0.00584
Total   47  0.37963

S = 0.07644   R-Sq = 32.28%   R-Sq(adj) = 27.67%


                                   Individual 95% CIs For Mean Based on
                                   Pooled StDev
Level         N     Mean    StDev  ----+---------+---------+---------+-----
Raw-Perm     11  0.37867  0.06303                     (-------*-------)
Alum-Perm    12  0.28359  0.12737      (------*-------)
PACl-Perm    16  0.25165  0.03919  (-----*-----)
Ferric-Perm   9  0.34126  0.04450              (--------*-------)
                                   ----+---------+---------+---------+-----
                                     0.240     0.300     0.360     0.420

Pooled StDev = 0.07644


Grouping Information Using Tukey Method

              N     Mean  Grouping
Raw-Perm     11  0.37867  A
Ferric-Perm   9  0.34126  A B
```

```
Alum-Perm    12  0.28359    B C
PACl-Perm    16  0.25165      C

Means that do not share a letter are significantly different.


Tukey 95% Simultaneous Confidence Intervals
All Pairwise Comparisons

Individual confidence level = 98.95%


Raw-Perm subtracted from:

                Lower    Center     Upper
Alum-Perm    -0.18036  -0.09508  -0.00980
PACl-Perm    -0.20704  -0.12702  -0.04700
Ferric-Perm  -0.12924  -0.03741   0.05442

               -+---------+---------+---------+--------
Alum-Perm         (-------*--------)
PACl-Perm      (-------*-------)
Ferric-Perm            (--------*--------)
               -+---------+---------+---------+--------
             -0.20     -0.10     -0.00      0.10


Alum-Perm subtracted from:

                Lower    Center    Upper
PACl-Perm    -0.10996  -0.03194  0.04608
Ferric-Perm  -0.03243   0.05766  0.14775

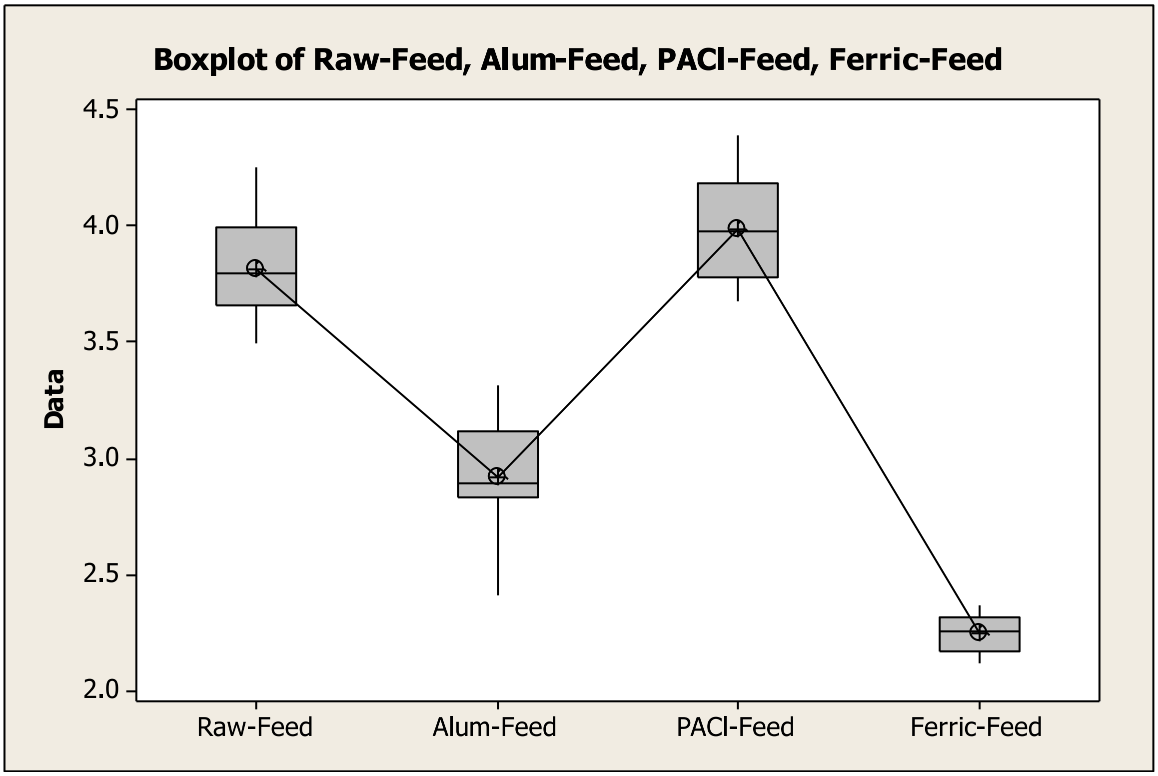
               -+---------+---------+---------+--------
PACl-Perm                (-------*-------)
Ferric-Perm                      (--------*--------)
               -+---------+---------+---------+--------
             -0.20     -0.10     -0.00      0.10


PACl-Perm subtracted from:

               Lower   Center    Upper
Ferric-Perm  0.00448  0.08961  0.17474

               -+---------+---------+---------+--------
Ferric-Perm                         (--------*-------)
               -+---------+---------+---------+--------
             -0.20     -0.10     -0.00      0.10
```

Feed TOC



One-way ANOVA: Raw-Feed, Alum-Feed, PACI-Feed, Ferric-Feed

```
Source  DF       SS      MS       F      P
Factor   3  22.3365  7.4455  151.50  0.000
Error   45   2.2115  0.0491
Total   48  24.5480

S = 0.2217   R-Sq = 90.99%   R-Sq(adj) = 90.39%


                                 Individual 95% CIs For Mean Based on
                                 Pooled StDev
Level         N    Mean   StDev  -----+---------+---------+---------+----
Raw-Feed     12  3.8107  0.2259                           (--*-)
Alum-Feed    12  2.9157  0.2825             (--*-)
PACl-Feed    16  3.9889  0.2183                               (*-)
Ferric-Feed   9  2.2444  0.0842  (-*--)
                                 -----+---------+---------+---------+----
                                    2.40      3.00      3.60      4.20

Pooled StDev = 0.2217


Grouping Information Using Tukey Method

              N    Mean  Grouping
PACl-Feed    16  3.9889  A
Raw-Feed     12  3.8107  A
Alum-Feed    12  2.9157    B
Ferric-Feed   9  2.2444      C
```

```
Means that do not share a letter are significantly different.


Tukey 95% Simultaneous Confidence Intervals
All Pairwise Comparisons

Individual confidence level = 98.94%


Raw-Feed subtracted from:

               Lower   Center    Upper
Alum-Feed    -1.1363  -0.8950  -0.6537
PACl-Feed    -0.0474   0.1783   0.4040
Ferric-Feed  -1.8269  -1.5663  -1.3057

                +---------+---------+---------+---------
Alum-Feed                (-*-)
PACl-Feed                           (-*-)
Ferric-Feed       (-*--)
                +---------+---------+---------+---------
             -2.0      -1.0       0.0       1.0


Alum-Feed subtracted from:

               Lower   Center    Upper
PACl-Feed     0.8476   1.0733   1.2990
Ferric-Feed  -0.9319  -0.6713  -0.4107

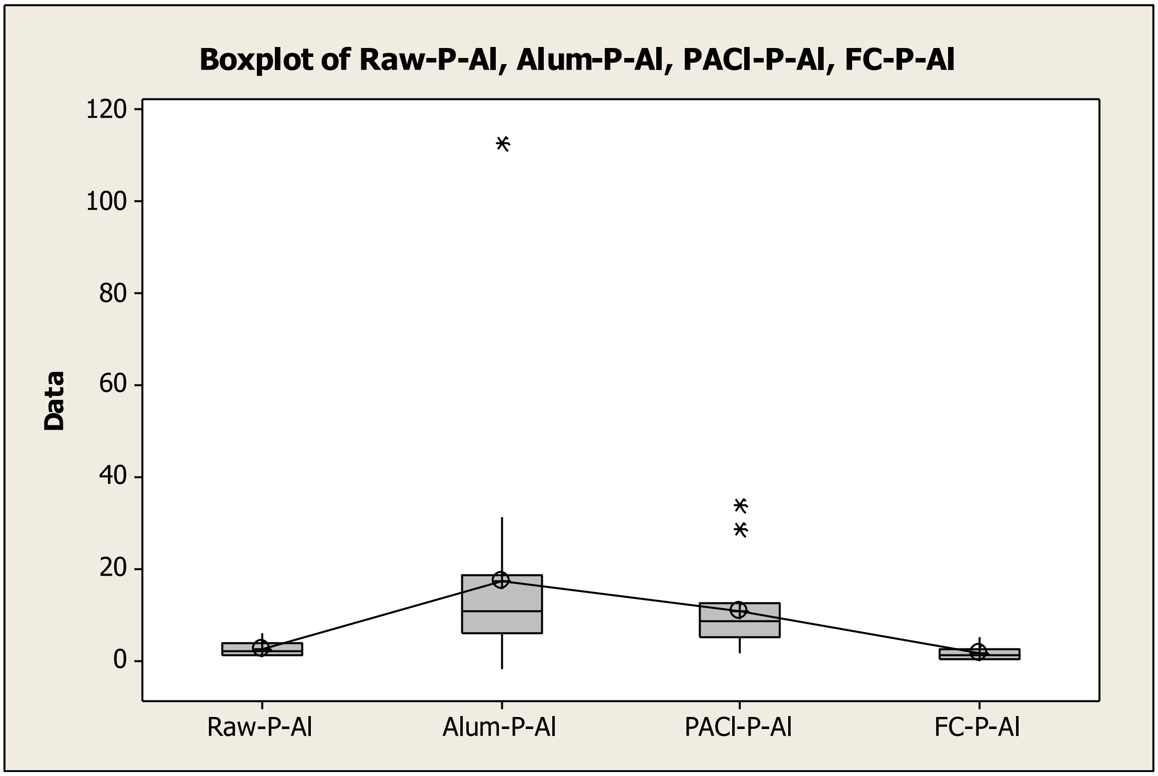
                +---------+---------+---------+---------
PACl-Feed                                   (--*-)
Ferric-Feed                (-*--)
                +---------+---------+---------+---------
             -2.0      -1.0       0.0       1.0


PACl-Feed subtracted from:

               Lower   Center    Upper
Ferric-Feed  -1.9908  -1.7445  -1.4983

                +---------+---------+---------+---------
Ferric-Feed     (--*-)
                +---------+---------+---------+---------
             -2.0      -1.0       0.0       1.0
```

Perm Metals-Al



One-way ANOVA: Raw-P-Al, Alum-P-Al, PACl-P-Al, FC-P-Al

```
Source  DF     SS   MS     F      P
Factor   3   2143  714  2.76  0.053
Error   46  11905  259
Total   49  14048

S = 16.09   R-Sq = 15.25%   R-Sq(adj) = 9.73%


                              Individual 95% CIs For Mean Based on
                              Pooled StDev
Level       N   Mean  StDev  --------+---------+---------+---------+-
Raw-P-Al    9   2.79   1.72  (----------*----------)
Alum-P-Al  16  17.66  26.77                    (-------*-------)
PACl-P-Al  14  11.17   9.25         (--------*--------)
FC-P-Al    11   1.90   1.45  (---------*---------)
                             --------+---------+---------+---------+-
                                     0        10        20        30

Pooled StDev = 16.09


Grouping Information Using Tukey Method

            N   Mean  Grouping
Alum-P-Al  16  17.66  A
PACl-P-Al  14  11.17  A
Raw-P-Al    9   2.79  A
FC-P-Al    11   1.90  A

Means that do not share a letter are significantly different.
```

```
Tukey 95% Simultaneous Confidence Intervals
All Pairwise Comparisons

Individual confidence level = 98.94%


Raw-P-Al subtracted from:

            Lower  Center  Upper  ------+---------+---------+---------+---
Alum-P-Al   -3.00   14.87  32.74                 (-------*--------)
PACl-P-Al   -9.95    8.37  26.70             (--------*--------)
FC-P-Al    -20.16   -0.89  18.39        (---------*--------)
                                  ------+---------+---------+---------+---
                                      -20         0        20        40

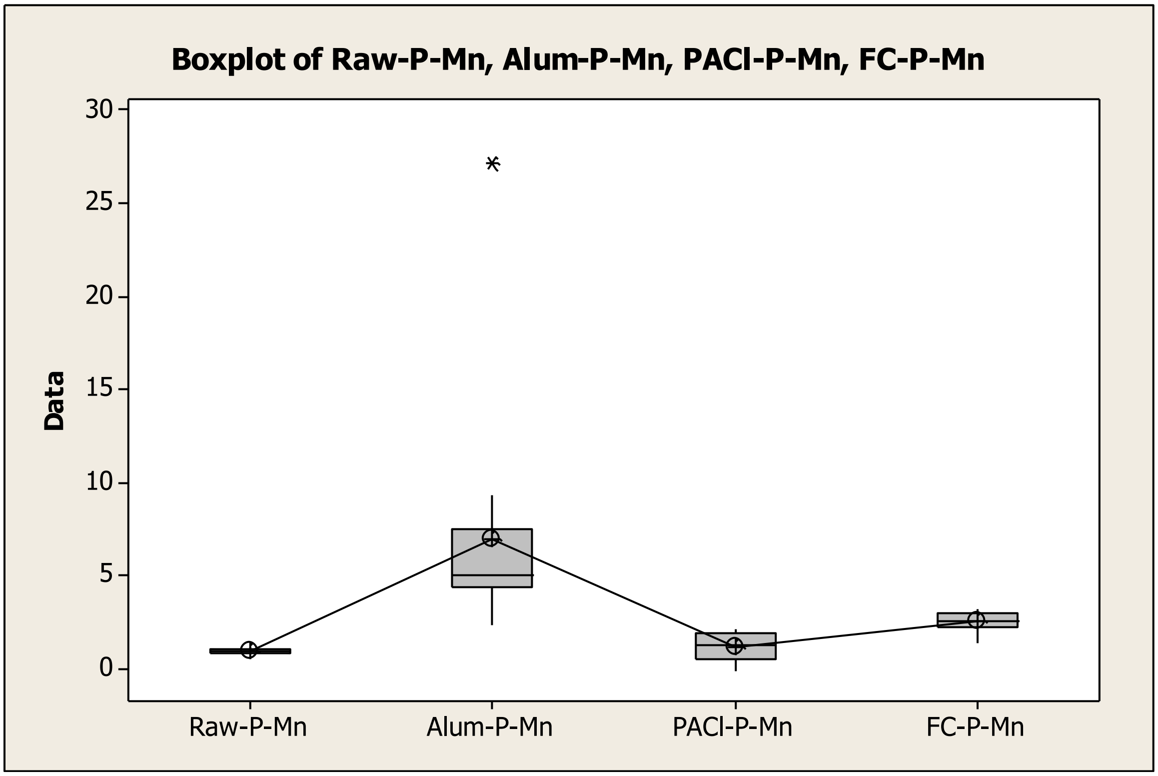

Alum-P-Al subtracted from:

            Lower  Center  Upper  ------+---------+---------+---------+---
PACl-P-Al  -22.19   -6.50   9.20       (-------*-------)
FC-P-Al    -32.56  -15.76   1.04  (-------*--------)
                                  ------+---------+---------+---------+---
                                      -20         0        20        40


PACl-P-Al subtracted from:

          Lower  Center  Upper  ------+---------+---------+---------+---
FC-P-Al  -26.54   -9.26   8.02     (-------*--------)
                                ------+---------+---------+---------+---
                                    -20         0        20        40
```

```
Perm Mn
```



One-way ANOVA: Raw-P-Mn, Alum-P-Mn, PACl-P-Mn, FC-P-Mn

```
Source  DF     SS     MS      F      P
Factor   3  337.6  112.5  10.40  0.000
Error   46  498.0   10.8
Total   49  835.6

S = 3.290   R-Sq = 40.41%   R-Sq(adj) = 36.52%


                             Individual 95% CIs For Mean Based on
                             Pooled StDev
Level       N   Mean  StDev  -----+---------+---------+---------+----
Raw-P-Mn    9  0.935  0.110  (--------*--------)
Alum-P-Mn  16  7.004  5.701                            (------*------)
PACl-P-Mn  14  1.198  0.761     (------*------)
FC-P-Mn    11  2.562  0.531         (-------*-------)
                             -----+---------+---------+---------+----
                                0.0       2.5       5.0       7.5

Pooled StDev = 3.290


Grouping Information Using Tukey Method

            N   Mean  Grouping
Alum-P-Mn  16  7.004  A
FC-P-Mn    11  2.562    B
PACl-P-Mn  14  1.198    B
Raw-P-Mn    9  0.935    B

Means that do not share a letter are significantly different.
```

```
Tukey 95% Simultaneous Confidence Intervals
All Pairwise Comparisons

Individual confidence level = 98.94%


Raw-P-Mn subtracted from:

            Lower  Center  Upper  --------+---------+---------+---------+-
Alum-P-Mn   2.414   6.068  9.723                         (------*------)
PACl-P-Mn  -3.485   0.263  4.010             (-------*------)
FC-P-Mn    -2.315   1.627  5.569               (-------*-------)
                                  --------+---------+---------+---------+-
                                       -5.0       0.0       5.0      10.0

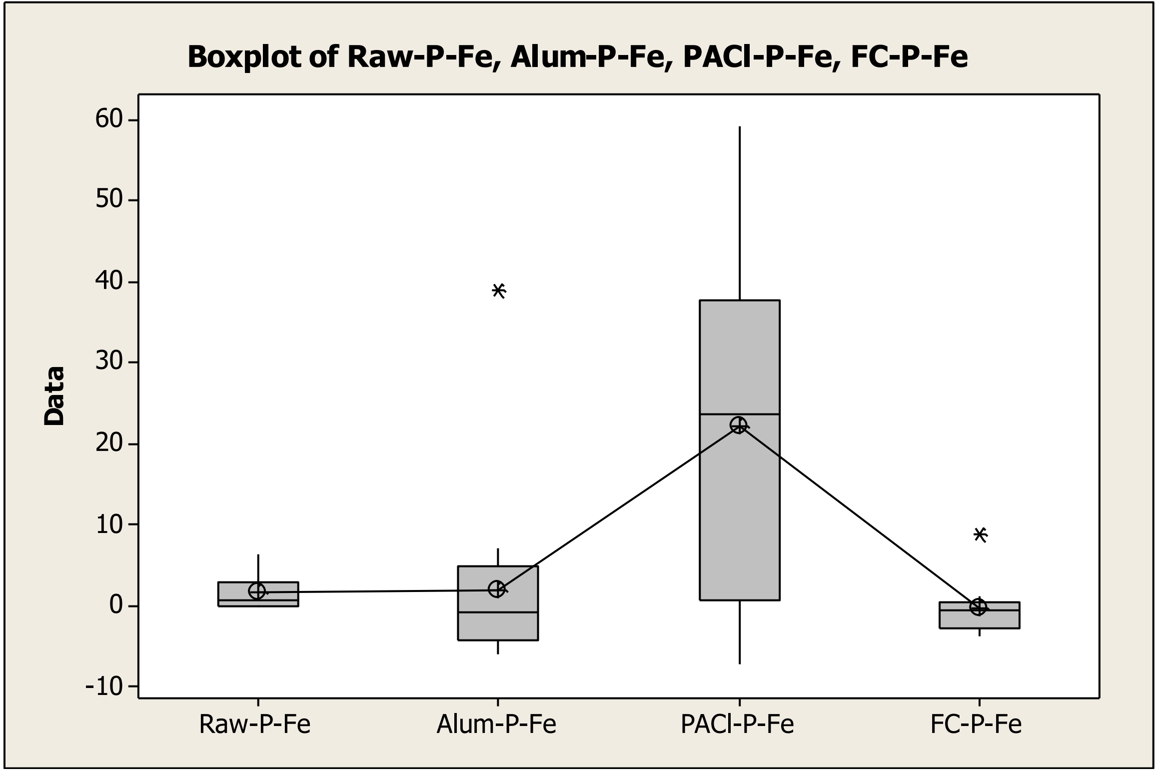

Alum-P-Mn subtracted from:

            Lower  Center   Upper  --------+---------+---------+---------+-
PACl-P-Mn  -9.015  -5.805  -2.596  (-----*------)
FC-P-Mn    -7.877  -4.441  -1.006    (------*------)
                                   --------+---------+---------+---------+-
                                        -5.0       0.0       5.0      10.0


PACl-P-Mn subtracted from:

          Lower  Center  Upper  --------+---------+---------+---------+-
FC-P-Mn  -2.170   1.364  4.898                (------*------)
                                --------+---------+---------+---------+-
                                     -5.0       0.0       5.0      10.0
```

Metals perm Fe



One-way ANOVA: Raw-P-Fe, Alum-P-Fe, PACl-P-Fe, FC-P-Fe

```
Source  DF     SS    MS     F      P
Factor   3   4416  1472  8.65  0.000
Error   46   7824   170
Total   49  12239

S = 13.04   R-Sq = 36.08%   R-Sq(adj) = 31.91%


                             Individual 95% CIs For Mean Based on
                             Pooled StDev
Level       N   Mean  StDev  --------+---------+---------+---------+-
Raw-P-Fe    9   1.78   2.24   (--------*--------)
Alum-P-Fe  16   2.01  10.88     (------*------)
PACl-P-Fe  14  22.09  21.29                       (------*------)
FC-P-Fe    11  -0.29   3.43  (-------*-------)
                             --------+---------+---------+---------+-
                                     0        10        20        30

Pooled StDev = 13.04


Grouping Information Using Tukey Method

            N   Mean  Grouping
PACl-P-Fe  14  22.09  A
Alum-P-Fe  16   2.01    B
Raw-P-Fe    9   1.78    B
FC-P-Fe    11  -0.29    B

Means that do not share a letter are significantly different.
```

```
Tukey 95% Simultaneous Confidence Intervals
All Pairwise Comparisons

Individual confidence level = 98.94%


Raw-P-Fe subtracted from:

            Lower  Center  Upper  --------+---------+---------+---------+-
Alum-P-Fe  -14.26    0.23  14.71             (------*------)
PACl-P-Fe    5.45   20.31  35.16                       (------*-------)
FC-P-Fe    -17.70   -2.07  13.55           (-------*-------)
                                  --------+---------+---------+---------+-
                                        -20         0        20        40

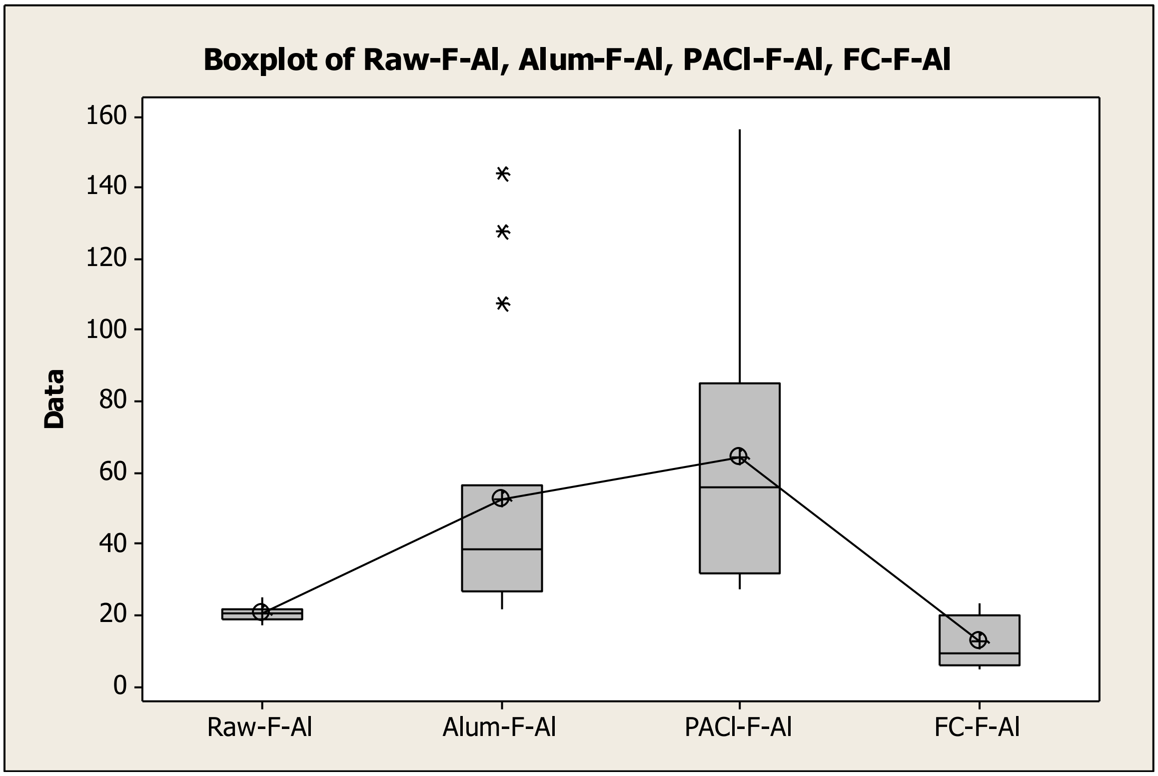

Alum-P-Fe subtracted from:

            Lower  Center  Upper  --------+---------+---------+---------+-
PACl-P-Fe    7.36   20.08  32.80                        (-----*-----)
FC-P-Fe    -15.92   -2.30  11.32            (------*------)
                                  --------+---------+---------+---------+-
                                        -20         0        20        40


PACl-P-Fe subtracted from:

          Lower  Center  Upper  --------+---------+---------+---------+-
FC-P-Fe  -36.39  -22.38  -8.37  (------*------)
                                --------+---------+---------+---------+-
                                      -20         0        20        40
```

Feed Al



One-way ANOVA: Raw-F-Al, Alum-F-Al, PACl-F-Al, FC-F-Al

```
Source  DF     SS    MS     F      P
Factor   3  22114  7371  7.51  0.000
Error   46  45131   981
Total   49  67245

S = 31.32   R-Sq = 32.89%   R-Sq(adj) = 28.51%


                             Individual 95% CIs For Mean Based on
                             Pooled StDev
Level       N   Mean  StDev  --+---------+---------+---------+-------
Raw-F-Al    9  20.64   2.24    (-------*--------)
Alum-F-Al  16  52.71  38.64                   (-----*-----)
PACl-F-Al  14  64.14  41.32                       (------*-----)
FC-F-Al    11  12.88   7.12  (------*-------)
                             --+---------+---------+---------+-------
                               0        25        50        75

Pooled StDev = 31.32


Grouping Information Using Tukey Method

            N   Mean  Grouping
PACl-F-Al  14  64.14  A
Alum-F-Al  16  52.71  A B
Raw-F-Al    9  20.64    B C
FC-F-Al    11  12.88      C
```

```
Means that do not share a letter are significantly different.


Tukey 95% Simultaneous Confidence Intervals
All Pairwise Comparisons

Individual confidence level = 98.94%


Raw-F-Al subtracted from:

            Lower  Center  Upper  -------+---------+---------+---------+--
Alum-F-Al   -2.72   32.08  66.87                  (------*------)
PACl-F-Al    7.83   43.50  79.18                     (------*------)
FC-F-Al    -45.29   -7.76  29.77          (------*-------)
                                  -------+---------+---------+---------+--
                                       -50         0        50       100

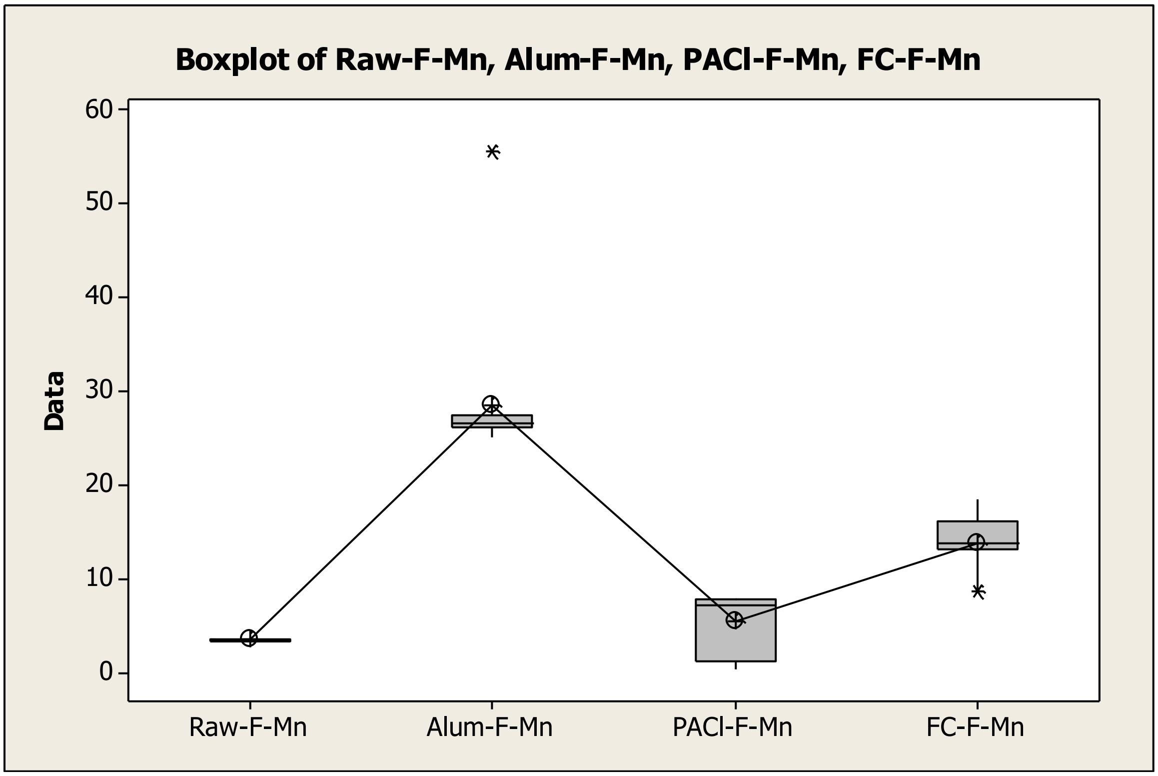

Alum-F-Al subtracted from:

            Lower  Center  Upper  -------+---------+---------+---------+--
PACl-F-Al  -19.13   11.43  41.99               (-----*-----)
FC-F-Al    -72.54  -39.83  -7.13    (------*------)
                                  -------+---------+---------+---------+--
                                       -50         0        50       100


PACl-F-Al subtracted from:

          Lower  Center   Upper  -------+---------+---------+---------+--
FC-F-Al  -84.90  -51.26  -17.62  (------*-----)
                                 -------+---------+---------+---------+--
                                      -50         0        50       100
```

Feed Mn



One-way ANOVA: Raw-F-Mn, Alum-F-Mn, PACl-F-Mn, FC-F-Mn

```
Source  DF      SS      MS      F      P
Factor   3  5340.4  1780.1  80.39  0.000
Error   46  1018.6    22.1
Total   49  6359.0

S = 4.706   R-Sq = 83.98%   R-Sq(adj) = 82.94%


                              Individual 95% CIs For Mean Based on Pooled StDev
Level       N    Mean  StDev    +---------+---------+---------+---------
Raw-F-Mn    9   3.533  0.189    (---*---)
Alum-F-Mn  16  28.454  7.282                                 (--*--)
PACl-F-Mn  14   5.477  3.142        (--*--)
FC-F-Mn    11  13.862  3.075                  (--*---)
                                +---------+---------+---------+---------
                              0.0       8.0      16.0      24.0

Pooled StDev = 4.706


Grouping Information Using Tukey Method

            N    Mean  Grouping
Alum-F-Mn  16  28.454  A
FC-F-Mn    11  13.862    B
PACl-F-Mn  14   5.477      C
Raw-F-Mn    9   3.533      C
```

```
Means that do not share a letter are significantly different.


Tukey 95% Simultaneous Confidence Intervals
All Pairwise Comparisons

Individual confidence level = 98.94%


Raw-F-Mn subtracted from:

            Lower  Center   Upper  --------+---------+---------+---------+-
Alum-F-Mn  19.694  24.921  30.147                                 (---*--)
PACl-F-Mn  -3.415   1.944   7.304                  (--*---)
FC-F-Mn     4.690  10.329  15.967                       (---*---)
                                   --------+---------+---------+---------+-
                                         -15         0        15        30

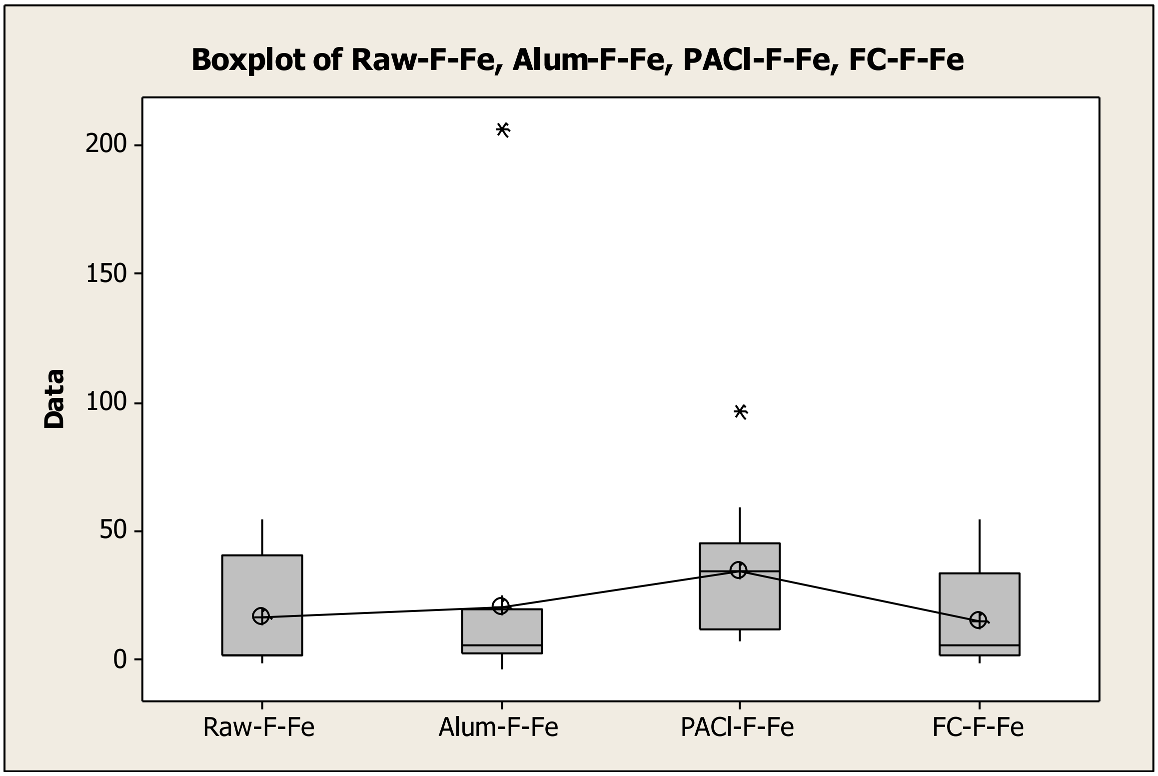

Alum-F-Mn subtracted from:

             Lower   Center    Upper  --------+---------+---------+---------+-
PACl-F-Mn  -27.567  -22.976  -18.386  (--*--)
FC-F-Mn    -19.505  -14.592   -9.679       (--*---)
                                      --------+---------+---------+---------+-
                                            -15         0        15        30


PACl-F-Mn subtracted from:

         Lower  Center   Upper  --------+---------+---------+---------+-
FC-F-Mn  3.330   8.384  13.439                      (---*--)
                                --------+---------+---------+---------+-
                                      -15         0        15        30
```

Feed Fe



One-way ANOVA: Raw-F-Fe, Alum-F-Fe, PACl-F-Fe, FC-F-Fe

```
Source  DF     SS    MS     F      P
Factor   3   2996   999  0.86  0.470
Error   46  53560  1164
Total   49  56556

S = 34.12   R-Sq = 5.30%   R-Sq(adj) = 0.00%


                             Individual 95% CIs For Mean Based on
                             Pooled StDev
Level       N   Mean  StDev  ----+---------+---------+---------+-----
Raw-F-Fe    9  16.84  22.24  (--------------*--------------)
Alum-F-Fe  16  20.44  50.24        (-----------*----------)
PACl-F-Fe  14  34.59  24.25                 (-----------*-----------)
FC-F-Fe    11  15.16  20.25  (-------------*-------------)
                             ----+---------+---------+---------+-----
                                 0        15        30        45

Pooled StDev = 34.12


Grouping Information Using Tukey Method

            N   Mean  Grouping
PACl-F-Fe  14  34.59  A
Alum-F-Fe  16  20.44  A
Raw-F-Fe    9  16.84  A
FC-F-Fe    11  15.16  A
```

```
Means that do not share a letter are significantly different.


Tukey 95% Simultaneous Confidence Intervals
All Pairwise Comparisons

Individual confidence level = 98.94%


Raw-F-Fe subtracted from:

            Lower  Center  Upper  ---------+---------+---------+---------+
Alum-F-Fe  -34.30    3.60  41.50          (-----------*------------)
PACl-F-Fe  -21.11   17.76  56.62              (------------*------------)
FC-F-Fe    -42.56   -1.67  39.21       (------------*-------------)
                                  ---------+---------+---------+---------+
                                         -30         0        30        60


Alum-F-Fe subtracted from:

            Lower  Center  Upper  ---------+---------+---------+---------+
PACl-F-Fe  -19.13   14.16  47.45               (----------*----------)
FC-F-Fe    -40.90   -5.27  30.36       (-----------*-----------)
                                  ---------+---------+---------+---------+
                                         -30         0        30        60


PACl-F-Fe subtracted from:

          Lower  Center  Upper  ---------+---------+---------+---------+
FC-F-Fe  -56.08  -19.43  17.22  (------------*-----------)
                                ---------+---------+---------+---------+
                                       -30         0        30        60
```