Fouling Mechanisms in Nanofiltration Membranes used for Surface Water Treatment

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Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners. I understand that my thesis may be made electronically available to the public.

Contribution of Authors

This is a manuscript style (sandwich) thesis with one manuscript that consists of contributions from Nisha Jha (author), Dr. Zsolt L. Kiss & Dr. Beata Gorczyca (co-authors). All the authors provided valuable inputs in the conception and design of study. The experiments and data analysis were carried out by Nisha Jha with the assistance of Dr. Zsolt L. Kiss. The interpretation of results from the acquired data, characterization of samples and image analysis by using atomic force microscopy was done by Nisha Jha. The manuscript was written by Nisha Jha, and Dr. Beata Gorczyca & Dr. Zsolt L. Kiss provided critical feedback and helped shape up the manuscript. The project was supervised by Dr. Beata Gorczyca.

Abstract

In this study, the influence of calcium concentration on flux decline and fouling mechanisms in NF90 membrane used for filtration of constant high DOC in synthetic water was observed and analyzed. The synthetic water was composed of sodium alginate (17 mg/L as DOC) and calcium chloride (50, 200, and 350 mg/L as $CaCO_3$). Several fouling models, resistance-in-series model and Atomic Force Microscopy (AFM) were used to analyze the flux decline curves, hydraulic resistances due to various fouling mechanisms and membrane surface morphology, respectively. Results of fouling experiments identified that reversibility of fouling increased with increasing calcium concentration due to increase in cohesive forces between calcium and alginate molecules. However, the flux decline and total hydraulic resistance was highly dependent on the concentration of both calcium and alginate in feed water forming Ca-alginate complexes. Also, at high calcium concentrations, gel layer formation becomes the dominant fouling mechanism offering maximum hydraulic resistance.

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List of Acronyms and Symbols

NOM	Natural Organic Matter
DOC	Dissolved Organic matter
DBP	Disinfection By-products
HAA	Haloacetic Acid
THM	Trihalomethane
THMFP	Trihalomethane Formation Potential
NF	Nanofiltration
RO	Reverse Osmosis
MF	Microfiltration
UF	Ultrafiltration
WTP	Water Treatment Plant
TFC	Thin Film Composite
MWCO	Molecular Weight Cut-off
AFM	Atomic Force Microscopy
DOM	Dissolved Organic Matter
POM	Particulate Organic Matter
HA	Humic Acid
FA	Fulvic Acid
DI	Deionized Water
PVWC	Pembina Valley Water Coorp.
PES	Polyethersulfone
R	Retention [%]

C	Permeate concentration [mg/L]
C_0	Concentration in the feed solution [mg/L]
J	Flux [L m^{-2} h^{-1}]
J_0	Initial Flux [L m^{-2} h^{-1}]
k	Fouling Coefficient
R^2	Regression Coefficient
η	Dynamic Viscosity [Pa. s]
ΔP	Pressure Difference between the feed and permeate side of membrane [Pa]
Da	Dalton
R_m	Membrane Resistance [m^{-1}]
R_t	Total Resistance [m^{-1}]
R_P	Concentration Polarization Layer Resistance [m^{-1}]
R_g	Gel Layer Resistance [m^{-1}]
$R_{f, org}$	Reversible Organic Pore Fouling Resistance [m^{-1}]
$R_{f, inorg}$	Reversible Inorganic Pore Fouling Resistance [m^{-1}]
$R_{f, irrev}$	Irreversible Pore Fouling Resistance [m^{-1}]
R_a	Mean plane roughness
R_q	Root mean squared roughness

Chapter 1: INTRODUCTION

1.1. Background

In the recent years, membrane technology has gained a lot of popularity for its application in water treatment and drinking water production, complying the increasingly strict water quality regulations. Implementation of membranes for water treatment has progressed over the years using advanced materials for membrane manufacturing in various configurations. The technology has come up as a good alternative to the traditional separation and purification processes. Membrane filtration is basically a separation process, where pollutants carried by the raw water are separated from the clean water. A driving force is applied across a semi-permeable thin layer of membrane which acts as a selective barrier and separates substances from water. Pollutants such as bacteria, microorganisms, particulates, natural organic material, and inorganic matter, which can impart color, taste, and odor to water and can react with disinfectants to form disinfection byproducts (DBP), are generally removed by the membrane processes.

Nanofiltration (NF) membranes have been widely used as low pressure-driven membrane processes for liquid-phase separation (Marchetti et al., 2014). NF membranes, having a pore size between 1-10 nm, typically operate at a pressure between 350-1000 kPa with a molecular weight cut-off (MWCO) of 300-500 Da (Mohammad et al., 2015). The properties of NF membranes lie between those of porous ultrafiltration membranes (UF) and non-porous reverse osmosis (RO) membranes i.e., the separation process is based on both size exclusion criteria and solution-diffusion mechanism, respectively. Most of the commercially available NF membranes possess negatively charged surface. Therefore, the NF membranes allow ions to be separated by a

combination of size and charge exclusion of UF and ionic interaction mechanisms of RO (Bowen & Welfoot, 2002). Due to lower energy consumption and higher flux rates, NF has successfully replaced reverse osmosis in many different applications (Cadotte et al., 1988). Similar to RO membranes, NF membranes are capable of separating natural organic matter (NOM) as well as some inorganic salts (hardness). However, unlike RO membranes, NF membranes have reasonably low retention capacity for monovalent ions, while high retention capacity for multivalent or divalent ions (Mohammad et al., 2015). These properties have allowed NF to be used in various field of applications, such as water and wastewater treatment, pharmaceutical and biotechnology, textile, metal recovery, and food engineering. Especially in water treatment plants using surface water as the source, NF membranes have successfully replaced conventional treatment systems such as lime-soda softening & activated carbon filters, due to these properties.

1.2. Problem Statement

Surface water reservoirs on the Canadian Prairies, often have unacceptable water quality for consumption due to high concentration of natural organic matter and inorganic salts imparting hardness to water. In the Province of Manitoba (Canada), high DOC has been observed and reported in surface water sources. However, the hardness of surface water has been observed to vary from very low to high ranges between different sources (40 – 400 mg/L as $CaCO_3$). Many water treatment plants in Manitoba have replaced their conventional water treatment systems with dual integrated membrane systems, mostly using Microfiltration (MF) and Nanofiltration (NF) membranes. NF membranes have been very efficient in the removal of divalent cations and NOM contributing hardness and Dissolved Organic Carbon (DOC), respectively, in surface waters (Schäfer et al., 1998).

However, like any other membrane process, NF is also highly susceptible to membrane fouling, limiting the successful application of the membrane technology. Membrane fouling is one of the significant challenges in any membrane process and therefore understanding the fouling mechanism and identifying a suitable control option is one of the essential components of membrane applications (Hong & Elimelech, 1997). Membrane fouling describes the reduction in filtration efficiency of membrane surface, due to deposition and accumulation of rejected contaminants from the feed stream on the membrane. Membrane fouling results in the reduction of permeate flux and increases operating pressures, ultimately affecting the energy requirements and the plant economy (Darton et al., 2004). The fouling process is highly influenced by membrane characteristics (pore size, permeability), feed solution composition (pH, temperature), NOM properties (molarity) and hydrodynamic and operating conditions (feed flow rate, cross-flow velocity) (Kilduff et al., 2004). In water treatment, presence of NOM and multivalent cations (such as Ca^{2+} and Mg^{2+}) in many raw water supplies has made the membrane filtration process even more challenging, due to both chemical and physical interactions between NOM, multivalent cations and the membrane itself (Hong & Elimelech, 1997). Various techniques have been developed to reduce the effect of membrane fouling, such as, improving the membrane properties to make it more fouling resistant, pretreatment of feed water, and optimizing operational parameters such as transmembrane pressure and cross-flow velocity.

1.3. Research Objectives

The main objective of this research was to investigate the fouling mechanisms in NF membranes, used for the treatment of feed water with high DOC and varying hardness concentration. This study was based on the use of synthetic water, representative of three typical surface water

sources (Rainy river, Assiniboine river & Red river) in Manitoba and NW Ontario (Table 3), composed of sodium alginate and calcium chloride as the model compounds for DOC and hardness, respectively. The DOC and calcium concentrations in the synthetic water were used as per maximum annual averaged values reported for the three rivers mentioned earlier. The study was carried out to identify the potential dominant mechanism (offering maximum hydraulic resistance) responsible for membrane fouling and resulting in maximum flux decline over time at a constant operating pressure. In addition to these, the study was also intended to provide an insight to the reversibility (or irreversibility) of NOM fouling under the influence of various calcium concentrations. The flux decline due to compaction of membrane and fouling was studied separately. The precompaction of membrane was studied for a range of compaction hours, to identify the number of hours required for pre-compaction.

This thesis comprises of a manuscript styled chapter (Chapter 3) which focuses on the main objectives of this research. Chapter 3 will be submitted for review in the Journal of Desalination and Water Treatment.

Chapter 2: LITERATURE REVIEW

2.1. Nanofiltration Membranes

Nanofiltration (NF) membranes were first recognized in the late 1980's, when Reverse Osmosis (RO) membranes were modified to obtain a reasonable water flux at relatively low pressures (Marchetti et al., 2014). RO membranes were used as high-pressure membranes resulting in low flux and considerably high energy cost. Nanofiltration was defined as an intermediate process between reverse osmosis and ultrafiltration that rejects molecules having a size around one nanometer (Bruggen et al., 2008). NF membranes have specific features for the range of rejection of particles, such as very high rejections for multivalent ions (85-95%) with low to moderate rejections for monovalent ions (0–70%), and the high rejection (90-95%) for organic compounds with a molecular weight above the MWCO of the membrane (Kilduff et al., 2004). However, the physicochemical interactions and the transport mechanisms between the NF membranes and the water being treated is still a major area of study for researchers and membrane manufacturers.

2.1.1. Design and Operation of NF Membranes

The majority of commercial NF membranes are available as thin film composite (TFC) membranes composed of three different layers i.e., a nonwoven polymeric support (about 150 microns), a micro porous polysulfone layer (about 50 microns), and an ultra-thin separation layer consisting of cross-linked polyamide (200-300 nm) on the top (Li et al., 2008). The polyamide layer is mainly responsible for the high rejection of solute particles and permeability of water.

Membranes are designed in special type of modules using flat-sheet, hollow fibers, spiral wound, capillary or tubular membranes. Spiral wound membranes are widely used in drinking water treatment because of their considerably low cost and moderate fouling tendency compared to the other membrane configurations. Several layers of flat sheet membranes are wound around a perforated cylinder to form these spiral wound membranes.

In membrane filtration, two main modes of operation are generally used: dead-end filtration and cross-flow filtration. Cross-flow filtration is more commonly used for drinking water treatment. The cross-flow velocities acting on the membrane surface in cross-flow filtration is considered to have a significant influence on NOM fouling. Braghetta (1995) identified that the higher cross-flow velocities (increased shear forces) cause disruption of fouling layer, resulting in increased permeate flux. At higher cross-flow velocities, the turbulence near the membrane surface was increased which minimized the formation of concentration polarization and gel layer formation near to / on the membrane surface, further decreasing the hydraulic resistance to feed flow (Braghetta, 1995).

2.1.2. NF Membranes Application in Surface Water Treatment

Surface waters comprise of a complex mixture of dissolved organic matters, inorganic matters, colloidal particles and microorganisms. NF is one of the most promising surface water treatment technologies for the removal of natural organic matter and inorganic pollutants. NF membranes have been mostly used for water softening (Bergman, 1995; Schaep et al., 1998; Ghizellaoui et al., 2005) and the removal of color and disinfection by-product (DBP) precursors (Mijatovic et al., 2004; Lin et al., 2007; Chellam et al., 2008; Sobhani et al., 2012). In surface waters, natural

organic compounds having relatively larger molecules compared to the NF membrane pore size, can be removed by the sieving mechanism. Whereas, the inorganic compounds/salts can be removed by the charge effect of NF membranes and ions in the surface water (Thanuttamavong et al., 2001; Thanuttamavong et al., 2002).

Yeh et al. (2000) studied the hardness removal from a lake in Taiwan, using conventional process (ozone, granular activated carbon & pellet softening) and an integrated membrane system (UF/NF). Although softening was achieved by all the processes, the results showed that NF membranes were the most efficient in producing high quality water (90% hardness removal & 75% dissolved organics removal) (Yeh et al., 2000). Many researchers have also investigated the removal of NOM and DBP precursors from surface water sources. Jarusutthirak et al. (2007(a)) reported that NF membranes are highly efficient in the removal of NOM from surface waters. Cho et al. (1999) studied the NOM rejection using different NF membranes (based on DOC) and it was concluded that the NOM rejection is clearly controlled by size exclusion, electrostatic repulsion and hydrophobicity interactions between NOM, the membrane surface and pores. Siddiqui et al. (2000) investigated four 100–300 Da spiral-wound NF membranes and observed average reductions of 90, 97 and 94% in DOC, Trihalomethane (THM) and Haloacetic Acid (HAA) formation potentials, respectively. Lin et al. (2007) investigated the THM formation potential (THMFP) removal efficiency for two commercial NF membranes (NF70 & NF270) at various pH and found that the removal of THM precursors were reasonably well (72– 98% removal efficiency) for both the NF membranes at high pH conditions. It was also identified that charge exclusion is the prevailing mechanism for the rejection of smaller organic compounds (Lin et al., 2007).

2.1.3. NF90 Membrane

NF90 membrane is one of the most extensively used commercial membrane by many researchers for investigating the properties of nanofiltration membranes under varying operating and fouling conditions (Li & Elimelech, 2004(a); Bellona et al., 2010; Elazhar et al., 2013; Hussain et al., 2013; Hussain & Al-Saleh, 2014). These membranes are very well known as tight nanofiltration membranes with very small pore sizes (Bellona et al., 2010). The rejection properties of NF90 membranes are considered to be very close to RO membranes due to the small pore sizes and negatively charged surface exhibiting size and steric exclusion mechanism, respectively (Bellona et al., 2010; Elazhar et al., 2013). Based on manufacturer's specification, NF90 membrane has a MWCO of 200 Da, maximum pressure of 41 bars and surface roughness of 69.9 nm (DOW Filmtec., 2016).

NF90 membranes are TFC membranes with a complex three-layered structure, as shown in Figure 1. The thin polyamide layer at the top of the membrane is also known as the active layer, as it is mainly responsible for the actual selectivity of the membrane (Li et al., 2008; Bellona et al., 2010). The hydrodynamic pressure acting on the membrane causes change in thickness and porosity of the supporting layers. However, the flux decline is mainly attributed to the compaction of dense thin film layer in the membrane (Bellona et al., 2010). NF90 membranes are also known to have a very high surface roughness compared to other available NF membranes from different manufacturers ranging between 5.5 nm – 43.3 nm (Vrijenhoek et al., 2001; Li & Elimelech, 2004(a)). This can cause very high initial flux decline due to large surface area available for foulant attachment (Li & Elimelech, 2004(a)). The rough surface of these

membranes is also responsible for reducing the chemical cleaning efficiency and increased irreversible foulant deposition (Al-Amoudi & Lovitt, 2007).

Figure 1. Cross-sectional view of three layered TFC membrane

2.2. NF Membrane Fouling

Despite of all the advantages and benefits of using membrane processes over conventional water treatment processes, there exists one major drawback in the application of membrane processes which is membrane fouling. Membrane fouling is defined as the accumulation of pollutants in the water to be treated on the membrane surface and/or within the pores, resulting in a decreased membrane performance or productivity. Membrane fouling is problematic not only because it reduces the membrane productivity but can also affect the treated water quality (Nghiem et al., 2010). Fouling in NF membranes is generally indicated by a reduced flux or increased pressure. The fouling phenomena can lead to extensive limitations to the effective operation of membrane systems, including decline in flux, increase in costs due to increased energy demand, increased frequency of cleaning and chemicals requirement, decreased lifetime of membranes and cost of replacement (Jarusutthirak et al., 2007(a)).

Membrane fouling in NF membranes can be very complex due to the interactions resulting in fouling occurs at nanoscale which cannot be easily identified and is therefore very difficult understand (Bruggen et al., 2008). In the NF membrane process, depending on the quality of feed

water, several types of fouling can take place, such as inorganic fouling or scaling, particulate/colloidal fouling, organic fouling, and biofouling (Kimura et al., 2004). The nature of fouling also depends on the chemical and physical interactions between the pollutants in feed water and the membrane structure due to various operating conditions, charge interactions, pore size and hydrophobic interactions (Shon et al., 2013).

2.2.1. Types of Fouling in NF membranes

(a) Inorganic Fouling

Inorganic fouling, also known as scaling is due to the precipitation of salts at the membrane surface. NF membranes reject the divalent cations and are retained at the membrane surface, resulting in an increased concentration and further exceeding the solubility limits, forming precipitates of those inorganic salts. The most common inorganic foulants found in NF applications include carbonate, sulphate and phosphate salts of divalent ions, metal hydroxides, sulphides and silica (Schäfer et al., 2004). More specifically, the species with the greatest scale forming potential are $CaCO_3$ and $CaSO_4 \cdot 2H_2O$, while the other potential scaling compounds are $BaSO_4$, $SrSO_4$, $Ca_3(PO_4)_2$, and $Fe(OH)_3$ (Hasson et al., 2001).

(b) Colloidal Fouling

Colloidal fouling may occur in NF membranes, depending on the relative size of colloidal particles and the membrane pores. The size of the colloids ranges from a few nanometers to a few micrometers. The colloidal particles either accumulate on the membrane surface depending on the membrane surface roughness, forming a cake layer, or if smaller than the pore size, the

colloids can also get into the pores, further reducing the effective pore size (Bruggen et al., 2008).

(c)   Biofouling

Biofouling is a dynamic process involving biologically active organisms in feed water (Schäfer et al. 2004). Biofouling results in the formation of biofilm on the membrane surface, due to the colonization and growth of microbes. However, in NF membranes, biofouling is not a specific problem because of the relatively smaller pore size compared to the size of bacteria (Bruggen et al., 2008).

(d)   Organic Fouling

Organic fouling is caused due to various organic compounds in water, such as humic substances, proteins, polysaccharides, dead and living microorganisms (Escobar et al., 2005). The organic fouling can result in irreversible flux decline and reduced membrane permeability, due to adsorption or deposition of dissolved and suspended organic matters present in water (Schäfer et al., 2004). In the biotechnology and food industry, proteins are mainly responsible for fouling, however in the treatment of surface waters, natural organic matter (NOM) is the main fouling component (Kilduff et al., 2004).

2.2.2. Various Fouling Mechanisms in NF membranes

Depending on the membrane characteristics (membrane surface charge, roughness, porosity), feed water quality (organic, inorganic, colloids & microorganisms) and operating conditions (pH, temperature, pressure, cross-flow velocity), the mechanism of fouling can be different

(Zularisam et al., 2006). The decline in flux can be due to the accumulation of high concentration of pollutants near the membrane surface due to diffusion (concentration polarization), formation of a gel layer on the membrane surface or pore restriction and blocking by molecules in water that can penetrate into the membrane pores (Kaya et al., 2011).

Based on literature, the mechanisms of fouling in NF membranes have been characterized most commonly using a resistance-in-series model (Kaya et al., 2011; Fang & Duranceau, 2013). This model incorporates the sum of hydraulic resistances offered by different fouling mechanisms to describe the decline in flux of a fouled membrane. The occurrence of these fouling mechanisms is not completely independent of each other, and therefore the effect of each mechanism needs to be studied individually to observe its contribution to the decreased membrane performance (Shirazi et al., 2010).

(a)   Concentration Polarization

Concentration polarization is the phenomenon when the concentration of the retained particles in the vicinity of the membrane surface is higher compared to the bulk solution. Particles in water are transported towards the membrane surface due to convection. However, there is a back diffusion of those particles towards the bulk solution. When the rate of back diffusion equals the rate of accumulation, the concentration of particles near the membrane surface reaches a steady state. Due to the high selectivity of NF membranes, concentration polarization exists in all cross-flow filtration processes (Mulder, 1996). The concentration polarization phenomena result in hindered flow of solvent through the membrane (reduced flux) and as a long-term consequence,

can also result in the formation of a more compact and dense fouling layer on the membrane surface or internal pore fouling (Kaya et al., 2011).

(b) *Gel layer formation*

Gel layer formation is considered to be the result of precipitation and complexation of organic and inorganic matters which further gets adsorbed to the membrane surface (Schäfer et al., 2004). The formation of gel layer provides additional resistance to the flow due to its behavior as a secondary filter on the top of NF membrane and its thickness continues to increase until a steady state condition is reached. The gel layer formed can be reversible or irreversible depending on the method of membrane cleaning used (Nghiem et al., 2010). Particles that are retained on the membrane surface due to pore size exclusion by the NF membranes, can attach to the surface due to the charged membrane surface, resulting in decreased permeate flux (Jarusutthirak et al., 2007(b)). However, in surface waters that are high in NOM and inorganic content, the adsorption of foulants to the membrane surface involve both chemical and physical interactions (Hong & Elimelech, 1997).

(c) *Internal Pore Blockage / Fouling*

Internal pore blockage / fouling is generally caused by particles that are smaller than the membrane pore size. These particles tend to adsorb onto the internal walls of the pores and minimize the effective pore size used for the water filtration. Some particles that are similar in size to the membrane pores can cause immediate pore blockage which can further form a compact and dense cake/gel structure under the effect of deposition and compaction (Schäfer et al., 2004). However, particles that are not readily able to enter the pores can be pressurized into

the pores by the constantly applied pressure. Pore blockage in NF membranes are partially held responsible for the flux decline (Bellonaa et al., 2010).

2.2.3. Factors affecting Permeate Flux & NF Membrane Fouling

(a) Temperature

Temperature of feed water directly influences the viscosity of water and is generally encountered with seasonal variations. Therefore, a decrease in temperature of feed water can result in either decreased flux or increased pressure to produce a predetermined flux. According to Chellam and Zander (2005), a decrease in 5°C can result in 13% increase in viscosity and a corresponding 11.7% decrease in flux at a constant driving pressure. Thus, higher transmembrane pressure might be required in winter to produce the same flux as in summer.

Several previous studies have demonstrated that temperature plays a significant role in affecting the permeate flux and membrane fouling. According to Goosen et al. (2002), polymeric membranes are sensitive to changes in feed temperature. The study reported an increase of permeate flux by 60%, when the temperature was increased from 20 to 40°C. The increase in permeate flux with temperature was attributed to the thermal expansion of membrane material. Sharma et al. (2003) described this behavior as a result of increase in membrane pore size and decrease in pore density which leads to decreased rejection of pollutants in water. Some studies also suggested that the increase in feed water temperature can lead to an increase in permeate diffusion rate through the membrane which might result in increased flux and decreased fouling (Salahi et al., 2010; Dang et al., 2014).

(b)   Compaction

Hydration, swelling, and deformation of the membranes during the initial stage of operation is very common in high pressure driven membranes, such as NF and RO. The viscoelastic nature of polymeric membranes leads to the compaction and densification of the membranes in the direction of applied hydrodynamic pressure (Hussain & Al-Saleh, 2014). While the membrane is compacting, a significant decline in flux can be observed and also an increased rejection, until the membrane matrix reaches an equilibrium state i.e., permeate flux is constant (Hussain et al., 2013).

The membrane compaction causes reduction in both effective pore size and the pore channel length. The time required to optimally pre-compact a membrane is not very clear in literature and therefore, requires more detailed investigation (Vrijenhoek et al., 2001; Lee et al., 2005; Bellonaa et al., 2010; Nghiem et al., 2010). However, the time required for sufficient compaction mainly depends on the type of membrane and its fabrication method. The active layer in TFC membranes has very small pore size, and therefore decrease in thickness of this layer during compaction causes a linear flux decline, further resulting in reduction of pore size. However, for highly porous structure, there can be an increase in flux due to reducing pore channel length (Hussain & Al-Saleh, 2014). Besides, compaction can be both reversible and irreversible, i.e. permanent deformation in the membrane structure results in irreversible compaction. However, after some relaxation effect the membrane partially regains its structure which is knowns as reversible compaction (Vishvanathan et al., 1998; Stade et al., 2013). Stade et al. (2013) used a relaxation time of 16 hours (under wet conditions and no applied pressure) to monitor any flux recovery due to reversibility of compaction in ultrafiltration membranes. The extent of

compaction and flux recovery highly depends on the type of membrane material. However, there was no consistent information provided for membrane relaxation time in literature.

In addition to the effect of compaction on the membrane operation and performance, it is also considered to be very important factor during the investigation of fouling mechanisms. The compaction effect in NF membranes may combine with the fouling effect and interfere with the identification of potential fouling mechanisms for a particular type of water (Hussain & Al-Saleh, 2014). Therefore, to avoid such interference, membranes are often pre-compacted at a higher pressure than the operating pressure to ensure the flux stability during fouling studies (Schäfer et al., 2004).

Hussain et al. (2013) studied the compaction effect in NF90 membrane samples by observing the decline in flux for a compaction time of 2 hours. During this study, it was observed that the initial flux for replicate membrane samples significantly varied from each other and that these variations were more significant at lower pressures than higher pressures. The initial flux represents the original membrane permeability as per manufactured characteristics, while the final flux is the indication of the extent to which the NF membrane can be compacted. It was also found that in case of TFC membranes, the flux is controlled by the active skin layer and not the polysulfone support layers. The flux was observed to decrease by almost 40% within the experiment time of 2 hours due to compaction (Hussain et al., 2013).

*(c)   **Membrane Surface Properties***

Membrane properties such as hydrophobicity/ hydrophilicity, surface charge, porosity and surface roughness are also very important factors in determining the interaction between foulants and the membrane surface (Zazouli et al., 2010(b)). Hydrophobic top layers in the TFC membranes are considered to be more prone to the adsorptive fouling (Ahn et al., 2008). Hydrophobic membranes cause most of the flux decline (Bruggen et al., 2008) and therefore, hydrophilic membranes are mostly recommended to minimize fouling (Thorsen, 1999). Most of the commercial NF membranes are negatively charged and hydrophilic in nature which enhances the electrostatic repulsion between the membrane surface and the negatively charged organic matter. However, in the presence of positively charged ions, the negative surface charge can be neutralized and enhance membrane fouling (Ahn et al., 2008). When the pore size of the NF membranes is larger than the size of dissolved organic compounds, hydrophobicity is a major parameter in determining the retention of these compounds by binding in or on the membrane surface (Al-Amoudi & Lovitt, 2007). Membrane surface roughness also plays a vital role in enhancement of fouling by increasing the rate of attachment and deposition onto the membrane surface (Al-Amoudi, 2010). These membrane surface properties can also influence the dominant fouling mechanisms, such as gel layer formation or pore fouling (Kaya et al., 2011; Abdelrasoul et al., 2013(a)).

2.2.4. Study of Membrane Surface Morphology

Many surface analysis techniques are available for assessing the membrane fouling and cleaning efficiency based on visualization of membrane surface images. Atomic Force Microscopy (AFM) is the most commonly used technique to characterize the membrane surface morphology

and study the surface adhesion - membrane fouling behavior (Li and Elimelech, 2004(b); Fang & Duranceau, 2013). AFM images are also very helpful in evaluating the performance of chemical cleaning procedures. Karime et al. (2008) compared the surface of a fouled membrane and the surface of a chemically cleaned membrane, and a remarkable difference in surface roughness (141.19 nm and 92.32 nm, respectively) was found between both the membranes. AFM image analysis provides several key parameters that can be used to characterize the membrane surface roughness; such as mean plane roughness (R_a - arithmetic average of all surface height deviations measured from the mean plane), root mean squared roughness (R_q - RMS deviation of the peaks and valleys from the mean plane), and surface area difference (change in surface area due to fouling) in nanoscale. Both the mean plane and RMS roughness of membrane surface are quite close to each other, unless there is a large peak observed in the surface analysis which raises the RMS roughness (Boussu et al., 2005). In this research, mean plane (arithmetic average) surface roughness was used for analysis of change in membrane surface morphology due to fouling.

The surface roughness of membranes obtained from the AFM images can be directly correlated to the intensity of membrane fouling and resulting flux decline. Several researchers have identified increase in flux decline with increase in membrane surface roughness (Vrijenhoek et al., 2001; Song et al., 2004; Hobbs et al., 2006). Hirose et al. (1996) suggested that a linear relationship exists between the mean plane roughness of membrane surface and the permeate flux for crosslinked aromatic polyamide RO membranes. The higher the mean plane roughness, the larger is the surface area for adsorption which increases the deposition of particles onto the membrane surface, further resulting in severe flux decline (Hirose et al, 1996; Vrijenhoek et al.,

2001; Hoek et al., 2003; Hobbs et al., 2006). Particles preferentially get deposited into the valleys of a rough membrane surface causing valley-clogging and resulting in decreased flux (Al-Amoudi, 2010; Shirazi et al., 2010). Vrijenhoek et al. (2001) used the physical parameters obtained from AFM analysis to correlate them with the flux decline data of RO and NF membranes to predict the trend of fouling in membranes. This study identified a flux decline of almost 38 – 50% in RO membranes (33.4 – 52.0 nm) and 14 – 47% in NF membranes (10.1 – 43.3 nm) (increasing flux decline with increasing mean plane surface roughness). The dependency of fouling and flux decline on membrane surface roughness has been elaborated quite evidently in literature. Despite of these efforts, the relationship between the measured surface roughness and resistances offered due to various fouling mechanisms in NF membranes is still not well understood.

2.3. Fouling in NF Membranes used for Surface Water Treatment

NF membranes have been found to be highly efficient in the treatment of surface waters due to its high retention potential for organics and inorganics (especially divalent cations), and higher flux production (Mohammad et al., 2015). Surface waters comprise of a complex mixture of various compounds, but most predominantly of dissolved organic content in the form of natural organic matters (NOM) and inorganic content in the form of divalent cations contributing hardness (Liikanen, 2006). Based on findings, dissolved natural organic matters are considered to be the major cause of NF fouling during filtration of surface waters (Kilduff et al., 2004). Also, inorganic salts such as calcium and magnesium are capable of forming precipitates and scales in the system while degrading the membrane performance. The presence of NOM and hardness together in surface water has been confirmed to enhance the fouling by divalent cations

to metal-organic complexation, resulting in increased flux decline (Li & Elimelech, 2004(a)). However, the characteristics and mechanisms of fouling in NF membranes need to be further investigated for the coupled effect of NOM and hardness in water.

2.3.1. Role of NOM in NF Fouling

Natural organic matter in water is a complex mix of particulate and dissolved organic and inorganic matter that vary depending on the seasonal changes and source of origin. NOM in surface waters cause aesthetic concerns, such as adding color, taste and odor, and also can chemically bind with other inorganic contaminants (Metsämuuronen et al., 2014). The presence of NOM in water can also enhance bacterial growth as well as biodegradation of organics, and therefore removal of NOM from water is necessary for human consumption (Goel et al., 1995). Most of the water treatment plants use chlorine for the disinfection of water. Although NOM itself is not considered to be toxic, it has the potential to react with chlorine to form potentially hazardous disinfection by-products (DBP) that are highly carcinogenic (Goss, 2011). Therefore, removal of NOM is a major concern in most water treatment processes and NF membranes are most commonly used method due to its high NOM removal efficiency (Kilduff et al., 2004).

NOM is considered to be a heterogeneous mixture of compounds with varying ranges of molecular weight, functional groups (phenolic, hydroxyl, carbonyl groups and carboxylic acid) and sources (Zularisam et al., 2006). Suspended or particulate organic matter (POM) can be easily retained on a 0.45 µm filter and removed from surface waters by using treatment methods such as coagulation, flocculation, and filtration (Goss, 2011). Also, POM comprise of only about 10% of the total organic matter found in the natural surface waters (Leenheer & Croue, 2003).

Therefore, dissolved organic matter (DOM) is the major ubiquitous group of compounds present in surface waters which is also very difficult to remove by any conventional treatment method. Although NF membranes are designed to efficiently remove dissolved organics, DOM is found to have the most deleterious effect on the membrane performance due to irreversible fouling resulting from surface water filtration (Zularisam et al., 2006).

DOM are generally comprised of humic substances, polysaccharides, amino acids, fatty acids, and proteins. The molecular weight of DOM varies from 100 to 100,000 Daltons and the concentration in surface water is influenced by various environmental factors such as pH, alkalinity, salinity, nutrients, temperature, turbidity and water flow rate (Goss, 2011). DOM can be fractionated into three major components, hydrophobic, hydrophilic, and transphilic (acid, base or neutral), where hydrophobic fraction represents almost 50% of the dissolved organic carbon (DOC) with larger molecular weight. Hydrophilic fractions contribute almost 25-40% DOC with lower molecular weight and transphilic fractions contribute approximately 25% DOC (Zularisam et al., 2006). NOM is predominantly composed of humic substances (hydrophobic) which are also responsible for the color of natural water (Fan et al., 2001; Schäfer, 2001). Humic substances can further be divided into three categories, humic acid (HA), fulvic acid (FA), and humin.

Based on literature, NOM in surface waters is found to be the major foulant and its deposition on NF membranes is the most dominant factor resulting in severe flux decline (Zularisam et al., 2006; Jarusutthirak et al., 2007(b)). The membrane performance can be affected by various important NOM properties, such as hydrophobic or hydrophilic fraction, molecular weight and

functional groups. Many researchers have studied the effect of these NOM properties on membrane fouling (Cho et al., 1998; Speth et al., 2000; Fan et al., 2001; Lee et al., 2002; Bessiere et al., 2009). However, the results are conflicting due to varying hydrodynamic conditions, membrane and NOM properties.

Some previous studies suggest that humic substances cause more significant (irreversible) fouling than FA, due to their low solubility, high aromaticity, adsorptive behavior, and hydrophobic nature (Yuan & Zydney, 1999; Jones et al., 2000). However, some other studies identified the hydrophilic neutral fraction to contribute to major flux decline (Lin et al., 2000) and also in determining the rate and extent of flux decline (Carroll et al., 2000; Fan et al., 2001). Fan et al. (2001) ranked the major NOM fractions based on their fouling potential in the order of hydrophilic neutral > hydrophobic acids > transphilic acids > hydrophilic charged.

Higher molecular weight compounds were also identified to have larger impact on fouling, compared to smaller DOM. Lee et al. (2002) found that polysaccharides and proteins that have large molecular weights can cause severe membrane fouling due to its neutral adsorptive character. This finding was well supported by the study of Speth et al. (2000) who observed more fouling due to hydrophilic neutrals than hydrophobic acids. In this study, the fouling behavior of polysaccharides was associated to its bulky, macromolecular shape that makes it prone to adsorb and foul the membrane surface. Lin et al. (2000) also studied the effect of fractionated NOM on UF membrane fouling and identified that both hydrophobic and hydrophilic components caused flux decline, however, the hydrophilic fraction was found to induce the worst fouling conditions. Lee et al. (2006) studied the fouling of RO membranes

using alginate (hydrophilic) and Suwanee River natural organic matter (hydrophobic), and reported that hydrophilic fouling was more severe than the hydrophobic fouling. The findings of the study were associated to the high intermolecular bridging capacity of alginate and also high molecular weight of hydrophilic compounds (Lee et al., 2006). Svenda and Gorczyca (2014) analyzed the foulants on NF membranes treating Red River water in Manitoba (Canada). The foulants were fractionated to determine the composition of DOC. It was identified that almost 74% of the total DOC was hydrophilic and mainly hydrophilic neutral fraction was responsible for contributing to maximum fouling (Svenda and Gorczyca, 2014).

2.3.2. Role of Hardness in NF Fouling

Along with NOM in surface water, a variety of inorganic salts and minerals are present, contributing hardness to the water. The presence of high concentration of inorganic salts in surface water can result in inorganic scaling (Shirazi et al., 2010). Mostly in NF and RO systems, membrane scaling is a common phenomenon occurring at the membrane surface due to concentration of salts in water exceeding the solubility limits and forming precipitates or crystals. Scaling is a thermodynamic process involving a change of phase that requires a degree of supersaturation depending on the ion activities in the precipitation reaction (Bruggen et al., 2008). Water treatment systems using NF membranes encounter inorganic foulants such as carbonate, sulphate and phosphate salts of divalent ions, metal hydroxides, sulphides, and silica (Schäfer et al., 2004).

Many water treatment processes use NF membranes not only for the removal of organic pollutants, but also for water softening, due to its high retention capacity for divalent cations.

Surface waters tend to have a high concentration of divalent cations such as Ca^{2+} and Mg^{2+} which is responsible for imparting hardness to the water, and varieties of monovalent cations. These alkaline earth metal cations when combined with polyanions such as carbonate (CO_3^{2-}), sulphate (SO_4^{2-}) and phosphate (PO_4^{3-}) ions, can lead to more fouling problems on NF membranes (Jarusutthirak et al., 2007(a)). Jarusutthirak et al. (2007(a)) studied the effect of monovalent and divalent cations on NF membrane fouling using NaCl and $CaCl_2$, and found that divalent cations cause more flux decline than monovalent cations, indicating that calcium ion has a significant effect on membrane fouling (Table 1). This finding was also supported by the studies carried by Hong & Elimelech (1997) and Schaefer et al. (1998). Also, phosphate was observed to be responsible for higher flux decline, compared to carbonate and sulphate scalants.

2.3.3. Combined effect of NOM-Hardness in NF Fouling

NF membranes have been found to be very effective in removing natural organic matter (NOM), very widely known as disinfection by-product (DBP) precursors formed during chlorination of drinking water treatment. Besides, NF membranes have also been popularly used for water softening, due to their high rejection efficiency for multivalent and monovalent ions (Jarusutthirak et al., 2007(b)). Both the organic and inorganic compounds in surface water are responsible for individually inducing limitations to membrane performance by fouling the membranes and resulting in decreased flux or increased pressure which further affects the operation and maintenance costs. However, NOM fouling is considered to be more intense when it combines with divalent cations, such as calcium and magnesium to form Metal-NOM complexes, resulting in the formation of a strong and highly compacted fouling layer on the NF membrane surface (Seidel & Elimelech, 2002). According to Ahn et al. (2008), truly dissolved

NOM is not important in the fouling process, and it is the divalent cations that interact with the NOM and enhance the aggregation and deposition of foulants on the membranes (Table 1). The study confirmed that divalent cations are the main boosters of fouling, rather than the direct deposition of carboxylate groups onto the sulfonyl groups of polyethersulfone (PES) membranes.

The molecular structure of NOM is not very well-defined and are very complex in nature. However, NOM consist of various acidic functional groups and the organic acid characteristics of the NOM is determined by the concentration of carboxyl functional groups (Ahn et al., 2008). Most of the NOM oxidize very slowly and therefore, their solubility in water depends on the pH of water. The presence of high ionic strength in water can reduce the electrostatic double layer forces between the NOM and membrane surface, resulting in foulant deposition and subsequent membrane fouling (Braghetta et al., 1997). Moreover, along with the ionic strength effect, the complexation between divalent metal ions (such as Ca^{2+} and Mg^{2+}) and acidic groups of NOM in natural waters, further enhances the NOM fouling (Seidel & Elimelech, 2002).

Many researchers have extensively studied the binding of divalent and monovalent ions to the acidic groups of NOM. Although, both Ca^{2+} and Mg^{2+} are divalent metal ions, however, based on literature, Ca^{2+} appears to interact more strongly in comparison to Mg^{2+} or other ions such as sodium (Na^+) (Lee et al. 2006; Ahn et al., 2008; Al-Amoudi, 2010). Li & Elimelech (2004 (b)) identified that the flux declined more severely in the presence of calcium compared to magnesium i.e., the inter molecular adhesion between the humic acids and fouled membrane increased significantly in the presence of Ca^{2+} compared to Mg^{2+}. Lee et al. (2006) investigated the effect of feed solution chemistry on RO membrane fouling using alginate as the synthetic

organic content in water (Table 1). Based on their study, it was confirmed that a thick alginate layer was formed on the membrane surface in the presence of calcium, while no alginate layer was observed in the presence of magnesium. This fouling behavioral difference between calcium and magnesium is associated with the complex forming capacity of these cations with NOM. Ahn et al. (2008) described this behavior by a strong inner-sphere complexation capacity for Ca^{2+} and no complexation at all for Mg^{2+}, because of which Ca^{2+} forms stronger complexes with NOM carboxylate groups.

The combined fouling effect of divalent cations and NOM has been studied by several researchers and many of these studies have concluded that the presence of calcium along with NOM in surface water dramatically decreases the permeate flux due to the reduced charge of both the NOM and membrane surface (Hong & Elimelech, 1997; Jarusutthirak et al., 2007(b); Al-Amoudi, 2010). Unlike other ions, calcium ions bind specifically with the acidic functional groups of NOM and reduce the negative charge of NOM by forming Ca-NOM complexes (Hong & Elimelech, 1997). The presence of calcium ions also neutralizes the negatively charged membrane surface which further accelerates the deposition of Ca-NOM complexes onto the partially neutralized membrane surface (Ahn et al., 2008). The formation of Ca-NOM complexes can result in reduced inter-chain electrostatic repulsion of NOM, forming small, coiled NOM macromolecules. Also, calcium can act as a medium to form a bridge between these NOM macromolecules (Al-Amoudi, 2010). As a result of the chemical and physical interactions between calcium, NOM and membrane surface, the foulant deposition can form a compact and dense fouling layer on the membrane surface.

The concentration of calcium and NOM in feed water and NF membrane surface characteristics are highly responsible in affecting the nature and extent of interactions between them. These interactions can affect the membrane performance in terms of flux decline, hydraulic resistance due to fouling, fouling mechanism, reversibility (or irreversibility) and surface roughness of fouling layer. Several research works have been carried out for investigating the fouling in NF membranes under different feed water quality, specifically concentration of DOC and Calcium (Table 1). The reported NF feed water DOC ranged between 1.5 – 20 mg/L and Calcium concentration between 0.45 – 1016 mg/L. However, none of these studies actually investigated fouling mechanism in the feed water containing both extremely high DOC and Ca concentration higher than 100 mg/L. Also, the relationship between the effects of fouling such as, flux decline, hydraulic resistance, fouling mechanisms and surface roughness in most of the studies were not clearly understood. Therefore, this study was mainly carried out to fill the research gap of investigating the relations between these parameters and also determine the flux decline and fouling mechanisms in NF90 membranes used for the filtration of varying calcium concentrations in the presence of DOC.

Table 1. Research findings of past studies on membrane fouling under different calcium and NOM concentrations in feed water

PAPER	Type of feed water (synthetic vs. natural)	Calcium (mg/L as CaCO$_3$)	NOM (mg/L as DOC)	Research Findings
Ahn et al., 2008	Natural	0.45	2.43	Ca^{2+} associates with the carboxyl groups more strongly than Mg^{2+} due to the looser second hydration shell structure of Ca^{2+}.
Song et al., 2004	Natural	20.25	3.5 - 4	High DOC and Ca accumulation was found on the membrane surface in the form of gel on the

				membrane.
Lee et al., 2006	Synthetic	50	8.24	Severe alginate fouling in the presence of calcium results from calcium induced alginate gel formation at the membrane surface.
Jarusutthirak et al., 2007(a)	Synthetic	50	10	NOM fouling exhibited greater flux decline with calcium ions, while solution flux curves dominated cake formation model.
Katsoufidou et al., 2007	Synthetic	50,100, 200	4.12	With increased calcium addition, cake development becomes the dominant mechanism throughout the filtration step and fouling reversibility is increased with the increase of calcium concentration.
Li and Elimelech, 2004(a)	Synthetic	100	20	Increased flux decline in NF90 membrane in the presence of calcium ions is attributed to the metal-humic complexation and membrane surface roughness.
Gorzalski and Coronell, 2014	Natural	105.5-115.8	6.7-8.7	Increased calcium concentration could cause precipitations in the fouling (cake layer).
Bellona et al., 2010	Synthetic	123.5	9.9	Sieving mechanism of the NF90 membrane changed slightly with fouling as the effective pore size became smaller with a larger deviation in pore size after fouling.
Gwon et al., 2003	Natural	166.5	2.68	A significant amount of Ca was detected in the membrane acid cleaning disposals; the inorganic-bound Ca was the major foulants. Dissolved organics seemed to accumulate very near the membrane surface and the flat-board-like inorganic matter accumulated next to the organic fouling layer.
Jamal et al., 2014	Synthetic	15.62, 31.25, 46.85, 62.5, 125, 250, 556.25	4.12 – 8.24	Flux decline and irreversible fouling developed during filtration increased with the calcium addition due to the bonding and charge neutralization capacity of calcium on membrane filtration.

Rubia et al., 2008	Surface	181.75–1016.75	1.5 - 6.5	Higher NOM removal efficiencies were obtained with NF90 membrane for all the tested water. Flux decreases in the presence of NOM and decreases further in the presence of both NOM and calcium ions.
Hong and Elimelech, 1997	Synthetic	25 - 250	10	Product water flux due to NOM fouling decreases dramatically as calcium concentration increases.

2.3.4. Other factors affecting NF Fouling

In addition to the chemical factors influencing the nature of NOM fouling in NF membranes, hydrodynamic conditions such as applied pressure, initial permeate flux and cross-flow velocity also play a very important role (Lee et al., 2006). At higher initial permeate flux or low cross-flow rate, the rejected Ca^{2+} concentration near the membrane surface is very high due to concentration polarization. This phenomenon might enhance the Ca-NOM complexation and deposition (Seidel & Elimelech, 2002). An increase in the cross-flow velocity can minimize the foulant-foulant interaction and thus, reduce the growth of fouling layer. Therefore, a controlled operational condition can certainly improve the membrane performance and cause minimal fouling.

Chapter 3: INVESTIGATION OF FOULING MECHANISMS IN NANOFILTRATION MEMBRANES USED FOR THE FILTRATION OF HIGH DOC AND VARYING HARDNESS WATER

Abstract

This study investigates the behavior of flux decline and change in fouling mechanisms in nanofiltration membranes, for the treatment of high DOC water in the presence of divalent cations (Ca^{2+}) at different concentrations. A model synthetic water composed of sodium alginate concentration of 17mg/L as DOC and calcium chloride of three concentrations: low 50, medium 200, and high 350 mg/L as $CaCO_3$, was used for the fouling study. The synthetic water quality was based on the DOC and hardness concentrations reported in three potable water sources in the Province of Manitoba and Ontario, Canada. A thin-film composite (TFC) NF90 membrane (DOW Filmtec., USA) was used for the fouling studies. Resistance-in-series model and other fouling models were used to describe the permeate flux decline and changing fouling mechanisms in NF90 membranes. The fouling study demonstrated that low calcium concentration formed an irreversible fouling layer with a surface roughness of 15.38 nm, due to increased adhesive forces between foulants and the rough membrane surface. At high calcium concentration, a dense, compact and reversible fouling layer was formed, due to increased cohesive forces between calcium and alginate molecules, resulting in maximum Ca-Alginate complexation and aggregation. The aggregates further linked together to form a cross-linked foulant structure with a surface. roughness of 38.17 nm. However, for medium calcium concentration a complex (non-uniform porosity) matrix of foulants was formed with a very high

surface roughness of 67.97 nm, due to the insufficient calcium available to fulfill the binding sites on alginate molecules. The fouling layer so formed resulted in offering highest flux decline and total hydraulic resistance. Results of fouling experiments identified that the reversibility of alginate fouling increased with increasing calcium concentration. However, the flux decline and the total hydraulic resistance was dependent on both alginate and calcium concentrations for maximum complexation and aggregation. In addition to the aforementioned effects of Ca^{2+}, results also show that the dominance of gel layer formation fouling mechanism increases with increase in calcium concentrations.

3.1. Introduction

Surface water sources in Manitoba and Ontario have been reported to contain high concentrations of Dissolved Organic Carbon (DOC) and wide range of hardness levels. Therefore, the removal of DOC and hardness have been one of the major objective for many of the drinking water treatment plants (WTP). NF membranes have been found to be highly efficient in the treatment of these surface waters, due to its high retention potential for organics and inorganics (especially divalent cations), and high flux production (Mohammad et al., 2015). However, NF membranes are highly susceptible to fouling, thus, limiting the successful application of the membrane technology. Fouling of membranes can cause reduction of permeate flux or increase in operating pressures, ultimately affecting the energy requirements and the plant economy (Darton et al., 2004).

The fouling process and mechanisms are highly influenced by membrane characteristics, feed water composition, natural organic matter (NOM) properties and hydrodynamic and operating

conditions (Kilduff et al., 2004; Zularisam et al., 2006; Saravia et al., 2013). NF membranes are typically negatively charged at neutral pH (Li & Elimelech, 2004(a)) and both, charge effects and size exclusion mechanisms influence the rejection behavior in NF membranes (Bowen & Welfoot, 2002; Al-Amoudi & Lovitt, 2007). Flux decline in NF membranes can occur due to the accumulation of high concentration of pollutants near the membrane surface due to diffusion (concentration polarization), formation of a gel layer on the membrane surface or pore restriction and blocking by molecules in water that can penetrate into the membrane pores. The mechanisms of fouling in NF membranes have been characterized most commonly using resistance-in-series model (Kaya et al., 2011; Fang & Duranceau, 2013). The fouling in NF membranes can be both reversible and irreversible (after chemical cleaning) (Nghiem et al., 2010), depending on the fouling mechanisms and interactions between the foulants and membrane. The occurrence of these fouling mechanisms is not completely independent of each other, and therefore the effect of each mechanism needs to be studied individually to observe its contribution to the decreased membrane performance (Shirazi et al., 2010).

3.1.1. Feed Water Composition and Membrane Fouling

Surface waters comprise of a complex mixture of various compounds but most important for membrane filtration are NOM (typically reported as DOC) and divalent cations (primarily Ca^{2+} and Mg^{2+}) contributing hardness (Liikanen, 2006). The composition of NOM in surface water depends on the seasonal changes and source of origin. Dissolved NOM are considered to be the major cause of NF fouling during filtration of surface waters (Hong & Elimelech, 1997; Kilduff et al., 2004; Li & Elimelech, 2004(a)); Mohammad et al., 2015). Dissolved NOM are generally comprised of humic substances, polysaccharides, amino acids, fatty acids, proteins, etc. NOM

can be fractionated into three major components, hydrophobic, hydrophilic, and transphilic (acid, base or neutral), where hydrophilic neutral compounds (such as polysaccharides & proteins) are reported to have the highest fouling potential (Speth et al., 2000; Fan et al., 2001; Lee et al., 2002; Svenda & Gorczyca, 2014).

Along with NOM in surface water, another predominant compound present is the variety of inorganic salts and minerals. Divalent cations such as Ca^{2+} and Mg^{2+} are mainly responsible for imparting hardness to the water. These alkaline earth metal cations when combined with polyanions such as carbonate (CO_3^{2-}), sulphate (SO_4^{2-}) and phosphate (PO_4^{3-}) ions, can lead to more fouling problems on NF membranes (Jarusutthirak et al., 2007(a)). The presence of high hardness concentration in surface water can result in scaling (Shirazi et al., 2010). Membrane scaling is a very common phenomenon occurring at the membrane surface, mostly in NF and RO systems. Some of the most commonly found inorganic salts that are responsible for scale formation on the membrane surface are $CaSO_4$, $CaCO_3$, SiO_2 and $BaSO_4$ (Schäfer et al., 2004).

3.1.2. Interactions between NOM & Hardness in Surface Water Sources and Membrane Fouling

NOM fouling is considered to be more severe when NOM combines with divalent cations to form Metal-NOM complexes. Metal-NOM complexes can form a dense and highly compacted fouling layer on the NF membrane surface (Seidel & Elimelech, 2002). According to Ahn et al. (2008), dissolved NOM is not as important in the fouling process, as the divalent cations that interact with the NOM and enhance the aggregation and deposition of foulants on the membranes. Divalent cations are mainly responsible for enhancing the fouling phenomenon,

rather than the direct interaction of NOM carboxylate groups with the sulfonyl groups of polyethersulfone (PES) membranes (Ahn et al., 2008).

Many researchers have extensively studied the binding of divalent and monovalent ions to the acidic groups of NOM (Table 1) (Lee et al., 2006; Ahn et al., 2008; Al-Amoudi A. S., 2010). These studies reveal that Ca^{2+} interacts more strongly with NOM to form a thick fouling layer on the membrane surface, in comparison to Mg^{2+} or other ions such as sodium (Na^+). This fouling behavioral difference between calcium and magnesium is associated with the strong inner-sphere complexation capacity for Ca^{2+} and no complexation at all for Mg^{2+}, because of which Ca^{2+} forms stronger complexes with NOM carboxylate groups (Ahn et al., 2008).

Unlike other ions, calcium ions bind specifically with the acidic functional groups of NOM and reduce the negative charge of NOM by forming Ca-NOM complexes (Table 1) (Hong & Elimelech, 1997). Calcium ions also neutralize the negatively charged membrane surface which further accelerate the deposition of Ca-NOM complexes onto the partially neutralized membrane surface (Ahn et al., 2008). The formation of Ca-NOM complexes can result in reduced inter-chain electrostatic repulsion of NOM, forming small, coiled NOM macromolecules. Also, calcium can act as a medium to form a bridge between these NOM macromolecules, further resulting in a more compact and dense fouling layer on the membrane surface (Al-Amoudi, 2010). Based on literature review, investigation of NF fouling mechanisms with different feed water composition has been carried out to identify the importance of Ca-NOM complexation in NF fouling (Table 1).

3.1.3. Effects of Membrane properties on Flux Decline and Membrane Fouling

(a) Compaction of NF Membranes

Deformation of membrane structure, due to compaction, in the early stages of filtration is a very common phenomenon in high pressure driven membranes, such as NF and RO. While the membrane is compacting, a significant decline in flux can be observed and also an increased rejection, until the membrane matrix reaches an equilibrium state i.e., permeate flux is constant (Hussain et al., 2013; Hussain & Al-Saleh, 2014). However, compaction can be both reversible and irreversible in nature. A permanent deformation in the membrane structure results in irreversible compaction, however, when the membrane partially regains its structure, after some relaxation effect, is known as reversible compaction (Vishvanathan et al., 1998).

Hussain et al. (2013) studied the compaction effect in NF90 membrane samples by observing the decline in flux with time. The initial flux in the study represented the original membrane permeability as per manufactured characteristics, while the final flux indicated the extent to which the NF membrane can be compacted. It was also found that in case of TFC membranes, the flux is controlled by the active skin layer and not the polysulfone support layers. The flux was observed to decrease by almost 40% within the experiment time of 2 hours, due to compaction (Hussain et al., 2013). Due to the effect of compaction in TFC membranes, most of the studies for investigation of fouling mechanisms, include a precompaction step before the actual filtration tests. Membranes are precompacted at a higher pressure than the operating pressure to ensure the flux stability during fouling studies (Schäfer et al., 2004) , and to separate the effects on flux decline due to membrane compaction and fouling.

(b) Membrane Surface Morphology

Many surface analysis techniques are available for assessing the membrane fouling and cleaning efficiency based on visualization of membrane surface images. Atomic Force Microscopy (AFM) is the most commonly used technique to characterize the membrane surface morphology and study the surface adhesion - membrane fouling behavior (Li and Elimelech, 2004(b); Fang & Duranceau, 2013). AFM images are also very helpful in evaluating the performance of chemical cleaning procedures. Karime et al. (2008) compared the surface of a fouled membrane and the surface of a chemically cleaned membrane, and a remarkable difference in surface roughness (141.19 nm and 92.32 nm, respectively) was found between both the membranes. AFM image analysis provides several key parameters that can be used to characterize the membrane surface roughness; such as mean plane roughness (R_a - arithmetic average of all surface height deviations measured from the mean plane), root mean squared roughness (R_q - RMS deviation of the peaks and valleys from the mean plane), and surface area difference (change in surface area due to fouling) in nanoscale. Both the mean plane and RMS roughness of membrane surface are quite close to each other, unless there is a large peak observed in the surface analysis which raises the RMS roughness (Boussu et al., 2005). In this research, mean plane (arithmetic average) surface roughness was used for analysis of change in membrane surface morphology due to fouling.

The surface roughness of membranes obtained from the AFM images can be directly correlated to the intensity of membrane fouling and resulting flux decline. Several researchers have identified increase in flux decline with increase in membrane surface roughness (Vrijenhoek et al., 2001; Song et al., 2004; Hobbs et al., 2006). Hirose et al. (1996) suggested that a linear

relationship exists between the mean plane roughness of membrane surface and the permeate flux for crosslinked aromatic polyamide RO membranes. The higher the mean plane roughness, the larger is the surface area for adsorption which increases the deposition of particles onto the membrane surface, further resulting in severe flux decline (Hirose et al, 1996; Vrijenhoek et al., 2001; Hoek et al., 2003; Hobbs et al., 2006). Particles preferentially get deposited into the valleys of a rough membrane surface causing valley-clogging and resulting in decreased flux (Al-Amoudi, 2010; Shirazi et al., 2010). Vrijenhoek et al. (2001) used the physical parameters obtained from AFM analysis to correlate them with the flux decline data of RO and NF membranes to predict the trend of fouling in membranes. This study identified a flux decline of almost $38 - 50\%$ in RO membranes ($33.4 - 52.0$ nm) and $14 - 47\%$ in NF membranes ($10.1 - 43.3$ nm) (increasing flux decline with increasing mean plane surface roughness). The dependency of fouling and flux decline on membrane surface roughness has been elaborated quite evidently in literature. Despite of these efforts, the relationship between the measured surface roughness and resistances offered due to various fouling mechanisms in NF membranes has not been investigated.

3.1.4. Flux Decline and Membrane Fouling Mechanisms

Several mathematical models have been widely used to explain the permeate flux decline due to various fouling mechanisms. Some commonly used models based on various fouling mechanisms in a cross-flow filtration system are complete pore blocking, standard pore blocking, intermediate filtration and cake filtration (Jarusutthirak et al., 2007(b); Abdelrasoul et al., 2013(a); Iritani & Katagiri, 2016). The linearized form of equations (1- 4 in Table 2) for permeate flow at a constant pressure for each fouling model can be used for data analysis and

model identification. The regression coefficient (R^2) can be used as an index to investigate the agreement of experimental data with the used model. The closer the R^2 value of a particular model to 1, the more dominant is the fouling mechanism associated to that model (Garravanda et al., 2017; Lin., 2017).

Table 2. Fouling models

Fouling mechanism	Constant pressure filtration	
Complete pore blocking	$\ln J = \ln J_0 - k_b \cdot t$	(1)
Gradual pore blocking (standard pore blocking)	$\dfrac{1}{\sqrt{J}} = \dfrac{1}{\sqrt{J_0}} + k_s \cdot t$	(2)
Intermediate filtration	$\dfrac{1}{J} = \dfrac{1}{J_0} + k_i \cdot t$	(3)
Cake filtration	$\dfrac{1}{J^2} = \dfrac{1}{J_0^2} + k_c \cdot t$	(4)

In Equations (1) – (4), J is the flux (L m^{-2} h^{-1}) at time t (hours), J_0 is the initial flux (L m^{-2} h^{-1}), and the various k values represent the fouling coefficients.

Various factors can affect the flux decline in NF membranes, such as membrane compaction, concentration polarization, adsorption and pore blockage. Other than built-up of fouling layer on the membrane surface, these phenomena usually occur at much shorter time span from the beginning of filtration. The effect of these factors on the membrane performance can be investigated only after a period of operation. The fouling models (Table 2) do not allow the individual investigation of all these factors. Resistance-in-series model incorporates the effect of each factor affecting the fouling mechanisms in membranes, and allows for determinations of various hydraulic resistances.

3.1.5. Objectives of Study

The objective of this study was to investigate the influence of calcium concentration (principal constituent of water hardness) on the fouling mechanisms in NF90 membrane used to filter high DOC (17 mg/L) water. The study was intended to provide at a better understanding of the effect of calcium concentration on the reversibility (or irreversibility) of fouling layer in NF90 membrane. The study focused on investigating the change in behavior of fouling mechanisms and nature of resultant fouling layer due to the interactions between calcium, DOC and NF membrane. The study was carried out to identify the potential dominant mechanism responsible for maximum flux decline and hydraulic resistance to feed flow.

3.2. Materials and Methods

3.2.1. Synthetic Water & Chemical Reagents

The synthetic water composition used in this study was based on typical surface water quality reported for three rivers (potable water sources) in Manitoba and Ontario, (Canada). The raw water quality of Red River, Rainy River and Assiniboine River was obtained for past few years (2012-2015). These rivers were observed to be high in DOC and contained wide range of total hardness concentrations, as presented below in Table 3. Since DOC and calcium hardness have been reported to cause the most significant fouling in NF membranes (Liikanen, 2006; Jarusutthirak et al., 2007(a)), these two parameters were mainly considered for the preparation of synthetic water. This study was focused on understanding the flux decline and fouling mechanisms due to the interactions of only calcium ions with DOC in the feed water and NF

membrane. For that reason, alkalinity, though being an important water quality parameter in surface waters, was not added to the synthetic water.

Table 3. Raw Water Quality in three river in the Canadian Prairie

Source of raw water	DOC (mg/L)		Average DOC	Total Hardness (mg/L as $CaCO_3$)		Average Hardness
	March	August		March	August	
Red River	10.8	12.35	11.6	376.5	323	350
Assiniboine River	13.8	16.1	15	309	285	200
Rainy River	23.2	8.7	15.95	65	41.6	50

Sodium alginate was used as a model component for DOC (Lee et al., 2006; Zazouli et al., 2010(a); Xin et al., 2015) and calcium chloride for hardness (Li & Elimelech, , 2004(a)) in the synthetic water. Sodium alginate is an anionic polysaccharide (hydrophilic neutral compound) produced by bacteria and algae. Based on the range of DOC reported in the three rivers during (as shown in Table 3), the concentration of sodium alginate used in the synthetic water was 17 mg/L as DOC. The total hardness concentration for the three rivers discussed in this study, was reported to be in the range of approximately 40-400 mg/L as $CaCO_3$ and therefore, three different calcium concentrations (50, 200 and 350 mg/L as $CaCO_3$) were selected for the preparation of synthetic water. Both calcium and magnesium are responsible for contributing total hardness in surface water. However, in this study only calcium was considered to be responsible for the total hardness in synthetic water, due to its high complexation capacity with NOM compared to magnesium. Sodium Hydroxide (pH 12) and Citric Acid (pH 4) solutions were used for cleaning the fouled NF membranes. All the chemicals and reagents used for membrane filtration

experiments were purchased from Sigma Aldrich, USA, in powder form and stock solutions were prepared using deionized (DI) water.

3.2.2. Laboratory Membrane Filtration Setup

A flat sheet polyamide TFC NF membrane was used for all the experiments in this study (NF90, DOW Filmtec, USA). According to the manufacturer, the membrane rejects 85-95% of NaCl under the following test conditions: maximum applied pressure of 41 bars and temperature of 45°C. The NF90 membrane has a MWCO (molecular weight cut-off) of 200 Da (DOW Filmtec., 2016). NF90 is a commercial tight membrane consisting of a fully aromatic polyamide active layer supported by a porous polysulfone layer reinforced with a non-woven polyester layer (Yüksel et al., 2013; Azaïs et al., 2014). NF90 membranes are negatively charged under any chemical conditions and also the surface roughness of the membrane is considered to be very high (68 - 70 nm) compared to the surface roughness reported for several other available NF membranes (10.1 – 43.3 nm) (Li & Elimelech, 2004(a)).

A crossflow Sterlitech CF042D membrane filtration cell was used for all the filtration experiments. The internal dimension of the membrane cell was 42 cm^2 as membrane active area and a feed spacer thickness of 7 mm. Besides, the crossflow filtration setup consists of temperature control system, pumps, feed tank (40-liter capacity), pressure gauge and valves, flow meter, digital weighing scale and automatic data acquisition system (Figure 2). The temperature control system was used to maintain a constant temperature of feed water at around 21±1°C. The permeate was continuously collected and weighed using a weighing scale to monitor the permeate flux. The system was operated in a closed loop mode, as both the permeate and

concentrate were circulated back to the feed tank to maintain a constant feed concentration. The system was designed to operate at a constant pressure and variable flux, however vice versa can also be done (Abdelrasoul et al., 2013(a)). Water treatment plants operate at a constant predetermined flux production and variable pressure conditions.
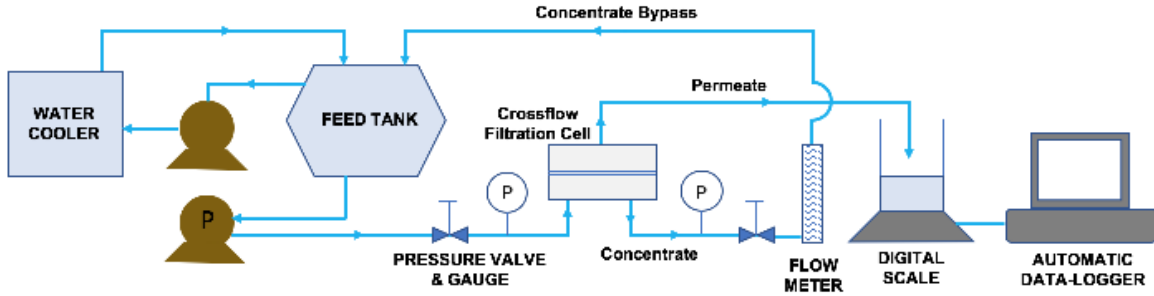
Figure 2. Schematic Diagram of the Bench-scale Experimental Setup

3.2.3. Experimental Procedure

(a) Resistance-in-series Model

Flux decline in a crossflow pressure driven membrane can be caused by several fouling mechanisms that introduce additional resistance to the flow. The permeate flux decline in NF membranes are most commonly described by resistance-in-series model based on Darcy's law, as given in equation (5) (Kaya et al., 2011; Fang & Duranceau, 2013).

$$J = \frac{\Delta P}{R_t \cdot \eta} \tag{5}$$

$$R_t = R_m + R_p + R_g + R_{f,org} + R_{f,inorg} + R_{f,irrev} \tag{6}$$

where, ΔP is the pressure difference between the feed and permeate side of the membrane (Pa), R_t is the total resistance (m^{-1}) and η is the dynamic viscosity of the feed solution (Pa. s). In this

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study, the total resistance (R_t) is equal to the sum of membrane resistance (R_m), concentration polarization layer resistance (R_p), gel layer resistance (R_g), reversible organic pore fouling resistance ($R_{f, org}$), reversible inorganic pore fouling resistance ($R_{f, inorg}$) and irreversible pore fouling resistance ($R_{f, irrev}$) as shown in equation (6). Other than the membrane resistance which is always present, all the other resistances are caused due to the various fouling mechanisms mentioned above.

The selectivity of the membrane was estimated by the percentage of retention (R) on NF membrane and is given by equation (7).

$$R = \left(1 - \frac{C}{C_0}\right) \times 100\% \qquad (7)$$

where R is the retention (%), C is the permeate concentration (mg/L) and C_0 is the concentration in the feed solution (mg/L).

(b) Membrane Precompaction

As a preconditioning step, all membrane samples were soaked for 24 hours in DI water (Hussain et al., 2013), prior to running any filtration tests. This preconditioning step removes any preservatives or residuals on the membranes and ensures that the membranes perform as expected. All the membrane samples were precompacted at a constant pressure of 40 bars for 8 hours (based on preliminary laboratory studies) to stabilize the flux before running any fouling tests. After the precompaction and relaxation of membranes for 12 hours, the flux was measured at an operating pressure of 10 bars for determination of membrane resistance after compaction. The relaxation time was provided to observe any flux restoration due to reversible compaction.

(c) ***Fouling Experiments***

The fouling experiments were carried out using three different composition of synthetic waters, where the concentration of sodium alginate was constant (17 mg/L as DOC) and only the concentration of calcium chloride was varied (50, 200 and 350 mg/L as $CaCO_3$). The experiments for each synthetic water composition was carried out in triplicates. Each fouling test was continuously carried out for 3 days, at a constant operating pressure of 10 bars. Also, flux measurements in all the experiments were done at the same operating pressure (10 bars).

The total fouling resistance was determined from the flux obtained in the end of the fouling experiment. After completing the fouling experiment, DI water was used for forward flushing of the membrane cell, without any applied pressure for around 10 minutes. The flux was measured to determine the resistance due to the presence of concentration polarization layer in the vicinity of membrane surface. The physical cleaning of membrane surface was done by carefully removing the membrane from the filtration cell and gently wiping out the side exposed to the crossflow, using Kimwipes (Kimberley Clark, USA) (Listiarini et al., 2009). The physical cleaning process removes any gel layer formed due to deposition of foulants on the membrane surface, and hence leaving only foulants deposited into the pores. The flux measured at an applied pressure of 10 bars after physical cleaning, was used to determine the gel layer resistance. For chemical cleaning, sodium hydroxide (pH 12) and citric acid (pH 4) solutions were used for the removal of organic and inorganic foulants, respectively, in the membrane pores. A high pH cleaning cycle should be done before the low pH cleaning cycle so as to avoid having the organic material lose their anionic charge. A loss of charge properties may cause the foulant to compact into the membrane and become more difficult to remove (Porcelli and Judd,

2008). The chemical cleaning process for each solution was carried out for 1 hour at a constant applied pressure of 4 bars, so that no permeate is produced with either highly acidic or basic qualities. The flux measured at an applied pressure of 10 bars after each chemical cleaning procedure was used to determine the reversible organic and inorganic pore fouling resistance. After these cleaning steps, the remaining resistance due to the presence of irreversible foulants in the membrane pores was determined. For each experiment, all the resistances are measured for membranes fouled and cleaned in one cycle only. The resistance-in-series model was used for the determination of resistances due to various fouling mechanisms observed during the fouling experiments (Figure 3).
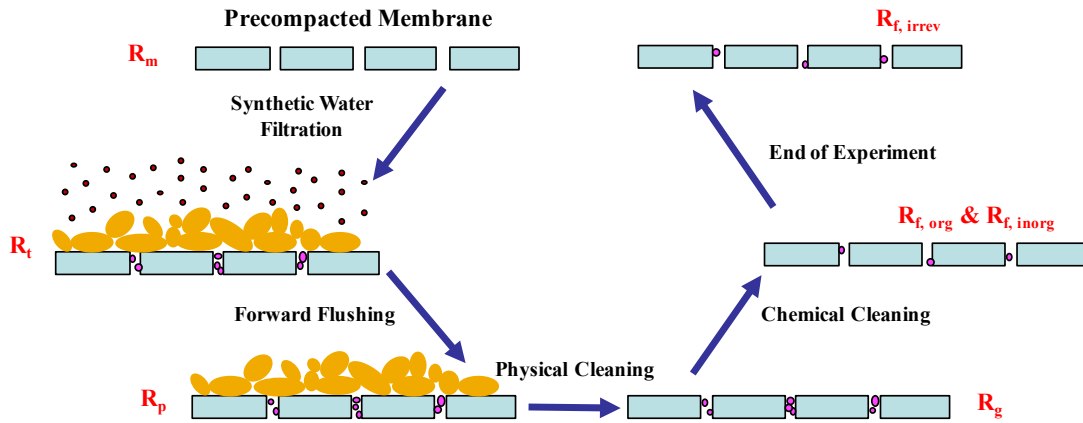
Figure 3. Flow chart for investigation of resistances due to various fouling mechanisms

3.2.4. Analytical Methods

A TOC (total organic carbon) analyzer (Teledyne Tekmar TOC Fusion Analyzer, USA) was used to measure the alginate (DOC) content in both the feed and permeate water. The water hardness was determined by using standard EDTA Titration method (Hach, USA) in both feed and permeate water. For DOC and hardness retention measurements, samples of feed and

permeate water were collected in the beginning and end of fouling experiments for each synthetic feed composition. Membrane surface roughness was measured using Atomic Force Microscopy (AFM) (Veeco D3100, USA) in tapping mode and the images were further analysed using NanoScope v6 software. The AFM measurements were done on NF membranes, prior to precompaction, after precompaction and after fouling to observe the changes in membrane surface morphology. The surface roughness presented in the study is the mean plane surface roughness (R_a – arithmetic average of the deviation from the centre plane) of different scanning spots.

3.3.   Results and Discussion

3.3.1. Effects of Membrane Compaction on Flux Decline

The first part of the study was carried out to investigate the adequate time required to pre-compact the membrane to obtain a stable flux after a relaxation time of 12 hours i.e., membrane compacted beyond that time does not affect the flux obtained after a relaxation time of 12 hours. Based on literature studies, the time required for compaction ranges from 2 to 24 hours (Vrijenhoek et al., 2001; Lee et al., 2005; Bellonaa et al., 2010; Mamun et al., 2017). In this study, the membrane was tested for compaction for 4, 6, 8 and 10 hours (Figure 4) by filtration of DI water through the NF membranes at a constant pressure of 40 bars. Each compaction time was tested in triplicate samples. The flux in the end of the experiment after 4 and 6 hours of precompaction was still decreasing, however, for 8 and 10 hours of precompaction, the flux was observed to be approaching a constant value.
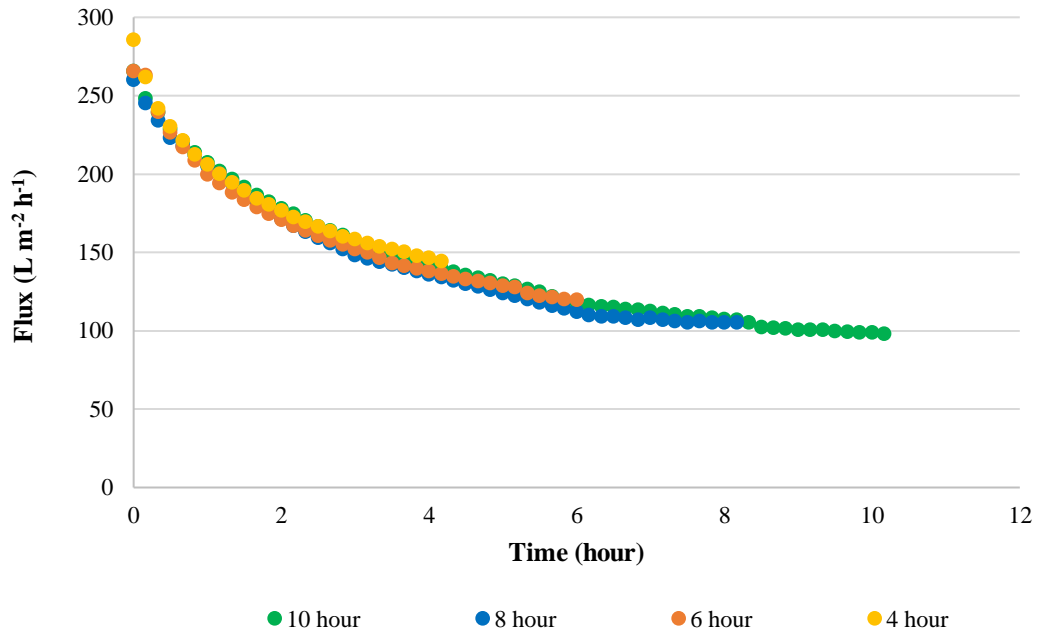
Figure 4. Flux Decline Curve for different hours of precompaction in NF90 membrane

The membrane resistances have been presented for pre-soaked virgin membrane (before applying any pressure), after precompaction and precompacted membrane with relaxation of 12 hours (Figure 5). It was observed that the difference in membrane resistance after precompaction as well as relaxation, between 8 and 10 hours, were within the standard deviation. Therefore, based on these preliminary laboratory studies, a precompaction time of 8 hours was selected for all the membranes, before starting the fouling experiments. Further, the choice (8 hours) was also validated by testing the membrane resistance after 3 days DI water filtration. It was observed that there was no significant decline in flux and the membrane resistance was almost constant (Figure 5).
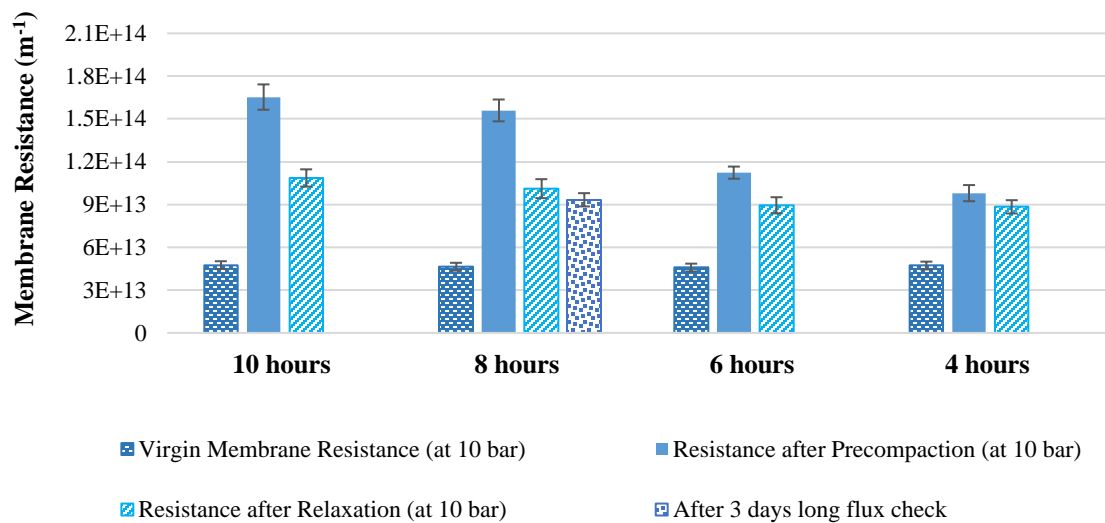
Figure 5. Change in membrane resistance due to precompaction

3.3.2. Effect of Calcium Concentrations on Flux Decline

After the precompaction of membranes, the NF membranes were fouled with the synthetic feed waters of varying calcium concentrations.
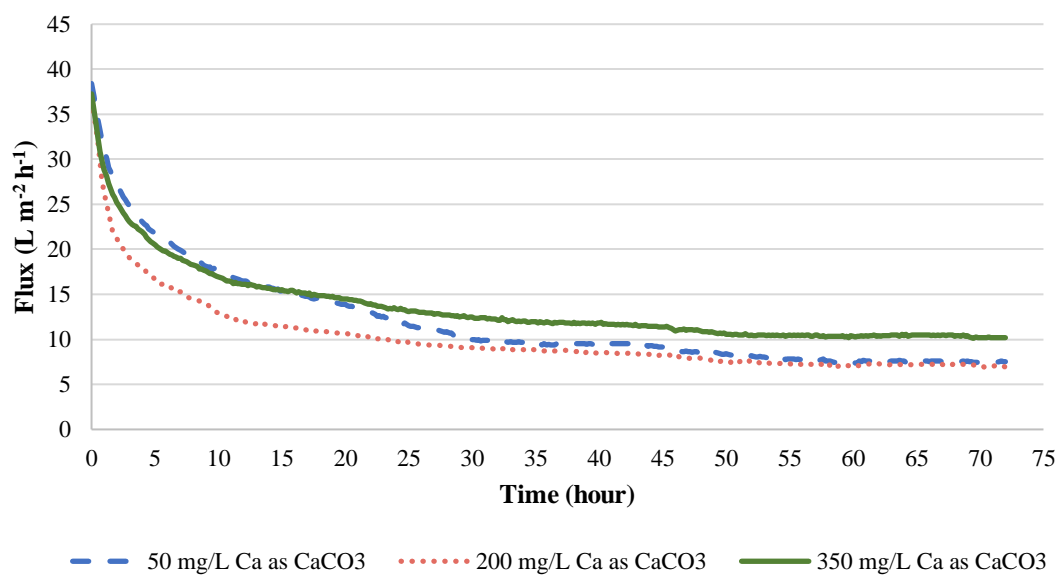
Figure 6. Flux Decline Curve for synthetic waters with different Calcium concentrations

It was observed that the flux decline in low Ca concentration was more gradual compared to the other two concentrations, throughout the fouling period, and exhibited high total resistance (due to membrane fouling) in the end of the fouling experiment (Figure 6). For medium and high calcium concentrations, the flux curves were almost parallel to each other, after first few hours of filtration. However, in the end of the fouling experiment, maximum flux decline was observed in the medium Ca concentration and minimum in the high Ca concentration. It was expected that the rates of flux decline will follow the increase in Ca concentrations, however, Figure 6 proves that this does not hold to be true.

The fouling models (Table 2) were used to identify the change in dominance between various fouling mechanisms during the course of filtration experiments. The fouling and regression coefficients were calculated for each calcium concentration for the beginning (1 hour) and end (72 hours) of the filtration experiments (Table 4 and Table 5).

Table 4. Model parameters from fouling models for 1 hour filtration

Calcium Concentration (mg/L as CaCO₃)	Complete Pore Blocking		Gradual Pore Blocking		Intermediate Filtration		Cake Filtration	
	k_b	R^2	k_s	R^2	k_i	R^2	k_c	R^2
50	3.63E-03	0.9986	3.07E-04	0.9991	1.04E-04	0.9993	5.94E-06	0.9987
200	5.57E-03	0.9904	4.99E-04	0.9869	1.80E-04	0.9826	1.17E-05	0.9714
350	4.33E-03	0.9956	3.79E-04	0.9973	1.33E-04	0.9983	8.20E-06	0.9986

Table 5. Model parameters from fouling models for 72 hours filtration

Calcium Concentration (mg/L as CaCO₃)	Complete Pore Blocking		Gradual Pore Blocking		Intermediate Filtration		Cake Filtration	
	k_b	R^2	k_s	R^2	k_i	R^2	k_c	R^2
50	2.81E-04	0.8664	4.00E-05	0.9176	2E-05	0.9515	4.00E-06	0.9787
200	2.18E-04	0.7835	3.34E-05	0.8585	2.09E-05	0.9125	4.30E-06	0.9696
350	1.80E-04	0.7952	2.38E-05	0.8501	1.28E-05	0.8927	1.90E-06	0.9467

At low Ca concentration, it was observed that in the first hour of filtration, intermediate pore blockage was the most dominant fouling mechanism (R^2 = 0.9993, Table 4). The mechanism changed to cake filtration immediately in the second hour and remained the same throughout the remaining filtration time (R^2 = 0.9787, Table 5). For medium Ca concentration, initially complete pore blockage was dominant (R^2 = 0.9904, Table 4), but changed to intermediate in the second hour and subsequently, cake filtration at the later stages (R^2 = 0.9696, Table 5). However, for high Ca concentration, cake filtration was observed to be dominant since the beginning (R^2 = 0.9986, Table 4), to the end (R^2 = 0.9467, Table 5) of the fouling experiments. These changes in fouling at different stages of filtration were associated to the changes in calcium concentration and its interaction with alginate molecules and membrane. It was identified that the R^2 values after 1 hour filtration for different fouling models were not significantly different, however, in the end of the fouling experiment, the R^2 values clearly indicate the difference in dominance of fouling mechanism at each calcium concentration.

For all the calcium concentrations, cake filtration was identified to be the most dominant fouling mechanism in the end of the fouling experiments. This finding was in agreement with the findings of Jarusutthirak et al. (2007(a)) when calcium chloride ($CaCl_2$) was used as the inorganic model foulant (10 and 50 mg/L as $CaCO_3$) in the synthetic feed water representing the surface water in Thailand. This study identified an increase in flux decline with increase in calcium concentration in the feed water and also cake formation was found to be the most well-fitted model among other models after a filtration period of 8 hours. However, when $CaCl_2$ was replaced by $CaCO_3$ in the feed water, the fouling phenomena behaved differently. The inorganic

scalant ($CaCO_3$) was found to foul both pores and surface of membrane, but pore blocking was mainly responsible for controlling the flux decline (Jarusutthirak et al., 2007(a)).

3.3.3. Effect of Calcium Concentrations on Resistance

For further understanding of the fouling behavior in the end of the fouling experiment, the resistances due to various fouling mechanisms in each set of fouling experiment were calculated using resistance-in-series model (Figure 7).

R (m-1)
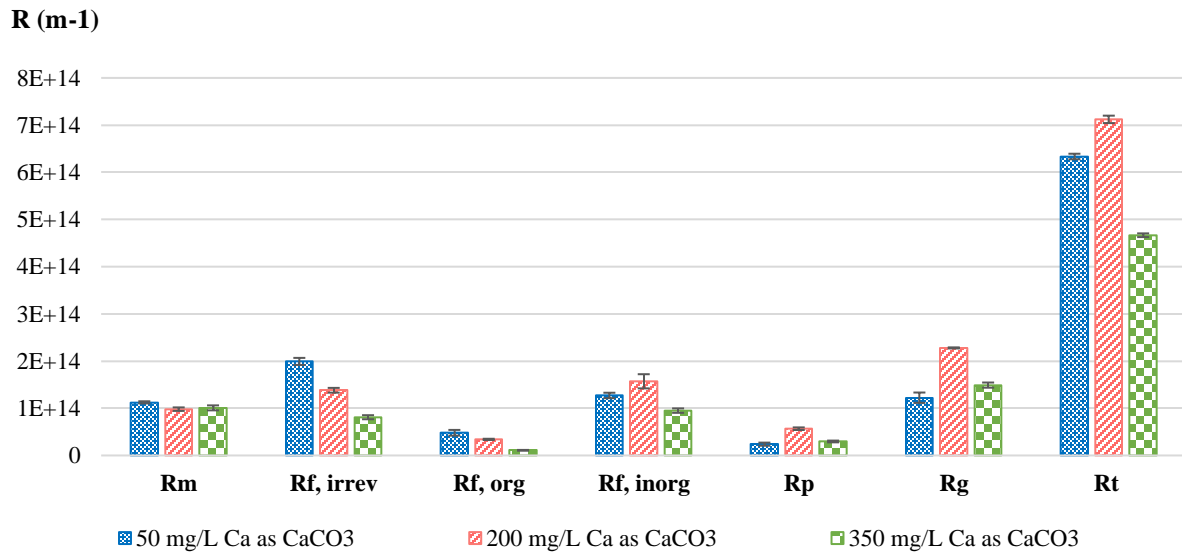
Figure 7. Resistances due to various fouling mechanisms in NF90 membranes

Comparing the total resistance in the end of the fouling experiment for the three different feed waters, medium Ca concentration was observed to exhibit the highest fouling resistance. The resistance due to gel layer formation, concentration polarization and reversible inorganic pore fouling were observed to behave similar to the total resistance for each feed water. However, the irreversibility of fouling inside the pores behaved completely different and was observed to be the highest in low Ca and decreased with increasing Ca concentration (Figure 7).

The change in behavior of fouling mechanisms in NF90 membrane can be explained by the interactions between alginate, calcium and membrane (Figure 8). At low Ca concentration, few Ca-Alginate aggregates were formed and smaller alginate molecules that could not bind with calcium got deposited in the valleys of the rough NF membrane surface or entered into the pores This resulted in a minimal gel layer formation with surface roughness of 15.38 nm, and high
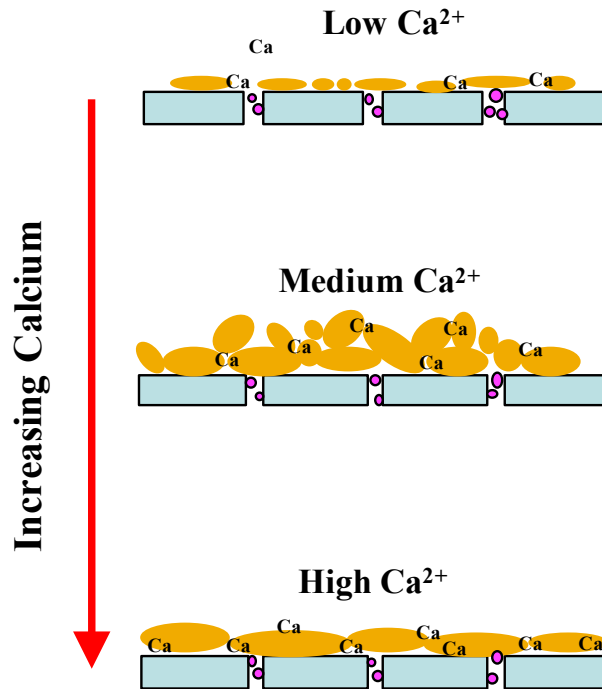
Figure 8. Behavior of gel layer formation with increasing Ca^{2+} concentration

irreversible and reversible pore fouling resistance (Figure 10 (c)). For medium Ca concentration, although there was complexation and formation of aggregates, the Ca concentration was not high enough to fulfill all the binding sites available on the alginate molecules. This resulted in the formation of a gel layer with surface roughness of 67.97 nm and a complex mixture of Ca-alginate complexes and smaller alginate molecules, offering substantial resistance to feed flow (Figure 10 (d)). However, at high Ca concentration, there was high Ca-Alginate complex formation, and the presence of high concentration of calcium ions allowed for intermolecular bridging between the aggregates, forming a cross-linked structure of the fouling layer. This resulted in the formation of a dense and compact gel layer with a surface roughness of 38.17 nm, offering reversible fouling on the membrane surface (Figure 10 (e)). This also demonstrated that gel layer formation becomes the most dominant fouling mechanism, at high calcium

concentrations. The consolidated gel layer also caused reduced deposition and fouling inside the pores (Figure 8).

The hypothesis of the nature of fouling layer demonstrated by comparison of different fouling resistances at each calcium concentration (Figure 8), correlates with the change in behavior of fouling models during the course of fouling experiments. At low calcium concentration, the intermediate pore blockage in the first hour of filtration explains the clogging of pores by the deposition of foulants on the rough membrane surface. The fouling layer is further smoothened by additional deposition and gel formation on the surface during the remaining filtration time. For medium calcium concentration, the alginate molecules formed complex with calcium and caused immediate flux decline, due to complete pore blockage. Some of the alginate molecules that could not bind with the available calcium were able to enter the pores, causing intermediate pore blockage. Later, the remaining alginates deposited on the membrane surface and the Ca-alginate complexes, resulting in subsequent gel formation with complex foulant structure. At high calcium concentration, the dominance of cake formation model since the beginning of filtration explains the maximum aggregation between calcium and alginate, resulting in a compact fouling layer on the membrane surface.

### 3.3.4. Analyses of Membrane Surface Morphology

The hypothesis on the fouling mechanisms obtained from the resistance-in-series model (resistance calculations) and flux decline models were also validated by the gel layer surface roughness observed using AFM (Figure 9 & Figure 10). The AFM images observed for clean non-precompacted membrane identified the very rough surface of NF90 membrane with a

surface roughness of 68.9 nm, which was further reduced to a value of 32.2 nm after precompaction. A significant difference was observed in the surface roughness of membranes fouled with feed water containing low, medium and high Ca concentration. The change in surface roughness is related to the interactions between foulants (alginate and Ca) and membrane surface. The AFM observations suggest that, at low Ca concentration the interaction between foulants and membrane is more adhesive i.e., individual foulants strongly bind with the membrane surface. However, when the Ca concentration is increased, the interaction tends to be more cohesive i.e., Ca-alginate complexation, aggregation and deposition. Therefore, although the surface roughness in low calcium is lesser compared to that of high calcium, the total hydraulic resistance is vice versa. The higher total hydraulic resistance in low calcium was due to the irreversible nature of fouling, especially in the pores (valley clogging and pore plugging). The value of membrane surface roughness for medium Ca concentration follows the same trend as the measured total resistance (Figure 7 & Figure 9) i.e., the membrane fouled with medium Ca concentration had the highest total resistance and surface roughness. This research was successful in application of AFM to provide a direct relationship between the fouled membrane surface roughness and total hydraulic resistances. The AFM observations of membrane surface roughness supports the hypothetical theory presented in this research (as suggested by the experimental results).
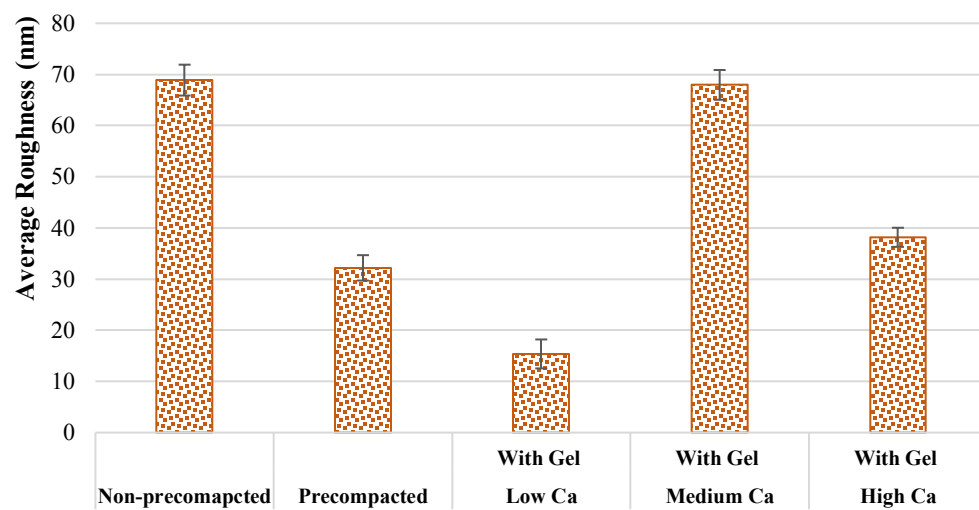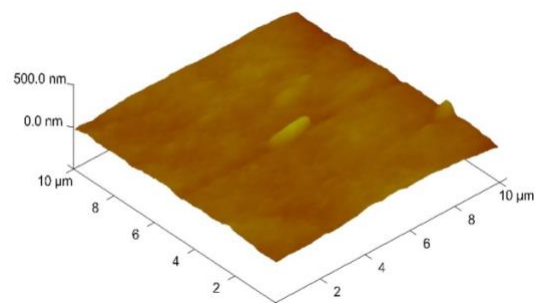
Figure 9. AFM Measured Mean Plane Surface Roughness of NF-90 membrane
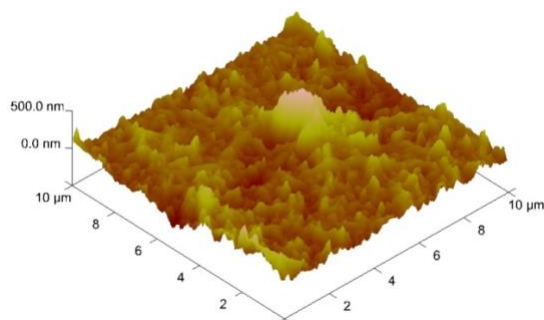
(a)
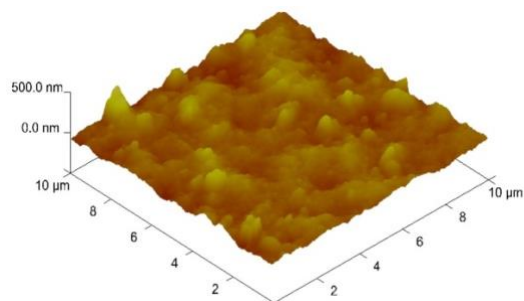
(b)

(c)
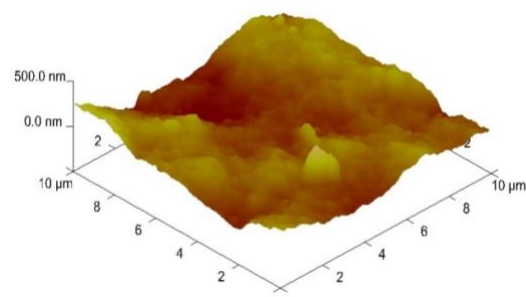
(d)
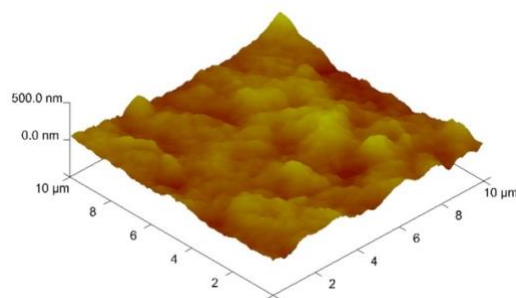
(e)

Figure 10. AFM Images of NF-90 membrane surface (a) Non-precompacted (b) Precompacted (c) 50 mg/L Ca as CaCO₃ (d) 200 mg/L Ca as CaCO₃ (e) 350 mg/L Ca as CaCO₃

The findings of this study were supported by many research studies that have concluded that the presence of calcium along with NOM in surface water dramatically decreases the permeate flux, due to the reduced charge of both the NOM and membrane surface (Hong & Elimelech, 1997; Kilduff et al., 2004; Lee et al., 2006; Jarusutthirak et al., 2007(a); Al-Amoudi A. S., 2010). Based on literature, the decline in flux and the fouling behavior is attributed to the increase in Ca-NOM complexation, with increasing calcium concentrations. However, in this study, the decline in flux and the resulting hydraulic resistance due to fouling obtained from the experimental results, did not exhibit a linear pattern of increase with increasing calcium concentrations. The maximum flux decline was observed with medium Ca concentration, instead of high Ca concentration (Figure 6).

The AFM analysis of the fouled membranes indicated that there is a relationship between the total hydraulic resistance and membrane surface roughness (Figure 7 & Figure 9). Both experimental results and AFM observations suggested that, at medium Ca concentration the

incomplete complexation of Calcium with NOM resulted in fouling mechanisms responsible for maximum hydraulic resistance to the feed flow and maximum flux decline.

Calcium is considered to exert more significant effect on the fouling layer when the binding site on NOM are completely saturated i.e., no more complexation after a certain limit of calcium concentration (also known as pseudo-maximum concentration) is reached (Hong & Elimelech, 1997; Kilduff et al., 2004). Also, when there is less calcium available to fulfill the binding sites on NOM, the small sized NOM and the complexed NOM can form a complex foulant structure, offering high resistance to feed flow. Therefore, it is understood from the experimental results and membrane surface analyses, that to minimize the complexity of the foulant structure and to maximize the reversibility of fouling, the Ca concentration should be just sufficient enough to fulfill all the binding sites available on the NOM in the feed water.

3.3.5. Results for Retention of DOC and Hardness

The NF90 membrane was also evaluated for the rejection of organic and inorganic content in the feed water (Figure 11). Rejection of DOC and hardness by the NF90 membrane was observed to be very high, as specified by the manufacturers. The increase in retention of hardness was observed due to the increasing concentration of calcium in feed water. However, the hardness of permeate water was independent of the calcium concentration in feed water.
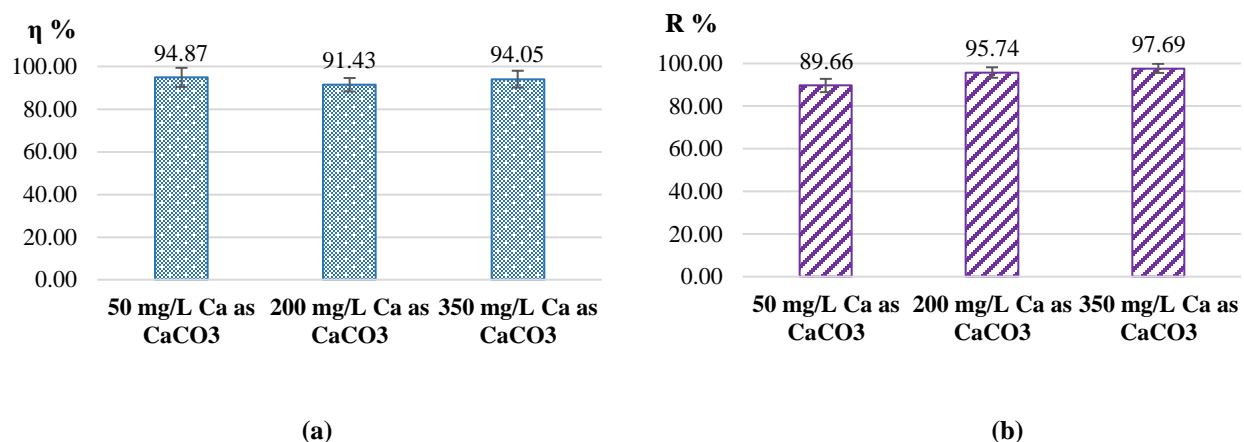
Figure 11. Retention on NF90 membranes (a) DOC (b) Hardness

3.4. Conclusion

The objective of this study was to investigate the fouling mechanisms in NF membranes for the filtration of high DOC water with a range of calcium concentration to represent hardness levels typical for Canadian surface water sources. NF90 membranes were fouled with synthetic waters comprising of high alginate concentration (17 mg/L as DOC) and calcium hardness of three concentrations: low 50, medium 200, and high 350 mg/L as $CaCO_3$. To the author's knowledge there have been no studies conducted on NF membranes for the filtration of water that contains such high concentration of DOC and Calcium. We postulate the following fouling mechanisms for low, medium and high Ca hardness waters.

1) At low Ca concentration, the alginate molecules in the synthetic feed water undergo lesser complexation and aggregation. Most of the alginate molecules and smaller aggregates preferentially accumulate in the valleys of rough membrane surface, due to increased adhesiveness between foulants and membrane. Pore fouling is the dominant fouling mechanism and therefore the fouling exhibit highly irreversible behavior. This

fouling mechanism results in low hydraulic resistance and low surface roughness of the membrane.

2) At high Ca concentration, the Ca-alginate complexation results in formation of a substantially compact gel layer on the membrane surface, due to high cohesive forces existing between foulants. The fouling layer in this case exhibits reversible fouling behavior with minimal foulants entering the pores (less troublesome). Formation of this gel layer is the dominant fouling mechanism at high calcium concentration, offering low hydraulic resistance and has low surface roughness.

3) At medium Ca concentration, the Ca concentration in the feed water was not sufficient enough to fulfill the binding sites on the alginate molecules. Due to which, fewer Ca-alginate complexes were formed and most of the smaller alginate molecules got accumulated along with the complexes on to the membrane surface. The resistance due to gel formation was the dominant fouling mechanism. The gel formed a complex matrix with a very rough surface and therefore offered maximum hydraulic resistance to flow, resulting in maximum flux decline compared to the other two concentrations.

4) The fouling mechanisms based on experimental results were consistent with the observed changes in gel layer surface roughness using the AFM images. The surface roughness of the gel layer formed with different calcium concentration was in agreement with the hypothetical theory of calcium ion interaction with DOC and NF membrane surface, proposed in this research.

Literature suggests that the flux decline due to fouling in the presence of DOC increases with increasing calcium concentrations. However, the results of this study identified a dramatic sensitivity to calcium concentration in terms of flux decline and hydraulic resistances. The study demonstrates that the flux decline is not solely dependent on the calcium concentration. Both the concentration of DOC and calcium in feed water affects the complexity of foulant structure formed on the membrane surface, further affecting the reversibility (or irreversibility) of membrane fouling. Also, this study was helpful in identifying that there is no linear relationship between the roughness of the fouling layer and the total resistance offered by the fouled membrane.

Chapter 4: SUMMARY AND CONCLUSION

This study was carried out with an aim to investigate the several possible fouling mechanisms in NF membranes, when used for the treatment of feed water with high DOC and a range of hardness concentrations. The research was focused on studying the influence of calcium concentration on the behavior of flux decline and hydraulic resistance due to each fouling mechanism. The objective of this study was also to establish an understanding of the effect of calcium concentrations on the reversibility and irreversibility of fouling

In this study, a synthetic water, representative of typical surface waters in Manitoba and Ontario was used as the feed water. The synthetic water was composed of sodium alginate and calcium chloride, used as model compounds for DOC and hardness in water, respectively. A flat-sheet TFC NF90 membrane manufactured by DOW Filmtec. was used in a cross-flow filtration set-up, for all the fouling experiments. The NF90 membranes were fouled with synthetic waters comprising of high DOC of 17mg/L and three calcium concentrations of 50, 200 & 350 mg/L as $CaCO_3$. Mathematical models such as complete pore blocking, standard pore blocking, intermediate filtration and cake filtration were used to analyze the flux decline curves for understanding the change in dominance of fouling mechanisms, during the filtration process. Resistance-in-series model was used to measure the hydraulic resistances due to membrane (after compaction) and each fouling mechanism after fouling and cleaning processes. Atomic Force Microscopy (AFM) was used to further analyze the membrane surface roughness, after fouling with different calcium concentrations.

Preliminary studies were carried out to identify a compaction time of 8 hours required for NF90 membranes, to achieve a constant flux before commencement of fouling studies. The results of the fouling investigations identified that the reversibility of fouling increases with increase in calcium concentration. It was also observed that the dominance of gel layer formation, in the presence of alginate molecules, becomes higher with increase in calcium concentration. This behavior of fouling layer can be explained by the tendency of forming Ca-alginate complexes in feed water. With increase in calcium, the tendency of complex formation increases, which further aggregates together to form a compact and dense cross-linked foulant structure. At low calcium, the complexation was minimal and maximum fouling was due to deposition of fewer aggregates and smaller alginate molecules on the rough surface and pores of NF90 membrane, and therefore was highly irreversible in nature. While for high calcium, due to maximum complexation, the fouling was more in the form of a consolidated and less porous gel layer. However, the fouling layer behaved quite differently in case of medium calcium concentration. Although, there was complex formation, the calcium ions were not adequate enough to bind with the available alginate molecules. Because of this, the foulant pore structure was very complex and rough compared to the other two concentrations, resulting in a maximum flux decline and total hydraulic resistance. It was observed that the flux decline and the total hydraulic resistance did not follow a linear pattern with increase in calcium concentrations. The finding of this study provided a meaningful insight to the importance of both calcium and NOM concentrations in affecting NF membrane performance. The concentrations of calcium and NOM should be in proportion to each other, so that all the binding sites are fulfilled and there is maximum complex formation. This would not only increase the reversibility of the foulants due to increased cohesive forces, but also enhance the membrane performance (decreased flux decline and total

hydraulic resistance), by minimizing the complexity of foulant layer. The experimental results and the hypothesis were very well supported by the AFM images obtained for the membranes fouled under different feed water conditions.

Chapter 5: ENGINEERING SIGNIFICANCE OF RESEARCH

Boyne river and Red river are used as raw water sources in different membrane WTPs (Stephenfield & Morris) operated by Pembina Valley Water Co-op. (PVWC). Both the rivers are reported to be very high in DOC and hardness concentrations (Table 6 & Table 3, respectively), however, manganese is of particular concern only in Stephenfield WTP. Therefore, in this research, only DOC and hardness were considered as the main parameters in the synthetic feed water used for the fouling studies. Also, literature suggested that these two parameters were mainly responsible for severe fouling in NF membranes. Besides the high DOC and hardness reported in Boyne & Red river, some other rivers such as Assiniboine and Rainy river in Manitoba and Ontario exhibited similar range of DOC, but very different range of hardness (40-310 mg/L as $CaCO_3$) concentrations. Considering the range of hardness concentrations reported in different rivers in the Canadian prairie, the synthetic water used in this study was composed of three different hardness concentrations and a constant high DOC. As shown in Table 6, both the DOC and hardness of natural (Boyne river) and synthetic (with high Ca concentration) water were in the similar range.

Stephenfield WTP in southern Manitoba has recently been upgraded from a conventional system to an integrated dual membrane system (MF followed by NF). This water treatment plant uses Boyne River (Manitoba) as the raw surface water source, which is reported to be very high in DOC, alkalinity, hardness and manganese (Table 6). Moran & Gorczyca (2015) carried out a detailed bench-scale study for comparison and identification of best NF membrane, among four

different membranes (NF90, NF270, BW30 & XLE), for high removal efficiency of these water quality parameters.

Due to higher permeate flux and lowered fouling over time observed in NF270 and NF90, they were considered to be the better option over the other two membranes. However, since NF90 is considered to be tight (smaller pores) NF membrane with a very high surface roughness, foulant deposition is higher in NF90 membranes compared to NF270. Therefore, NF270 was selected for testing the performance in a pilot scale study with three NF stages. The DOC removal was observed to be acceptable, and no post-treatment addition of hardness & alkalinity (84% & 77% removal respectively) was required using NF270. However, excessive manganese residual was reported in the effluent. Manganese removal being an important consideration for Stephenfield WTP, NF270 was replaced by NF90 in stage 2 &3 for improving the overall removal efficiency of manganese (Figure 12). The results from the pilot scale study demonstrated a very high removal efficiency of DOC, hardness and manganese (Table 6).
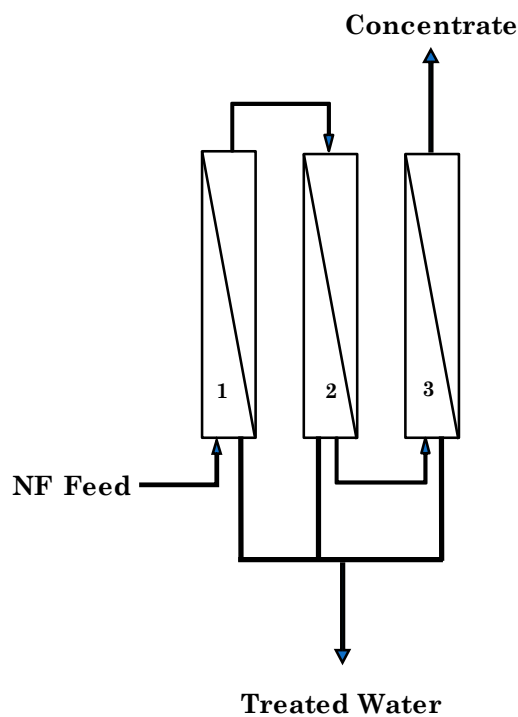
Figure 12. NF stages (Stage 1: NF270 and Stage 2 & 3: NF90) in pilot-scale filtration setup in Stephenfield Regional WTP

Table 6. Natural and Synthetic feed water (high Ca) parameters and removal efficiencies of NF90 membrane

Parameters	Natural water (Boyne River Stage 1 effluent)		Synthetic water – High Ca	
	Feed Water	% Removal (early stage)	Feed Water	% Removal
DOC (mg/L)	18.6	94.7	17	94.05
Hardness (mg/L as CaCO$_3$)	360	96.0	350	97.7
Alkalinity (mg/L as CaCO$_3$)	305	NA	N/A	N/A
Manganese (mg/L)	1.81	99.7	N/A	N/A

5.1. Comparison of NF90 Membrane Performance using Natural and Synthetic Water

This research was further continued to study the fouling in NF90 membranes, that was selected for the pilot scale study and later used in the full-scale membrane filtration system in Stephenfield WTP. The high surface roughness of NF90 membrane increases the vulnerability of fouling, especially in the presence of a complex mix of organics and inorganics. Also, the increased cost associated with use and maintenance of NF membranes, made this study of interest for understanding the membrane fouling in real WTPs. This research was carried out to provide meaningful insight to the flux decline and dominant fouling mechanisms affected by the high concentration of DOC & hardness in feed water. The effect of surface roughness of NF90 membranes on the behavior of foulant deposition and foulant structure was also studied thoroughly.

The laboratory bench-scale results for both DOC & hardness removal efficiency using NF90 membrane for filtration of synthetic water (high Ca concentration) was observed to be very similar to that of the Natural (Boyne river) water (Table 6). The natural feed water used for the bench-scale study was collected from stage 1 (NF270) effluent of the Stephenfield pilot plant (Table 6); the similar laboratory set-up was used as the one used for this research. The flux data obtained from the bench scale experiments using synthetic and natural water, when analyzed for the dominance of fouling mechanism after the first hour of filtration were in agreement with each other (Table 7). It was identified that cake filtration was the most dominant fouling mechanism right from the beginning of both the studies, with regression coefficients of 0.9986 and 0.9923, respectively.

Table 7. Model parameters from fouling models for 1 hour filtration of Synthetic water (high Ca) and Natural (Boyne river) water

Feed Water	Complete Pore Blocking		Gradual Pore Blocking		Intermediate Filtration		Cake Filtration	
	k_b	R^2	k_s	R^2	k_i	R^2	k_c	R^2
Synthetic Water (High Ca)	4.33E-03	0.9956	3.79E-04	0.9973	1.33E-04	0.9983	8.20E-06	0.9986
Natural Water (Boyne River)	1.2121	0.8515	0.0882	0.9165	0.0263	0.9612	0.0012	0.9923

Also, after one hour of filtration, the total hydraulic resistance measured using synthetic water was found to be coherent with that of natural water, as $1.216+E14$ m^{-1} & $1.250+E14$ m^{-1} respectively. The flux after one hour filtration was observed to be 25.24 Lm^{-2}h^{-1} (Figure 6) for synthetic water and 27.19 Lm^{-2}h^{-1} for natural water (Figure 13) (Moran & Gorczyca, 2016), at a

constant operating pressure of 10 bars and temperature of 21±1°C. The observed flux values, operating pressure and viscosity of feed water (operating temperature) were incorporated in the equation for resistance-in-series model (Equation 5 in Section 3.1.5.) to calculate the total hydraulic resistances for both synthetic and natural water. For filtration of natural water the membrane was not precompacted before running any fouling test. The similarity in total hydraulic resistance after first hour of filtration and the dominance of cake filtration in both the cases exhibit that Ca-alginate complexation is mainly responsible for the offered resistance. The effect of compaction on flux decline in NF90 membranes will be more evident when used for longer hours of filtration resulting in increased fouling and hydraulic resistance. Some recent observations by Pembina Valley Water Corp. from the pilot plant in Stephenfield was used for calculating the total hydraulic resistance after filtration of Boyne river water for 72 hours. The Stephenfield pilot plant (or any other WTP) operates at a variable pressure and constant flux, unlike the lab-scale setup that worked on constant pressure and variable flux. The pilot plant operated at a constant flux of 20.41 L/m^2/h, pressure of 2.7 bar and temperature of 9.4°C for 72 hours, to offer a total hydraulic resistance of 3.59E+13 m^{-1}. This resistance was much lower compared to the total hydraulic resistance observed in this research for synthetic water (high Ca) filtration for 72 hours i.e., 4.67E+14 m^{-1}. This difference was obviously because of the much lower operating pressure (2.7 bar) in the pilot plant compared to the one used in bench-scale study (10 bar) and resistance being directly proportional to the operating pressure (Equation 5).
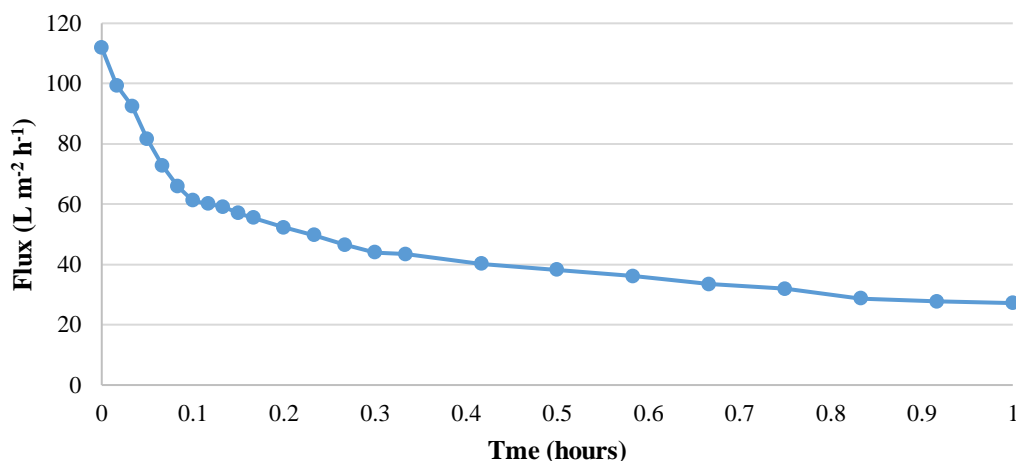
Figure 13. Flux Decline Curve for natural water (Boyne river Stage 1 effluent) (Moran & Gorczyca, 2016)

The results of experiments conducted on a bench-scale cross-flow filtration setup using NF90 membranes for synthetic (high Ca) and natural (Boyne river) water, very well correlated with each other. The feed water used in both the studies were from different sources, but consisted of similar DOC and hardness concentration. Since the type of feed water used in this research was not natural, but synthetic, the complex nature of natural surface waters can possibly lead to variations in foulants and membrane interaction when operated for a longer period of time. However, the similarity between total hydraulic resistances due to fouling, measured for both synthetic and natural (Boyne river) water, justifies the choice of model parameters in synthetic water. Besides, in both cases (representing high Ca concentration), the cake formation was identified to be the most dominant fouling mechanism. Similar to synthetic water, natural water was also observed to cause less pore fouling compared to membrane surface fouling (Table 7). The results of this research can be attributed to the presence of high calcium concentrations binding with the available DOC in feed water affecting the fouling behavior. This results in maximum complexation and aggregation, which directly causes increase in reversibility of fouling and decrease in irreversibility of fouling by allowing minimal pore fouling in

membranes. The consistency in fouling mechanisms and total hydraulic resistance in both Boyne river water (with high alkalinity) and synthetic water with high calcium concentration (without alkalinity), indicates that alkalinity might not play a major role in flux decline and membrane fouling. However, at low or medium calcium concentrations (as used in this research), in the presence of high alkalinity, precipitates smaller than the membrane pore size might be able to enter the pores and cause scale formation, by adsorption and pore plugging. Antiscalant are generally used in WTPs to avoid any scale formation in the system, which might otherwise interfere with the membrane performance and lifetime.

The findings of this study suggest that NF90 membrane, when used in pilot/full scale systems in Stephenfield WTP, will be prone to foul easily due to its high surface roughness, and high DOC and hardness in feed water. However, most of the fouling will be on the membrane surface, due to the formation of a compact and dense fouling (gel) layer, that will be mostly reversible by regular chemical cleaning procedures.

5.2. Recommendations for use in Full-Scale Membrane Systems

Based on the findings of this study, several suggestions can be provided for optimization or better performance of full-scale membrane systems. As per the observations in this study, calcium concentration seemed to be a very important parameter regulating the intensity and complexity of fouling in NF membranes in the presence of DOC in feed water. It was also concluded that calcium and NOM when present in concentrations sufficient enough to bind with each other, results in the most reversible fouling. Detailed investigations can be carried out to identify the maximum concentration of calcium required to sufficiently bind with the DOC

present in any source of water. The results of this investigation can be compared to the calcium hardness reported in the particular source of water, to identify whether calcium needs to be removed or added to the feed water for maximizing reversibility of fouling in full-scale membrane systems. The formation of reversible fouling layer on membrane surface and less fouling in membrane pores can increase the chemical cleaning efficiency of the membrane system. However, implementation of this technique needs to be confirmed with more study, as calcium is a potential scalant and adding more calcium in feed water can also cause degradation of membrane performance and system.

Another important suggestion to minimize fouling would be pretreatment of feed water before used for filtration through NF membranes. Pretreatment methods such as coagulation or use of oxidants such as ozone can be applied to reduce the DOC in feed water. Coagulation has been known as a very well-known pretreatment method before membrane filtration. A linear relationship has been observed to exist between the ability of coagulation to remove DOC and to improve membrane performance (Howe & Clark, 2006). However, organic matters with low molecular weight and large solubility organic cannot be easily removed by coagulation (Sun et al., 2013). Ozone is a powerful oxidant which has high potential to reduce the size of NOM in feed water to form small functional groups with high surface zeta-potential. This can further enhance the interaction of these NOM functional groups with the available calcium in feed water resulting in Ca-NOM complex formation. Through ozone oxidation, macromolecular organics can be oxidized into small molecules which can further be oxidized into inorganic matters. This method is capable of reducing the concentration of pollutants participating in membrane fouling (You et al., 2007; Sun et al., 2013).

Chapter 6: RECOMMENDATIONS FOR FUTURE RESEARCH

1) From this research, it was clear that concentration of calcium in the presence of alginate molecules, highly influences the reversibility and irreversibility of membrane fouling. Therefore, further investigations can be done to identify the relationship between the concentration of calcium and Ca-alginate complex formation. When the concentration of calcium is adequate to bind all the available NOM in feed water, there is formation of a cohesive fouling layer on the membrane surface. This fouling layer is relatively reversible in nature compared to individual foulants attachment to the membrane surface. This study can be helpful in maximizing the reversibility of fouling layer by enhancing the Ca-alginate complex and aggregates formation, that acts as a secondary barrier to the feed flow and minimizes irreversible foulant deposition inside the membrane pores.

2) Surface waters are generally expected to have high levels of alkalinity. Water treatment plants use antiscalant to avoid any scale formation in the system due to the alkaline feed water. The behavior of flux decline and change in fouling mechanisms can be investigated by adding alkalinity (calcium carbonate instead of calcium chloride as a model compound for hardness) and antiscalant to the synthetic water.

3) Morris water treatment plant in Manitoba uses TMG20 (Toray element) NF membranes, primarily for the removal of hardness and DOC. Our research group conducted some preliminary studies for investigating the compaction in TMG20 NF membranes. It was identified that the compaction was not the same as observed in case of NF90 membranes,

although both the membranes are TFC. It would be interesting to know if the fouling mechanisms behave differently for thin film composite NF membranes provided by different manufacturers.

4) Literature suggests that oxidants like ozone can be very helpful in increasing the zeta-potential of the NOM by dissociating them into small functional groups. These functional groups can attach to the calcium present in water to form larger aggregates. The role of calcium in enhancing the NOM fouling was elaborately discussed in this research. However, it would be useful to investigate the contribution of ozone in any significant increase in enhancement of Ca-NOM complex formation, further affecting the increased rejection and reversibility of fouling. This study can be helpful in investigating the efficiency of ozone as a pretreatment method prior to NF membrane filtration.

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