MODELING IRREVERSIBLE FOULING IN SUBMERGED HOLLOW FIBER MEMBRANE SYSTEMS FOR DRINKING WATER TREATMENT

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ABSTRACT

The use of low pressure membrane filtration processes in water and wastewater treatment fields has been increasing rapidly due to evolving health concerns and the development of new and lower-cost membranes. Among diverse types of operating mode and membrane modules, submerged hollow fiber membrane systems are very competitive because of their simpler operation, greater ability to resist against fouling, lower maintenance cost and smaller footprint. However, membrane fouling still remains the main disadvantage and limitation of these systems. Membrane fouling decreases the permeate flux which in turn increased the capital and operating costs of membrane systems, and also affects pretreatment needs, cleaning requirements and operating conditions. Therefore, fouling control is an important consideration in the design and operation of a membrane filtration system. A lot of research has been conducted to seek effective methods to control fouling. Based on the understanding of fouling mechanisms and the influence of operating parameters on membrane fouling, numerical models have been developed to quantitatively predict fouling. Nevertheless, most of the studies and models developed to date combine reversible and irreversible fouling together. Irreversible fouling, the main cause of the long term fouling has received limited attention. As a result, there remains a knowledge gap in terms of the mechanisms that govern irreversible fouling as well as the fouling behavior. This research was undertaken to investigate irreversible fouling, and moreover, attempt to develop a simple and reliable model to accurately predict irreversible fouling in submerged hollow fiber membrane filtration systems for drinking water treatment.

The study results revealed that even though all experiments were performed with an operating flux that was less than the critical flux, a substantial amount of fouling was observed when filtering over extended periods of time. The extent of fouling was observed to be related to both the operating permeate flux and the system hydrodynamic conditions. Irreversible fouling observed in this study was due to both extensive internal/pore fouling and surface/cake fouling. Internal fouling was the predominant mechanism that governed irreversible fouling.
A semi-empirical relationship was developed to model the extent of fouling when filtering over extended periods of time for conditions where the operating permeate flux was less than the critical flux. The relationship was based on the membrane characteristics, the extent of surface/cake fouling and the extent of internal/pore fouling, respectively.

The extent of surface/cake fouling was determined to be governed by the operating permeate flux and the system hydrodynamic conditions (i.e. the cross-flow velocity). The extent of internal/pore fouling was determined to be governed only by the operating permeate flux. In addition, the results from the present study indicated that when operating the membrane filtration system below critical flux conditions, for a given volume of permeate filtered, the extent of overall fouling increased as the operating permeate flux increased and decreased as the cross-flow velocity increased.
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LIST OF SYMBOLS

\[ J \] the permeate flux \([m^3/m^2s]\) or \([L/m^2 \text{ hr}]\)

\[ \Delta P \] the trans-membrane pressure \([N/m^2]\)

\[ \mu \] the water viscosity \([Ns/m^2]\),

\[ R_t \] the total filtration resistance \([m^2/m^3]\)

\[ R_m \] the intrinsic membrane filtration resistance \([m^2/m^3]\)

\[ R_r \] the reversible resistance \([m^2/m^3]\)

\[ R_{ir} \] the irreversible filtration resistance \([m^2/m^3]\)

\[ k_i \] the fouling strength of dissolved organic matter \([m/g]\)

\[ S_T \] the dissolved organic matter concentration \([g/m^3]\)

\[ J_0 \int_0^t J \, dt \] the total volume of the filtrate per unit area of the membrane \([m^3/m^2]\)

\[ A \] the rate of pore blockage,

\[ R_{p0} \] the initial resistance of the protein deposit \([m^2/m^3]\)

\[ R' R' \] the rate of cake growth

\[ k_T \] the total fouling coefficient

\[ k_R \] the reversible fouling coefficient

\[ k_I \] the irreversible fouling coefficient

\[ P_v \] the trans-membrane pressure after filtering a given permeate volume [psi],

\[ P_0 \] the initial trans-membrane pressure [psi]

\[ P_{20^\circ C} \] the trans-membrane pressure value at temperature 20.0 \(^{\circ} C\) \([N/m^2]\)

\[ P_T \] the trans-membrane pressure value at temperature \(T\) \([N/m^2]\)

\[ T \] the operating temperature \([^{\circ}C]\)

\[ \mu_{20^\circ C} \] water viscosity values at temperature of 20.0 \(^{\circ} C\) \([Ns/m^2]\)

\[ \mu_T \] water viscosity values at temperature of \(T\) \([Ns/m^2]\)

\[ Jv \] the operating permeate flux \([m^3/m^2s]\) or \([L/m^2 \text{ hr}]\)
$\tau_L$ flow path length [m]

$N$ number of pores [No./m$^2$]

$R$ membrane pore radius [m]

$r_0$ initial membrane pore radius [m]

$r'$ membrane radius after filtering $V$ of water [m]

$A_0$ the initial active surface area of a given membrane module

$K_1$ a constant related to membrane module and raw water characteristics [Nm$^6$/L]

$K_1''$ a constant related to membrane module and raw water characteristics [Nm$^4$/L]

$K_1'$ a constant related to membrane module and raw water characteristics [m$^2$]

$K_2$ rate of pore number reduction (i.e. rate of surface fouling) [1/m]

$K_3$ rate of pore radius reduction (i.e. rate of internal fouling) [1/m]

$CFV$ cross-flow velocity applied to the membrane system [m/s]

$V$ volume of water filtered [m$^3$]
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CHAPTER 1 INTRODUCTION AND RESEARCH OBJECTIVES

The use of low pressure membrane filtration processes in water and wastewater treatment fields has been increasing rapidly due to evolving health concerns and the development of new and lower-cost membranes. According to the definition given by USEPA, a low pressure membrane filtration process is “a pressure or vacuum-driven separation process in which particulate matter larger than 1 μm is rejected by an engineered barrier primarily through a size exclusion mechanism and which has a measurable removal efficiency of a target organism that can be verified through the application of a direct integrity test” (USEPA, 2005).

Based on sieving mechanisms, low pressure membrane filtration is capable of removing suspended or colloidal particles larger than the membrane pore size. Compared with traditional granular media filtration processes used in drinking water treatment, low pressure membrane filtration removes more disinfection by-product precursors (USEPA, 2005) and pathogens, uses reduced amount of treatment chemicals, has a smaller footprint and a lower labor requirement (Metcalf and Eddy, 2003). Four main membrane technologies exist: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). MF and UF are low pressure membranes while NF and RO are typically classified as high pressure membranes. Consequently, in this document, low pressure membranes will hereafter be referred to simply as membranes. MF and UF were firstly commercialized in the early 1990’s and have now become widespread in water and wastewater treatment applications. The pore sizes for MF membranes range from 0.1 to 0.2 μm (nominally 0.1 μm), while the pore size for UF membranes range from 0.01 to 0.05 μm (nominally 0.01μm) or less (USEPA, 2005).

Membrane properties such as surface charge, hydrophobicity, pH and oxidant tolerance, strength and flexibility are mainly determined by the materials used for manufacturing the membranes (USEPA, 2005). Currently, most of the membranes used for drinking water production are typically made of low-cost polymeric material (i.e. polyacrylonitrile (PAN)).
Membrane modules are the smallest operational units in membrane filtration systems. Usually, a membrane system consists of the membrane modules, bulkheads into which the membranes are potted, pressure support structures, feed inlet, concentrate outlet ports and permeate collection points (Malleialle et al., 1996). There are four major types of membrane modules: hollow fiber, plate and frame, spiral wound, and tubular modules. The application of hollow fiber modules is becoming the most popular type of membranes because of the lower energy cost and back-flushing capability of these modules. Hollow fiber modules are generally bundled together (100 to 10,000 fibers) and both ends are potted using resin into bulkheads to form membrane systems. Each fiber usually has an outside diameter of 0.5 to 2.0 mm, an inside diameter of 0.3 to 1.0 mm, a wall thickness of 0.1 to 0.6 mm and a fiber length of 1 to 2 meters (USEPA, 2005). A large surface area per unit volume and a high shear rate can be achieved by compactly packing membrane modules together. Large surface area leads to large permeate flow, while the very small flow channels between the compactly packed modules provides a high shear rate (Malleialle et al., 1996). All these contribute to lower the cost of hollow fiber modules when compared to other types of membrane modules. In addition, the ability to back-flush hollow fiber modules typically results in better fouling controlling (Malleialle et al., 1996). Hollow fiber membrane modules may operate in either “inside-out” or “outside-in” mode (see Figure 1.1). In inside-out configurations, feed water from the inside (i.e. fiber lumen) permeates through the wall of membranes to the outside; while in outside-in mode, feed water from the outside of the membranes permeates along and passes the membrane surface, and filtrate is collected inside the lumen (USEPA, 2005). The driving force for hollow fiber modules is the trans-membrane pressure difference, which is either supplied by providing a positive or a negative (vacuum) pressure.
Based on the operating mode, membrane filtration systems can be typically divided into two categories: submerged and external, as seen in Figure 1.2. External systems typically use the inside-out flow configuration and pressure is used as the driving force, while submerged systems typically use an outside-in flow configuration and a vacuum is used as the driving force. The high shear rates needed to minimize fouling are typically achieved through applying a high cross-flow velocity along the membrane surface in external systems, while a high shear rate is typically achieved by sparging air along the membrane surface in submerged systems. Typical operating trans-membrane pressure ranges from 21 kPa to 276 kPa (3 to 40 psi) in a pressure-driven hollow fiber membrane system; while a vacuum of approximately -21 kPa to -83 kPa (-3 to -12 psi) is typically applied in a vacuum-driven hollow-fiber membrane system (USEPA, 2005).
Submerged hollow fiber systems are very competitive when compared to other types of operating mode and membrane modules. The advantages of these systems include simpler operation, greater ability to resist against fouling, lower maintenance cost and smaller footprint (Fane et al., 2002; Yoon et al., 2004). The present thesis deals exclusively with submerged hollow fiber membrane systems. Consequently, in this document, submerged hollow fiber membranes will hereafter be refereed to simply as membranes.

Although there are a number of advantages associated with membrane systems, when compared to other filtration processes such as conventional sand filtration, membrane fouling
still remains the main disadvantage and limitation of membrane systems. Membrane fouling, which is caused by the deposition and accumulation of materials on the membrane surface, or inside the membrane pores, decreases the permeate flux which in turn increases the capital and operating costs of membrane systems. In addition, membrane fouling affects pretreatment needs, cleaning requirements and operating conditions (Metcalf & Eddy, 2003). Therefore, fouling is an important consideration in the design and operation of a membrane filtration system. A lot of research has been conducted to seek effective methods to control fouling. Based on the understanding of fouling mechanisms and the influence of operating parameters on membrane fouling, a number of numerical models (Ho and Zydney, 2000; Yuan et al., 2002; Katsoufidou et al., 2005; Bolton et al., 2006a; Bérubé and Lei, 2006; etc) have been developed to quantitatively predict fouling. Corresponding strategies have also been developed and applied to control and minimize membrane fouling (Bellara et al., 1996; Smith et al., 2002; Smith et al., 2005; Cui et al., 2003; Bérubé and Lei, 2006; Hilal et al., 2005; etc). Operating membrane filtration systems under critical permeate flux, back-washing and controlling the system hydrodynamic conditions are some strategies that have been widely used to control fouling. However, there remains a knowledge gap in terms of the mechanisms that govern irreversible fouling. Most of the studies and models developed to date combine reversible and irreversible fouling together. Irreversible fouling, which is typically the main cause of long term fouling has received limited attention. As a result, the mechanisms that govern irreversible fouling, as well as the fouling behavior, are poorly understood. Due to this knowledge gap, there is currently no accurate model to predict irreversible fouling, or to develop effective strategies to prevent and control irreversible fouling.

This research studied irreversible fouling in submerged hollow fiber membrane filtration systems for drinking water treatment. The objectives of this research were to firstly gain a better understanding of the mechanisms of irreversible fouling, secondly quantify the relationships between the extent of irreversible fouling and the operating parameters, thirdly develop a mechanistic model to accurately predict irreversible fouling, and ultimately propose practical suggestions to the engineering application of membrane filtration systems.
All experiments were performed at sub-critical flux conditions. As discussed in Chapter 2, when operating below critical flux, only irreversible fouling, that is fouling which is not impacted by back-transport mechanisms, should theoretically occur. The specific hypotheses that were tested are:

1. that irreversible fouling, when operating below critical flux, is not impacted by back-transport mechanisms (i.e. extent of air sparging), and
2. that for a given permeate volume filtered, the extent of irreversible fouling is not affected by the operating permeate flux
CHAPTER 2 LITERATURE REVIEW

There are two obstacles that prevent the widespread application of membrane filtration systems: concentration polarization and membrane fouling. Concentration polarization is the increase in the concentration of retained material at the membrane surface, while membrane fouling refers the adsorption or deposition of material in or on the membranes. Both concentration polarization and membrane fouling increase the membrane resistance by limiting mass transfer at membrane surface, and cause a decrease in the permeate flux. They are also interrelated: severe concentration polarization can aggravate the extent of membrane fouling (Ghosh, 2006). The negative impact of concentration polarization on the permeate flux is relatively constant. On the other hand, the negative impact of membrane fouling increases with time, and is generally more significant than that from concentration polarization. Membrane fouling is generally regarded as the main cause of the decrease in the permeate flux in membrane filtration systems. Fouling and strategies for fouling control are reviewed in the follow sections.

2.1 Permeate Flux Decline and Membrane Fouling

2.1.1 The phenomenon of permeate flux decline

During the membrane filtration process, the permeate flux decreases with respect to time. The general form of Darcy’s law (Equation 2.1) describes the overall characteristics of flux reduction.

\[ J = \frac{\Delta P}{\mu R_t} \]  \hspace{1cm} (2.1)

where \( J \) is the permeate flux \([m^3/m^2s]\), \( \Delta P \) is the trans-membrane pressure \([N/m^2]\), \( \mu \) is the water viscosity \([Ns/m^2]\), \( R_t \) is the total filtration resistance \([m^2/m^3]\). The driving force for the transport of water across membranes is the pressure gradient from one side of the membrane to the other (i.e. trans-membrane pressure). The total filtration resistance, which increases over time as fouling progresses, limits the transport of water across the membrane.
Membrane fouling is due to the accumulation of material on or in the membrane skin and can be classified into two categories: reversible fouling and irreversible fouling. Reversible fouling is the fraction of fouling that can be impacted by the rate of mass transfer away from the membrane surface, while irreversible fouling is not impacted by the rate of mass transfer away from the membrane surface (Bérubé and Wong, 2007). Reversible fouling can be controlled hydraulically. However, irreversible fouling can only be removed by chemical cleaning. The total fouling resistance is the sum of the resistance due to the membrane itself, which is constant, the resistance due to reversible fouling and the resistance due to irreversible fouling as presented in Equation 2.2 (Aimar and Howell, 1989).

\[ R_t = R_m + R_r + R_{ir} \]  

where \( R_m \) is the intrinsic membrane filtration resistance \([m^2/m^3]\), \( R_r \) is the reversible resistance \([m^2/m^3]\), \( R_{ir} \) is the irreversible filtration resistance \([m^2/m^3]\). Darcy's law can then be written as Equation 2.3.

\[ J = \frac{\Delta P}{\mu(R_m + R_r + R_{ir})} \]  

2.1.2 Mechanisms of membrane fouling

As illustrated in Figure 2.1, there are four classical models that have been popularly accepted and applied to explain membrane fouling mechanisms.

![Four classical fouling models](Adapted from Hermia, 1982)
Cake fouling occurs when a permeable cake layer forms on the membrane surface with increasing thickness that creates an additional layer of resistance to permeate flow. Standard blocking assumes material accumulates and absorbs inside the membrane wall, leading to the reduction of pore radius and an increase in the membrane resistance. Complete blocking assumes pores are completely plugged by particles and no flow can go through the plugged pores. Intermediate blocking assumes that some of the particles seal off the pores and the rest accumulate on the top of other deposited particles. The reduction of effective pore size and pore numbers caused by standard blocking and cake fouling are typically the main causes for the permeate flux decrease (Minegish et al., 2001). The four models are also commonly referred to as pore blocking (complete blocking), direct adsorption (standard blocking), long term adsorption (intermediate blocking) and boundary layer resistance (cake fouling) (Bowen et al., 1995).

Each of these models has been used individually or in combination to explain experimental observations. However, membrane fouling is an extremely complicated physico-chemical phenomenon, which can involve several fouling mechanisms occurring simultaneously.

2.1.3 Behavior of particle back-transport at membrane surface

While the permeate flux carries particles towards a membrane surface through convection, this mass flux is balanced by a number of back-transport mechanisms that carry particles away from a membrane surface (Belfort et al., 1994). Four particle back-transport mechanisms (i.e. Brownian diffusion, shear-induced diffusion, lateral migration by inertial lift and surface transport) are typically used to explain the behavior of particulate and macromolecular solutions at membrane surfaces. Brownian diffusion is only significant for submicron particles (less than 1 μm) and is typically not a significant back-transport mechanism in low pressure membrane (i.e. MF and UF) systems. Shear-induced diffusion on the other hand is significant for larger micron-sized particles (from 1 μm to 30-40 μm) and is proportional to the shear rate at a membrane surface. Inertial lift is strongest for large particles (greater than 30 to 40 μm), and is due to pressure differences that arise at the extremities of large particles when exposed to a
velocity gradient. Surface transport can be significant when a membrane is exposed to a relatively high tangential flow, causing retained particles to slide along the membrane surface (Belfort et al., 1994).

All four back-transport mechanisms depend strongly on the shear rate and/or particle size. The shear rate or shear stress near a membrane surface is an important hydrodynamic parameter in describing the particle back-transport. Induced surface shear forces are regarded as a major strategy to control fouling because they increase the mass transfer away from the membrane surface (Mallevalle et al., 1996). The experimental results from Bian et al. (2000) indicated that the velocities of back-transport away from a membrane surface increased as the shear rate increased, resulting in a decrease in membrane fouling.

It should be noted that of the four fouling models, standard blocking, which is due to the adsorption of foulants within the membrane pores, is not impacted by the back-transport mechanisms discussed above, since these mechanisms manifest themselves at the membrane surface and not within the membrane pores.

2.1.4 The concept of critical flux

The concept of critical flux hypothesizes that there exists a flux below which fouling does not occur; above this flux, fouling is observed (Field et al., 1995). At critical flux, the rate of mass transfer towards a membrane surface, due to particle convection towards the membrane surface, is balanced by the rate of mass transfer away from the membrane surface, due to one or more back-transport mechanisms. Therefore, the critical flux for a particular application depends on the system hydrodynamics and the particle size.

It should be noted that true critical flux conditions are typically never achieved, because solutions typically contain particles of various sizes, each with different back-transport rates, and
because the critical flux concept assumes that fouling due to adsorption within the membrane pores (i.e. standard blocking) does not occur.

A number of researchers have demonstrated that the concept of critical flux can not be applied directly (Wisniewski et al., 2000; Cho and Fane, 2002; Ognier et al., 2004; Ye et al., 2006). Wisniewski et al. (2000) found that for solutions of particles of non-uniform size as well as the presence of the soluble compounds, which are not influenced by hydrodynamic conditions, the critical flux concept could not be applied. A number of researchers have reported a two-stage increase in trans-membrane pressure when operating bioreactors at a permeate flux substantially below the critical flux (Ognier et al., 2002a; Ognier et al., 2004; Cho and Fane, 2002; Nagaoka et al., 1996). The first stage consisted of a long term slow and gradual increase in the trans-membrane pressure, while the second stage was characterized by a rapid rise in the trans-membrane pressure. The gradual fouling in the first stage was reported to be “hydraulically irreversible” and could not be avoided even when operating the system under critical flux conditions (Ognier et al., 2004). Cho and Fane (2002) suggested that the fouling that occurred when operating below critical flux was due to non-homogeneous flux conditions at a membrane surface. They suggested that due to fouling, the localized fluxes in some membrane areas were reduced (i.e. first stage). Therefore, for membrane systems operated with a fixed permeate flux, the reduced localized flux in some areas must be accompanied by an increase in the localized flux in other membrane areas that were not yet fouled. When the increase in the localized flux exceeded the critical flux, fouling occurred and was accompanied by a sudden rise in the trans-membrane pressure (i.e. second stage). The length of the first fouling stage has been observed to be related to the operating flux. When applying lower sub-critical fluxes, the first fouling stage was observed to last longer (Cho and Fane, 2002; Ognier et al., 2002b; Le Clech et al., 2003).

It should also be noted that the critical flux measured in the studies presented above was usually determined based on the flux stepping experiments which only lasted a few hours. Le
Clech *et al.* (2003) indicated that critical flux values might be affected by the period of each flux step and the time delay between flux steps. Therefore, care must be taken when interpreting critical flux values and the use of critical flux to assist in investigating fouling (*Ye et al.*, 2006).

As an alternative, the concept of pseudo-steady-state permeate flux has been proposed. For a constant trans-membrane pressure system, the magnitude of the permeate flux after the initial period of rapid decrease in the flux was defined as pseudo-steady-state flux. The pseudo-steady-state permeate flux was found to be governed by the hydrodynamic conditions applied to the membrane systems. Hydrodynamic studies conducted by Bérubé and Lei (2006) indicated that membranes operated with dual-phase cross-flow (i.e. with air sparging) could increase the pseudo-steady-state permeate flux by 20-60% when compared to membranes operated with single phase cross-flow (i.e. without air).

### 2.2 Strategies of Fouling Control

Strategies to avoid fouling or decrease the extent of fouling have been explored for decades. The methods employed for the control of fouling in low pressure membranes was reviewed comprehensively by Hilal *et al.* (2005). Pretreatment of the feed water, membrane material/surface modification, optimization of operating parameters/conditions and recovery cleaning are the four main approaches to control membrane fouling.

#### 2.2.1 A review of general methods for fouling control

Pretreatment typically involves a physical and/or chemical process designed to remove solute, colloidal and/or particulate material that can foul the membrane. Typically, physical processes are used to remove large suspended particles that may block the membrane pores or accumulate on the membrane surface. Typically, chemical processes are used to reduce internal adsorption inside membranes pores through coagulation and flocculation to convert solute and colloidal foulant into larger particles (Hilal *et al*., 2005).
Membrane material/surface modification aims to reduce the adsorption of foulant on the membrane surface by changing the properties of the membrane surface. The methods of membrane material/surface modification consist of either reducing the attractive forces or increasing the repulsive forces between the solute (i.e. foulant) and the membrane (Belfort et al., 1994). It has been generally known that membranes with a hydrophilic surface have a lower fouling potential and fouling of hydrophilic surfaces is often reversible. Since many commercial membranes are made from hydrophobic polymers, because of the superior chemical resistance and thermal and mechanical properties of these polymers, there is interest in coating hydrophobic polymers with hydrophilic materials (Hilal et al., 2005). Techniques used for surface modification include coating and photo-induced grafting.

Membrane type and configuration also affect fouling (Hilal et al., 2005). For example, hollow fiber membranes are back-washable. In addition, submerged hollow fiber systems are relatively simple, low cost (Cui et al., 2003) and require a relatively small footprint (Yoon et al., 2004).

A number of operating parameters/conditions can be modified to reduce membrane fouling. Commonly used approaches include back-flushing, back-pulsing, back-washing, air sparging and the use of high cross-flow velocities, mixers, turbulence promoters and vortex generators. Back-flushing and back-pulsing consist of periodically reversing the flow through the membrane to remove foulants that have plugged membrane pores. Back-washing is similar to back-flushing except that the reversed flow contains chemical cleaning agents. Air sparging, high cross-flow velocities, mixers, turbulence promoters and vortex generators generate high shear forces at the membrane surface and as a result increase the extent of back-transport of foulants away from the membrane surface. In addition, operating the membrane system under critical flux conditions can also reduce membrane fouling (Hilal et al., 2005).
Recovery cleaning procedures usually involve physical and/or chemical cleaning. Physical scouring, using pressurized water or air, can typically be used to effectively remove surface fouling. Chemical cleaning is necessary to remove foulants from membrane pores and to remove heavily consolidated surface foulants.

2.2.2 Air sparging in hollow fiber ultrafiltration membranes

Air sparging is an effective way to generate high surface shear at membrane surfaces (Cui et al., 2003). By injecting air directly in the concentrate compartment during the filtration process, air sparging creates a gas-liquid two-phase flow along a membrane surface, increasing the surface shear, and reducing fouling. Air sparging has been recognized as a very effective approach for fouling control and permeate flux enhancement. The mechanisms by which air sparging reduces fouling in a cross-flow tubular membrane system have been summarized by Cui et al. (2003). However, the mechanisms by which air sparging reduces fouling in submerged hollow fiber membranes are relatively poorly understood.

It has been well recognized that fouling in submerged hollow fiber membrane systems is greatly reduced by air sparging (Bellara et al., 1996; Smith et al., 2002; 2005; Cui et al., 2003; Bérubé and Lei, 2006; etc). However, the mechanisms of the flux enhancement as well as the performance of the sparged air in hollow fiber membranes are different from those in tubular membranes.

In a review paper by Cui et al. (2003), the main mechanisms of permeate flux enhancement by air sparging in submerged hollow fiber membrane systems were identified to be due to (1) scouring induced by the falling film that can surround a confined rising bubble (Bellara et al., 1996; Smith et al., 2005), (2) shear forces induced by oscillating flows that are present in the wake of a rising bubble (Bellara et al., 1996; Smith et al., 2005; Bérubé and Lei, 2006), (3) high bulk cross-flow velocities induced by the rising bubbles, and (4) pressure instabilities induced by the rising bubbles (Cui et al., 2003).
Cui et al. (2003) argued that gas flow rate, fiber orientation, fiber size and flexibility all had an impact on the flux enhancement in submerged hollow fiber membranes. The benefit of air sparging could be measured either by the degree of flux increase or the degree of deposit resistance decrease. Cui et al. (2003) reported that increasing the intensity of air sparging typically increased the flux and reduced the magnitude of resistance (also see Figure 2.2). However, a plateau is typically observed above which an increase of air sparging intensity does not result in an increase of the permeate flux (Chang and Fane, 2000b; Bérubé and Lei, 2006). Cui et al. (2003) reported that smaller fibers responded more positively to air sparging because they were more flexible and could move laterally and remove the deposited material on the membrane surface.

Bérubé and Lei (2006) suggested that both the lateral velocity of a swaying fiber and the physical contact between swaying fibers could generate high shear forces at a membrane surface. Promoting lateral swaying could potentially increase the physical contact between membrane fibers, and mechanically remove the foulant layer on the membrane surface. The magnitude of the surface shear forces was related to the configuration of the membrane system and the air sparging practice (Bérubé et al., 2006).

2.3 Irreversible Fouling

To minimize fouling in membrane filtration systems, physical membrane cleaning methods such as back-washing, high cross-flow velocity or scouring with air bubbles are routinely used in many existing full-scale membrane plants. Back-washing changes the direction of the flow and removes foulants that plug membrane pores and/or accumulate on membrane surfaces. High cross-flow velocities and air sparging create shear along the membrane surface, thus removing the material accumulating on the surface. However, membrane fouling can not be totally prevented by the above physical methods. This is partly because fouling due to adsorption within the membrane pores, cannot be controlled by physical membrane cleaning methods. As a
result, regardless of the physical membrane cleaning methods applied, a membrane becomes irreversibly fouled over time (Katsoufidou et al., 2005; Kimura et al., 2004). Bérubé and Wong (2007) defined irreversible fouling as the fraction of the total fouling that is not impacted by the rate of mass transfer away from a membrane surface.

Since physical membrane cleaning methods cannot control irreversible fouling, chemical cleaning is eventually needed to eliminate irreversible fouling. However, membrane systems need to be shut down during chemical cleaning, leading to a reduction in plant production. The waste produced from chemical cleaning also needs to be disposed of. Also, frequent chemical cleaning can reduce the membrane life. In addition, the costs of the cleaning chemicals are relatively high. As a result, compared with the physical cleaning methods applied to reduce reversible fouling, chemical cleaning is more expensive and complicated. Consequently, irreversible fouling poses a great challenge when optimizing the operation of membrane filtration systems (Crozes et al., 1997; Kimura et al., 2004).

2.3.1 Causes of irreversible fouling and corresponding prevention strategies

To date, there has been no comprehensive research study conducted to investigate irreversible fouling. The very few studies that have focused on irreversible fouling have focused more on water chemistry aspects such as the interactions between natural organic matter and membrane materials. Crozes et al. (1993) found irreversible fouling was caused mainly by the adsorption of low molecular weight natural organic matter inside the membrane pores. This study also revealed that adsorption occurred more severely in a hydrophobic membrane than a hydrophilic membrane, when filtering surface water. Kimura et al. (2004) found that polysaccharide-like organic matter was the main cause for irreversible fouling in hydrophobic membrane systems. In addition, iron and manganese also contributed to irreversible fouling to some extent. Kimura et al. (2006) concluded that the degree of irreversible fouling was a function of the membrane properties and the types of organic matter in the solute. Although hydrophilic natural organic matter was observed to produce irreversible fouling regardless of the type of
membrane used, the exact composition of the organic material that caused irreversible fouling was reported to vary for different membrane materials. Irreversible fouling was also found to be proportional to the volume of solute filtered. When operated at the same trans-membrane pressure, UF membranes, which had a lower permeate flux, showed less irreversible fouling than MF membranes which had a higher permeate flux (Kimura et al., 2006).

Pretreatment of the water matrix to remove material that can potentially adsorb inside membrane pores and change the physicochemical properties of the membrane surface has been regarded as the major strategy for the prevention of irreversible fouling (Crozes et al., 1997; de Amorim and Ramos, 2006). However, research conducted by Kimura et al. (2005) found that although pre-coagulation/sedimentation did reduce reversible fouling significantly, it was ineffective at reducing irreversible fouling. This was because pre-coagulation/sedimentation was not able to remove polysaccharide/protein-like organic matter which was reported to cause irreversible fouling in this study. The effectiveness and efficiency of other pre-treatment methods need to be investigated in future research.

In terms of modification of the physicochemical properties of membrane surfaces, blending Pluronic F127 with poly (ether sulfone) (PES) increased the hydrophilicity of UF membranes, and was reported to be less prone to irreversible fouling (Wang et al., 2005). de Amorim and Ramos (2006) observed that the irreversible fouling of hydrophilic PVDF membranes was reduced when treated by a hydrophilic polymer solution. Kimura et al. (2006) observed that the irreversible fouling of polyacrylonitrile (PAN) membranes by naturally occurring organic matter was relatively low, while polyvinylidene fluoride (PVDF) and polyethylene (PE) suffered severe irreversible fouling.

2.3.2 Operating factors that influence irreversible fouling

Crozes et al. (1997) investigated the impact of operating parameters on irreversible fouling. The cross-flow velocity, the operating permeate flux, the back-washing frequency and the
trans-membrane pressure all influenced irreversible fouling. Both reversible and irreversible fouling could be controlled by increasing the cross-flow velocity, reducing the permeate flux, and increasing the back-washing frequency. It was empirically observed that irreversible fouling in LED (membrane developed by Lyonnaise des Eaux) UF membranes could be avoided by limiting the increase of trans-membrane pressure to a critical value. Above the critical value, irreversible fouling increased exponentially with the increase of trans-membrane pressure.

The extent of irreversible fouling related to permeate flux, back-washing frequency and time was measured by Kim and DiGiano (2006). The rate of irreversible fouling decreased substantially when the flux decreased from 65 to 50 L/m²h and back-washing frequency increased from every 15 to 10 minutes. Increase of back-washing time did result in a slight decrease in the fouling rate, but an increase of back-washing frequency was more effective at decreasing the fouling rate. Nevertheless, irreversible long-term fouling could not be completely avoided by the increase of back-washing frequency and back-washing time. Both internal fouling and cake formation were observed to be responsible for irreversible long-term fouling.

Air sparging was observed to be able to reduce irreversible fouling to some extent (Chang and Fane, 2000a). The resistance associated with reversible and irreversible fouling during filtration with and without air sparging is shown in Figure 2.2. As presented, the air sparging could reduce both reversible and irreversible filtration resistance. The reversible resistance was reduced significantly with an increase of superficial velocity. On the other hand, the irreversible resistance was much less significantly reduced with an increase of superficial velocity.
Other research indicates that reversible fouling and irreversible fouling are related to some extent. Bérubé and Wong (2007) observed that material that initially reversibly fouled a membrane surface could consolidate and generate irreversible fouling. This conclusion is somewhat consistent with those observed by other researchers. Nagaoka et al. (1998) suggested that some irreversible fouling could result from the consolidation/compaction of accumulated material on the membrane surface. They suggested that the rate of material accumulation on the membrane surface was proportional to the trans-membrane pressure. Hong et al. (2002) observed that the extent of the consolidation was a function of the duration of the filtration cycle. Katsoufidou et al. (2005) also observed that although reversible fouling could be removed by back-washing, the combined influence of pore blocking and cake formation could result in long term flux decline and eventually the formation of irreversible fouling.

### 2.3.3 Quantification of irreversible fouling

Liang et al. (2006) developed a relationship to determine the magnitude of irreversible fouling resistance $R_f$, based on the fouling strength of dissolved organic matter $k_i$ [m/g], the dissolved organic matter concentration $S_f$ [g/m$^3$], and the total volume of the filtrate per unit area of the membrane $\int_0^t J dt$ [m$^3$/m$^2$] as presented in Equation 2.4.
The fouling strength factor of dissolved organic matter $k_i$ was regarded to be operation-specific, and a function of the characteristics of dissolved organic matter and the membrane materials (Liang et al., 2006).

2.4 Modeling of Fouling in Submerged Hollow Fiber Membrane Systems

Using Darcy’s law and the four classical fouling models described in Section 2.1.2, individually or in combination, a number of studies have been conducted to attempt to explain the mechanisms that occur during membrane fouling. Usually, only one of the four fouling models is applied at one time. However, fouling kinetics suggest more than one fouling mechanism occurs at one time, and therefore, two or more of the four classical fouling models need to be considered successively or simultaneously (Jacob et al., 1998).

2.4.1 Models that account for the effect of different fouling mechanisms either separately and or in succession

Most early studies expressed fouling behavior by identifying a dominant mechanism contributing to the evolution of flux decline (Katsoufidou et al., 2005). Tracy and Davis (1994) observed that during the filtration of bovine serum albumin (BSA) solutions through microfiltration membranes, both the standard blocking model and the pore blocking model initially fitted the experimental data well. However, with time, the cake filtration mechanism eventually dominated fouling behavior. Bowen et al. (1995) reported that all four classical fouling models could dominate the fouling process, but at different times, depending on the material in the solution being filtered and the membrane pore size. Theoretically, if the size of most membrane pores was larger than the material in the solution being filtered, the sequence of fouling started with standard blocking, complete blocking, followed by intermediate and cake fouling. If the size of most membrane pores was smaller than material in the solution being
filtered, the sequence of fouling started with complete blocking, followed by intermediate blocking and cake fouling. However, in practice, the fouling models are likely superimposed due to the membrane pore size distribution. In addition, although the initial and final steps could be identified, the transition between each dominant fouling model was gradual and complex. For membrane pore sizes studied in this research (smaller than material being filtered), the initial step was the complete blocking of the smallest pores, while the final step was the beginning of cake fouling. Nevertheless, for the smallest pore size membrane (nominal pore diameter 0.2 μm), the initial step seemed to be the combination of standard blocking and intermediate blocking (Bowen et al., 1995).

Minegish et al. (2001) observed that when hollow fiber UF membranes fouled, the decrease in the pore diameter and the decrease in the pore number occurred simultaneously. The decrease in the pore diameter was due to the adsorption of the low molecular weight substances (standard blocking model) inside the pore wall. The decrease in pore numbers was due to the accumulation of the high molecular weight humic substances (complete blocking model) on membrane surface. However, the mathematic model developed in their study only considered the effect of the primary fouling mechanism: the decrease of pore numbers by the high molecular weight humic substances.

2.4.2 Models that account for the effect of different fouling mechanisms in parallel

Recently, several studies considered more than one fouling mechanism to explain and model fouling behavior (Ho and Zydney, 2000; Yuan et al., 2002; Katsoufidou et al., 2005; Bolton et al., 2006a; Bolton et al., 2006b; Ye et al., 2006).

Ho and Zydney (2000) modeled the flux decline over time in membranes by taking both pore blockage and cake fouling into account. The filtration flow rate could be determined by three parameters: the rate of pore blockage $\alpha$, the initial resistance of the protein deposit $R_{p0}$ [$m^2/m^3$] and the rate of cake growth $f'R'$. The values of these parameters were estimated from
the experimental data and provided excellent agreement between the data and model predictions. The model also demonstrated a smooth transition from pore blockage, as the initial principal mechanism, to cake fouling, which eventually dominated fouling. For this study, one mathematical equation was able to explain fouling behavior regardless of the different phenomena and mechanisms occurring during the filtration process. This was regarded as the first model to combine the effect of two fouling mechanisms together (Bolton et al., 2006a).

Yuan et al. (2002) modified the combined pore blockage and cake fouling model developed by Ho and Zydney (2000) and found it was in good agreement with the flux decline behavior during microfiltration of Aldrich humic acid through 0.2 μm pore size membranes. Since the three parameters $\alpha$, $R_{p0}$ and $f'R'$ were all estimated from independent measurements of the physical properties of the humic acid systems, the changes of the solution condition could be reflected in the model calculation results. The model thus had the ability to analyze humic acid fouling under different conditions. In addition, a flux was observed below which the cake filtration could be negligible. This is similar to the critical flux concept developed for colloidal filtration (Yuan et al., 2002).

Katsoufidou et al. (2005) took the simultaneous effect of all fouling mechanisms: pore construction, pore blocking and cake development into account and developed a new model based on the previous study by Bowen et al. (1995) and Yuan et al. (2002). The model successfully described the experimental data collected when filtering humic acid solutions through a single hollow fiber UF membrane. Their results suggested that the internal pore adsorption caused relatively rapid irreversible fouling. In parallel, pore blocking became important with time and a fouling cake developed on the membrane surface. Although back-washing could partly reverse the effect of pore blocking and cake formation, the combined influences of these two mechanisms could persist for a long time and eventually contribute to irreversible fouling.
Based on the classical fouling models, Bolton et al. (2006a) generated five new models that accounted for the combined effect of individual fouling mechanisms. These models, such as caking and complete blockage model, assumed that cake formation and complete pore blocking occur simultaneously. When pores were blocked, although still permeable, the resistance for solutions to go through the membrane increased, and more cake would build upon the membrane surface. Eventually, more cake formation and less pore blockage occurred. Explicit equations were also derived from Darcy’s Law under constant pressure and constant flow conditions. The equation could also be reduced to a single form of either the complete blocking model or a cake fouling model. Experimental results from the filtration of sterile IgG demonstrated that the combined caking and complete blockage model was the most useful since it provided good fits for both data sets, and was confirmed to be useful for a wide range of applications. The combined cake-standard and caking-intermediate models could give good fit to data as well and would also be effective in certain applications (Bolton et al., 2006a).

Bolton et al. (2006b) also developed a new adsorptive model that incorporated the effects of the permeate flux on irreversible fouling. While the standard model assumed all foulants entering into membrane pores deposit and accumulate uniformly along the pore wall, the adsorptive model allowed some foulants to deposit at the wall following zero order kinetics. This new adsorption model was combined with cake fouling, intermediate blocking and complete blocking models to predict fouling behavior. The combined intermediate-adsorption model was observed to be the best at matching the experimental data. Because this new model accounted for the effect of the flow rate and adsorption, it could be applied to membrane systems operated under different flow rates.

When using a membrane bioreactor for wastewater treatment, Ye et al. (2006) observed that fouling, when operating at subcritical flux conditions, was initially due to the standard pore blocking, and subsequently due to cake fouling. They also observed that the rate of standard pore blocking and cake fouling increased exponentially with respect to the permeate flux.
2.4.3 Models that combined reversible and irreversible fouling together

Very few studies were found that considered the effect of reversible fouling and irreversible fouling in parallel.

A series of studies are being undertaken at the University of British Columbia to attempt to develop a model that can be used to accurately predict the evolution of the trans-membrane pressure over time in a submerged hollow fiber membrane system. These studies investigate the effects of the hydrodynamic conditions and the system configurations on membrane fouling. The results to date indicate that the increase in the trans-membrane pressure during one filtration cycle, can be modeled using a simple exponential relationship as presented in equation 2.5 (Bérubé and Watai, 2005).

\[
P_v = P_o e^{[k_r]v} = P_o e^{[k_r + k_i]v}
\]

(2.5)

where \( k_r \) is the total fouling coefficient, which is the sum of the reversible (\( k_r \)) and irreversible (\( k_i \)) fouling coefficients, \( P_v \) is the trans-membrane pressure after filtering a given permeate volume [psi], \( P_o \) is the initial trans-membrane pressure [psi], which is equivalent to the clean water flux. The reversible fouling coefficient was reported to be proportional to the different between the operating permeate flux and the pseudo-steady-state permeate flux (Bérubé and Watai, 2005). The irreversible fouling was initially estimated to be proportional to the inverse of the permeate flux (Bérubé and Lei, 2006). However, this initial estimate was derived based on experiments with heavily fouled membranes operated over relatively short periods of time (i.e. 8 hours) and with a constant trans-membrane pressure and variable permeate flux. Therefore, it is not clear whether this initial estimate can be applied to a properly operated (i.e. not extensively fouled) membrane with a constant permeate flux and variable trans-membrane pressure.

Liang et al. (2006) also described membrane fouling in submerged membrane bioreactor systems for wastewater treatment with a relationship that included both reversible and
irreversible fouling parameters. Reversible fouling was attributed to the mixed liquor suspended solids in solution, while long-term irreversible fouling was attributed to dissolved organic matter. Based on their study, reversible fouling was determined to be responsible for the initial rapid increase in the membrane resistance, and irreversible fouling was responsible for the subsequent and relatively slow increase in the membrane resistance.

2.5 The Knowledge Gap: Mechanisms occurring in irreversible fouling and a reliable model to predict irreversible fouling

As discussed above, membrane fouling has been extensively studied for decades. While the previously developed models have provided insight into the fouling mechanisms, they have certain limitations. Most of these studies and the models developed to date, combine reversible and irreversible fouling together. Irreversible fouling, the main cause of long-term fouling, has received limited attention. As a result, the mechanisms that govern irreversible fouling, as well as the fouling behavior, are poorly understood. Particularly, better knowledge of the impact of back-transport mechanisms (i.e. extent of air sparging) and the operating permeate flux on irreversible fouling is needed. Due to this knowledge gap, there is currently no accurate model to predict irreversible fouling, or to develop effective strategies to prevent and control irreversible fouling.
CHAPTER 3 MATERIALS AND METHODS

This study was designed to investigate the impact of system hydrodynamics on irreversible fouling in a submerged hollow fiber membrane system. All experiments were conducted at a constant permeate flux and variable trans-membrane pressure conditions. The specific experimental conditions investigated are presented in the following sections.

3.1 Bench-scale Membrane System

The bench-scale membrane system used in the present research is illustrated in Figure 3.1. It consisted of a submerged membrane system (system tank and membrane module), an aeration system (air line, air flow controller, central aerators), a permeate flux generation, collection and measurement system (Masterflex variable speed pump and digital scale), and a vacuum measurement system (digital pressure gauge, pressure transducer and data logger).

Figure 3.1 Schematic of the bench-scale submerged membrane system
Trans-membrane pressure for the system was defined as the difference between the magnitude of the vacuum inside the permeate line and the atmospheric pressure. Trans-membrane pressure was automatically measured by a transducer and recorded through a data-logger once every minute. The permeate flux was periodically (once every 4-5 hours during daytime hours) monitored by a digital scale to ensure that it remained constant over time.

![Picture of laboratory bench-scale experimental setup]

Figure 3.2 Picture of laboratory bench-scale experimental setup

3.1.1 *Submerged membrane system*

The submerged membrane system consisted of a system tank with flow control baffle inside, and a membrane module.

*System tank*

The system tank consisted of an open top cylindrical tank with an open ended concentric cylindrical baffle inside. The cylindrical tank had a diameter of 0.142 m and a height of 1.4 m. The working depth of the system tank was 1.0 m, resulting in a total working volume of 16 L. A
valve was located at the bottom of the tank to allow the fluid used in the experiment to be
drained after each experiment.

The cylindrical baffle, with a diameter of 0.07 m and a height of 0.8 m, was located along
the vertical center line of the cylindrical tank, and 0.025 m from the bottom of the tank, as shown
in Figure 3.3. The cylindrical baffle enabled the hydraulics and air sparging in the submerged
membrane system to be controlled by using the aeration system, as described in Section 3.1.2.

Figure 3.3 Schematic diagram of system tank with cylindrical baffle
**Membrane module**

The membranes used in the present research were outside-in flow hollow fiber membranes, produced by Zenon Environmental Inc (Oakville ON). The physical characteristics of the membrane are presented in Table 3.1.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Outside diameter</th>
<th>Surface properties</th>
<th>Nominal pore diameter</th>
<th>Typical operating TMP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Outside-in hollow fiber</td>
<td>1.77 mm</td>
<td>Non-ionic &amp; hydrophilic</td>
<td>0.04μm</td>
<td>1-8 psi</td>
</tr>
</tbody>
</table>

For the present research, single membrane fiber modules were used. Membrane modules were produced by potting the membrane fibers into a top and bottom bulkheads as illustrated in Figure 3.4. Epoxy was used to pot the membrane fibers into the bulkheads. While the top bulkhead was open to allow for the permeate collection, the bottom bulkhead was sealed.

![Figure 3.4 Schematic of membrane module](image)
The membrane fiber was 0.42 m long. It was held tightly and located inside the cylindrical baffle along the vertical center line, and was placed 0.195 m from the bottom of the system tank as illustrated in Figure 3.5. The total membrane surface area was 0.0023 m$^2$.

![Figure 3.5 Membrane module position inside the system tank](image)

3.1.2 Aeration system

The aeration system was used to control the hydrodynamic conditions in the system tank by changing the bulk cross-flow pattern and cross-flow velocities along the membrane surface.

According to previous studies, higher permeate flux could be achieved under dual-phase flow (air and water cross-flow along membrane surface) (Bellara et al., 1996, Smith et al., 2002, Smith et al., 2005, Cui et al., 2003, Bérubé and Lei, 2006, etc). Therefore, dual-phase bulk cross-flow conditions were adopted throughout the present research. Dual phase cross-flow was generated by aerating the system tank with the central aerator.
The central aerator, located at the bottom of the cylindrical tank, consisted of a perforated plate with eight 2 mm diameter holes arranged in a circle (see Figure 3.6). Air was added to the system tank through the central aerator.

![Figure 3.6 Schematic of center aerator](image)

The rising air bubbles, which were confined to the inside of the cylindrical baffle, entrained water upwards along the inside of the cylindrical baffle. The air and the entrained water flowed upwards along the membrane surface, on the inside of the cylindrical baffle, thus forming a dual phase cross-flow condition. A schematic of the flow path for the dual phase cross-flow is illustrated in Figure 3.7.

![Figure 3.7 Schematic of dual phase cross-flow aeration system](image)

(Arrows indicate the direction of listed flow)
The velocities of bulk cross-flow were controlled by varying the air flow rate. For the present study, bulk cross-flow velocities of 0.2, 0.3 and 0.4 m/s were considered. The corresponding air flow rates (and air flow meter readings), to achieve these bulk cross-flow velocities for the dual phase cross-flow system, are presented in Table 3.2, and were obtained as part of a previous study which focused on the impact of different hydrodynamic conditions on submerged membrane systems (Lei, 2005).

Table 3.2: Operating bulk cross-flow velocities and air flow rate for dual phase system (Lei, 2005)

<table>
<thead>
<tr>
<th>Bulk cross-flow velocities (m/s)</th>
<th>Air flow rate (ml/min)</th>
<th>Air flow meter readings</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>3200</td>
<td>25</td>
</tr>
<tr>
<td>0.3</td>
<td>5300</td>
<td>42</td>
</tr>
<tr>
<td>0.4</td>
<td>7500</td>
<td>60</td>
</tr>
</tbody>
</table>

The air flow rate to the aerator was controlled by using a valve and an air flow meter (model: Cole-Parameter: N034-39(ST)) connected to a compressed air line, as illustrated in Figure 3.1.

3.1.3 Permeate flux generation, collection and measurement system

A peristaltic pump was used to provide the driving force that enabled the permeate to flow through the membrane. The pump was connected to the membrane module via a quarter inch hard tubing (1/4” OD food Grade Polyethylene Green Line G800-04). Hard tubing was used to prevent any collapse in the tube since the system was operated under vacuum (see Section 3.4). A Masterflex pump (model number 7521-50) with two Masterflex pump heads (model number 7013-21) operated in parallel was adopted. Each of the pump head rotors were offset to minimize pressure fluctuations. An additional set of two pump heads were used to pump raw water to the system tank to maintain the constant working volume of 16 L during every experiment. The
pump speed was adjusted to achieve the required permeate flux (see Section 3.4).

Permeate flux was collected in a 5L flask. The change in weight of permeate in the flask was monitored over time using an electronic scale (Scout Pro 4000 g Scale) to ensure that a constant permeate flux was maintained during every experiment. The permeate flux was regularly measured every 4 to 5 hours (day time).

3.1.4 Vacuum measurement system

The use of the pump created a vacuum inside the membrane fibers, providing the driving pressure differential (i.e. trans-membrane pressure) that enabled the permeate to flow through the membrane.

Pressure transducer and data logger

A pressure transducer (Omega PX240 M0263/1100) was connected to the permeate line to measure the trans-membrane pressure. The transducer was connected to a data logger (National Instrument USB-6009) that conveyed data to a computer once every 1 minute using a custom Labview application (version 7.0).

Since the output from the pressure transducer was a voltage signal, a relationship was developed and used to convert the data from the pressure transducer to a pressure reading. The relationship was developed by applying several known vacuums to the transducer and recording the voltage signal obtained by the data logger for each vacuum. Prior to each experiment, the transducer was calibrated. Since the pressure transducer measured the relative pressure, all of the pressure readings obtained corresponded to pressure differences between the inside of the permeate line and the atmosphere (i.e. trans-membrane pressure).

Pressure gauge

A compound digital pressure gauge (Cole-Parameter, K-68950-00) was used to
periodically monitor the vacuum that was applied to the pressure transducer and ensure that the trans-membrane pressure measured by both the pressure transducer and pressure gauge were in agreement. Since all pressure measurements were relative measurements with respect to atmospheric pressure, prior to each experiment, the pressure gauge reading was set to zero.

3.2 Routine Membrane Integrity Testing and Maintenance

3.2.1 Membrane integrity testing

Before starting each experiment, the integrity of the membrane module used was verified using a pressure hold (bubble) test.

A schematic of the membrane integrity testing (pressure hold test) apparatus is illustrated in Figure 3.8. For the integrity testing, fully wetted and submerged membrane fibers were pressurized to 41 kPa (6 psi) using a compressed air line, the membrane was then isolated from the compressed air line by closing an isolation valve, and the pressure was monitored for 2 minutes. According to the information from the manufacturer, at a pressure of 41 kPa (6 psi), a breach of approximately 3 um in diameter in the integrity of membrane surface should be detected without damaging the membrane fibers. The membrane was considered breached if a significant decline in the pressure (10% of the testing pressure) as observed during the test. The membrane was also considered breached if bubbles were observed to escape from the membrane module.

If the integrity of the membrane was compromised, the membrane module was discarded.
3.2.2 Membrane cleaning

After each experiment, the membrane module was cleaned using a sodium hypochlorite (NaClO) solution (diluted from 6.0% Domestic Miroclean Bleach). As recommended by the membrane manufacturer, the membrane cleaning procedure used during the present study was as follows:

1. the used membrane fiber was soaked in a 750 ppm solution of sodium hypochlorite (NaClO) solution (diluted from 6.0% Domestic Miroclean Bleach) for 16 hours;
2. the 750 ppm solution of NaClO was then filtered through the membrane fiber at a -28 kPa (-4.1 psi) vacuum for a period of 20 minutes;
3. the membrane fiber was transferred into a fresh 50 ppm solution of NaClO, and the solution was then filtered through the membrane fiber at -28 kPa (-4.1 psi) for a period of 20 minutes;
4. the cleaned membrane fiber was then stored by soaking it in a 50 ppm solution of NaClO.

Before a cleaned membrane fiber was used for a filtration test, the membrane fiber was rinsed three times using distilled water. Distilled water was then filtered through the membrane fiber at -4.1 psi for a period of 20 minutes.
3.3 Source Water

The source water used in the present research was a mixture of raw water from the Capilano Reservoir and Jericho Pond. The Capilano Reservoir is located in North Vancouver and supplies 40 percent of the Great Vancouver Regional District’s drinking water. Raw water from the Capilano Reservoir is characterized by low turbidity (<1 NTU) and low organic content (approximately 2 ppm as Total Organic Carbon). Because of its high quality, raw water from the Capilano Reservoir had a very low fouling potential. Preliminary tests indicated that it would take a number of days to weeks for the membrane to foul. To enable a greater number of experimental conditions to be considered with a shorter time frame, raw water from the Capilano Reservoir was mixed with raw water from Jericho Pond, located in Vancouver. The resulting raw water mixture had a TOC of approximately 6 ppm, and a relatively higher fouling potential.

Approximately 80 L of raw water from Jericho Pond was collected on June 5th, 2005 and approximately 120 L on Aug 4th, 2005 and stored in a refrigerator at 4 °C in the Environmental Engineering Lab at UBC. Raw water from Capilano Reservoir was collected on the same dates and stored in the same refrigerator as the Jericho Pond water. Approximately 300 L of Capilano water was collected on June 5th, 2005 and approximately 600 L was collected on Aug 4th, 2005.

Prior to each experiment, Capilano and Jericho water was brought to room temperature and then mixed in a 5:1 ratio (5 parts Capilano : 1 part Jericho).

The TOC concentrations of different raw waters and their mixtures are summarized in Table 3.3. TOC tests revealed that even though the raw waters were stored in a refrigerator at 4 °C, the TOC of the raw water changed slightly over time as presented in Table 3.3.
Table 3. 3 TOC of raw water and their mixtures

<table>
<thead>
<tr>
<th>Water</th>
<th>First collection event</th>
<th>Second collection event</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Test date</td>
<td>Volume collected</td>
</tr>
<tr>
<td>Capilano*</td>
<td>2005/06/05</td>
<td>300 L</td>
</tr>
<tr>
<td>Jericho*</td>
<td>2005/06/05</td>
<td>80 L</td>
</tr>
<tr>
<td>Mixture</td>
<td>2005/06/05</td>
<td>4.26</td>
</tr>
</tbody>
</table>

*represents Capilano reservoir water and Jericho pond water, respectively

TOC tests were performed by the Persulfate-Ultraviolet Oxidation Method 5310 (APHA, AWWA and WEF) with the aid of a Dohrman Phoenix 8000 UV- Persulfate analyzer (Dohrman).

3.4 Experimental Program

3.4.1 Experimental conditions considered

The overall objective of the present research was to develop a simple and reliable relationship to accurately model irreversible fouling in a submerged membrane system under different hydrodynamic conditions. The impact of different hydrodynamic conditions on irreversible fouling was assessed by monitoring the evolution of the trans-membrane pressure over time when operating the system at a permeate flux that was less than the pseudo-steady-state (i.e. critical) permeate flux ($J_{SS}$) and when operating the system under different hydrodynamic conditions. The hydrodynamic conditions considered were dual-phase cross-flow at bulk cross-flow velocities of 0.2, 0.3 and 0.4 m/s.

As previously discussed, irreversible fouling was defined as the fouling that is not
impacted by the rate of mass transfer away from the membrane surface. Therefore, irreversible fouling can be observed when the operating permeate flux was less than the pseudo-steady-state permeate flux. Table 3.4 lists the pseudo-steady-state permeate fluxes for different operating conditions. These were obtained from previous studies using a similar source water and experimental apparatus (Lei, 2005). To ensure that the system was operating below pseudo-steady-state flux for all hydrodynamic conditions considered, operating fluxes of 40, 50, and 60 L/m²h were considered.

<table>
<thead>
<tr>
<th>Bulk dual phase cross-flow velocities</th>
<th>0.2 m/s</th>
<th>0.3 m/s</th>
<th>0.4 m/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo-steady-state permeate flux</td>
<td>65.0±1.30 L/m²h</td>
<td>91.8±4.24 L/m²h</td>
<td>93.7±1.0 L/m²h</td>
</tr>
</tbody>
</table>

Two series of experiments were performed to assess the impact of the system hydrodynamics on irreversible fouling. Series 1 was conducted using filtered and deionized water for all experimental conditions to estimate the clean water trans-membrane pressure. The source water used in Series 1 was filtered and deionized tap water (tap water was treated using a Reverse Osmosis Filtration System (model#: GXRM10G, Serial#: 04-1647). Series 2 was conducted using the 5:1 Capilano and Jericho raw water mixture. All experiments performed as part of Series 2 were performed in duplicate. The experimental series and experiment names are summarized in Table 3.5.

All experiments were performed at room temperature (range between 15-20 °C). Prior to the start of each experiment the waters were brought to room temperature. Water temperature was monitored throughout the experiment using a thermometer (Fisher 14-1997). All experiments were conducted until the trans-membrane pressure increased above 35 kPa (5 psi).
<table>
<thead>
<tr>
<th>Permeate flux (Lm²hr⁻¹)</th>
<th>Bulk cross-flow velocity (m/s)</th>
<th>Experiment names</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Series 1 (clean water)</td>
</tr>
<tr>
<td>40</td>
<td>0.2</td>
<td>1-T-1</td>
</tr>
<tr>
<td>40</td>
<td>0.3</td>
<td>1-T-2</td>
</tr>
<tr>
<td>40</td>
<td>0.4</td>
<td>1-T-1</td>
</tr>
<tr>
<td>50</td>
<td>0.2</td>
<td>1-T-2</td>
</tr>
<tr>
<td>50</td>
<td>0.3</td>
<td>1-T-2</td>
</tr>
<tr>
<td>50</td>
<td>0.4</td>
<td>1-T-2</td>
</tr>
<tr>
<td>60</td>
<td>0.2</td>
<td>1-T-1</td>
</tr>
<tr>
<td>60</td>
<td>0.3</td>
<td>1-T-2</td>
</tr>
<tr>
<td>60</td>
<td>0.4</td>
<td>1-T-1</td>
</tr>
</tbody>
</table>

3.4.2 Experimental monitoring

The experiments in Series 1 (i.e. clean water tests) lasted approximately 5 minutes. However, experiments in Series 2 lasted 6 to 15 days each. During this time, the permeate flux, the air flow meter readings, the pressure gauge readings and the water temperature were periodically monitored every 4-5 hours (day time) to ensure the system worked properly. The pressure transducer data were recorded automatically every minute as described in Section 3.1.4.

At the beginning of each experiment, a lag phase of up to 5 minutes was observed when the trans-membrane pressure increased as a vacuum was being formed inside the membrane and the tubing. The duration of the lag phase was relatively insignificant with respect to the duration of the entire experiments. To simplify the analysis of the data from the experiments in Series 2, the monitoring time was set to zero (i.e. time = 0) when the measured trans-membrane pressure reached the steady-state clean water trans-membrane pressure.
3.4.3 Trans-membrane pressure correction

After the experiments were completed, the data were collected from the data logger and converted into a Microsoft Excel file.

Factors such as temperature, atmospheric pressure, consistency of the system set up (e.g. length of tubing, height of the instruments), can all have effects on trans-membrane pressure measurements. Variations caused by system set up were avoided by keeping system configuration consistent throughout the study period. The effect of ambient atmospheric pressure changes could be neglected since a relative pressure transducer was used in the study. However, the effect of temperature changes needed to be considered. Variations in the temperature affect the viscosity of the liquid and directly impact the measured trans-membrane pressure, as presented in Equation 3.1.

\[
\Delta P = J \mu R_t
\]  

(3.1)

where \( \Delta P \) is the trans-membrane pressure \([N/m^2]\), \( J \) is the operating permeate flux \([m^3/m^2s]\), \( \mu \) is the water viscosity \([Ns/m^2]\), and \( R_t \) is the total filtration resistance \([m^2/m^3]\). To remove the effect of variation in the temperature on trans-membrane pressure, the measured trans-membrane pressure was standardized to a reference temperature of 20.0 °C using Equation 3.2.

\[
P_{20°C} = \frac{P_T \mu_{20°C}}{\mu_T}
\]  

(3.2)

where \( P_{20°C} \) \([N/m^2]\) and \( P_T \) \([N/m^2]\) are trans-membrane pressure values at temperatures of 20.0 °C and \( T \), respectively, and \( T \) is the operating temperature \([°C]\). \( \mu_{20°C} \) \([Ns/m^2]\) and \( \mu_T \) \([Ns/m^2]\) are water viscosity values at temperatures of 20.0 °C and \( T \), respectively. The temperature range in the present study was within 15-25 °C, and \( \mu_{20°C} = 1.002 \times 10^{-3} \text{ Ns/m}^2 \), \( \mu_{25°C} = 1.139 \times 10^{-3} \text{ Ns/m}^2 \), \( \mu_{25°C} = 0.890 \times 10^{-3} \text{ Ns/m}^2 \). Assuming the relationship between temperature and water
viscosity is linear within a temperature range of 15-20 °C, \( \mu_T \) can be calculated by Equation \( \mu_T = -2.74 \times 10^{-5}T + 1.55 \times 10^{-3} \) (see Figure 3.9 a), within temperature 20-25 °C, \( \mu_T \) can be calculated by Equation \( \mu_T = -2.24 \times 10^{-5}T + 1.45 \times 10^{-3} \) (see Figure 3.9 b). To simplify the calculation within the 15-25 °C range, average values were adopted, where the water viscosity at a temperature \( T \) (\( \mu_T \)) can be calculated by Equation 3.3.

\[
\mu_T = -2.49 \times 10^{-5}T + 1.50 \times 10^{-3} 
\]  

(3.3)

![Figure 3.9 Water viscosity vs Temperature](image)

The standardized trans-membrane pressure at a temperature of 20.0 °C can therefore be calculated using Equation 3.4.

\[
P_{20^\circ C} = \frac{P_T \mu_{20^\circ C}}{-2.49 \times 10^{-5}T + 1.50 \times 10^{-3}} 
\]  

(3.4)
CHAPTER 4 EXPERIMENTAL RESULTS

Two series of experiments, totaling 24 experiments were performed to obtain the data necessary to model irreversible fouling over time (see Table 3.5 for Experimental Program). Series 1 used a filtered and deionized water to measure clean water trans-membrane pressure under different operating permeate fluxes and cross-flow velocities. Series 2 used mixed source water to conduct a similar experimental program as series 1 to measure the evolution of trans-membrane pressure over time.

4.1 Evolution of Trans-membrane Pressure for Clean Water

When using clean water (i.e. filtered and deionized water), the trans-membrane pressure remained constant for a given operating permeate flux, regardless of the system hydrodynamic conditions (i.e. cross-flow velocity, and the volume of water filtered). However, the trans-membrane pressure increased when the operating permeate flux increased. The experimental results of series 1 are presented in Figure 4.1.

![Figure 4.1 Trans-membrane pressure for filtered and deionized water](image)

Figure 4.1 Trans-membrane pressure for filtered and deionized water
A linear relationship was observed between trans-membrane pressure and the operating permeate flux when filtering clean water as presented in Figure 4.2. The linear relationship (i.e. $\Delta P = 127.79\ Jv$) was expected since for clean water, the trans-membrane pressure is theoretically proportional to the permeate flux as presented in Equation 3.1.

![Figure 4.2 Linear relationship between operating permeate flux and trans-membrane pressure](image)

4.2 Evolution of Trans-membrane pressure over Time for Mixed Source Waters

As discussed in Section 3.4.1, 18 experiments were conducted in series 2. At least ten thousand trans-membrane pressure values were collected for each of the experiment. All the experiments showed a similar trend of increasing trans-membrane pressure over time. The trans-membrane pressure initially increased slowly. However, as more volume of water was filtered, the trans-membrane pressure increased at a faster rate. For a given operating permeate flux, the trans-membrane pressure increased more slowly at higher cross-flow velocity than at lower cross-flow velocity.

Figure 4.3, 4.4 and 4.5 show experimental trans-membrane pressure values with respect to the volume of water filtered (V) when operating at a permeate flux of 40, 50 and 60 L/m$^2$h. All
the data were normalized to 20 °C to account for the impact of temperature on the change of source water viscosity as discussed in Section 3.4.3.

Figure 4.3 Trans-membrane pressure vs Volume of water filtered at permeate flux 40 L/m²h
(The experiments in (b) were duplicates of experiments in (a); CFV standards for cross-flow velocity)

Figure 4.4 Trans-membrane pressure vs Volume of water filtered at permeate flux 50 L/m²h
(The experiments in (b) were duplicates of experiments in (a); CFV standards for cross-flow velocity)
Figure 4.5 Trans-membrane pressure vs Volume of water filtered at permeate flux 60 L/m²h

(The experiments in (b) were duplicates of experiments in (a); CFV standards for cross-flow velocity)

Three major observations can be made from the experimental results. First, for all experimental conditions, the trans-membrane pressures increased over time even though the experiments were performed with operating permeate fluxes that were less than the critical permeate flux. Second, for a given volume of permeate filtered, the extent of fouling (i.e. increase in trans-membrane pressure) was greater at a higher operating permeate flux. And finally, for a given volume of permeate filtered, the extent of fouling was lower at a higher cross-flow velocity.
CHAPTER 5 MODEL DEVELOPMENT, DATA ANALYSIS AND DISCUSSION

5.1 Model Development for Irreversible Fouling

Fouling is typically assumed to result from the accumulation of material at the membrane surface (cake fouling), the plugging of membrane pores (intermediate/complete blocking) and adsorption of material within membrane pores (standard blocking, i.e. internal fouling) (Field, et al., 1995; Hermia, 1982; Bolton et al., 2006a). When the operating permeate flux in a membrane system is less than the critical permeate flux, the extent of fouling that is due to cake fouling and/or intermediate/complete blocking is expected to be minimal (Field et al., 1995). Therefore, when operating below critical flux, fouling should be predominately due to standard blocking, i.e. internal fouling.

5.1.1 Model 1: Irreversible fouling is only due to internal fouling

The experiments performed in the present study were all conducted below critical flux conditions. Therefore, it was assumed that the sole mechanism responsible for fouling was material adsorption inside the membrane pore. Material adsorption causes a reduction in the pore radius. Based on this assumption, Model 1 was derived.

Derivation of Model 1

From Darcy’s law, the flow through a clean membrane can typically be expressed using Equation 5.1.

\[ J_v = \frac{n r^a \pi \Delta P}{8 \mu \tau L} \]  

(5.1)

Where \( J_v \): the operating permeate flux \([m^3/m^2s]\)

\( \tau L \): flow path length \([m]\)

\( n \): number of pores \([No./m^2]\)
r: membrane pore radius [m]

Rewriting Equation 5.1 to isolate the trans-membrane pressure yields Equation 5.2.

$$\Delta P = \frac{8 \mu \tau L J_v}{n r^4 \pi}$$  \hspace{1cm} (5.2)

Converting the units of operating permeate flux to L/m² h yields Equation 5.3.

$$\Delta P = \frac{8 \mu \tau L J_v}{n r^4 \pi} \times \frac{10^{-3}}{3600}$$  \hspace{1cm} (5.3)

Where Jv: the operating permeate flux [L/m² h]

For a given membrane, the pore radius was assumed to become smaller when a given volume of liquid (V) had been filtered as illustrated in Figure 5.1

Figure 5.1 Unit length membrane pore and its cross section (Where \( r_0 \) is the initial pore radius, and \( r' \) is the pore radius after filtering a unit volume of liquid).

The reduction of pore radius can be related to the volume of water filtered. The greater the volume of water filtered, the greater the amount of material adsorbed inside the pore (i.e. reduction membrane pore size). For a specific membrane pore, \( M_v \) was defined (see Equation 5.4) as the ratio of the volume of material adsorbed inside the pore wall to the volume of liquid that had passed through a pore of unit length.
\[
M_v = \left[ \frac{\text{Volume of materials adsorbed inside the pore wall}}{\text{Volume of liquid through the pore}} \right] 
\] (5.4)

Based on this assumption, the change in radius for a unit length of membrane pore, with respect to the volume of permeate filtered can be expressed using Equation 5.5.

\[
\frac{dr}{dV} = \frac{-M_v}{2\pi(1)} 
\] (5.5)

Where \( V \): volume of water filtered [m\(^3\)]

Integrating Equation 5.5 with \( r = r_0 \) at \( V = 0 \) and \( r = r' \) at \( V = V \) yields Equation 5.6.

\[
r = \sqrt{r_0^2 - \frac{M_v}{\pi} V} 
\] (5.6)

Combining Equation 5.6 into Equation 5.3 yields Equation 5.7.

\[
\Delta P = \frac{8\mu \tau L J_v}{n\pi (r_0^2 - \frac{M_v}{\pi} V)^2} \times \frac{10^{-3}}{3600} 
\] (5.7)

For a given membrane module and raw water matrix, \( \mu, \tau L, n \) and \( \pi \) are constants and can be grouped into a single parameter \( K_1'' \). Also, \( M_v/\pi \) can be grouped into a single parameter \( K_3 \), which is proportional to the extent to which material adsors inside the pores. As a result, Equation 5.7 can be rewritten as presented in Equation 5.8 (i.e. Model 1).

\[
\Delta P = \frac{J_v K_1''}{(r_0^2 - K_3 V)^2} 
\] (5.8)

Where \( K_1'' = \frac{8\mu \tau L}{\pi n} \times \frac{10^{-3}}{3600} \) represents all the constants in Equation 5.7 [Nm\(^4\)h/L]

\( K_3 = \frac{M_v}{\pi} \) is the volumetric reduction rate of pore radius [1/m]

\( r_0 \): initial membrane pore radius = 2e-8 m in the present study
Significance of coefficients

The parameter $K_1''$ is not expected to be affected by the experimental conditions investigated in the present study, since $K_1''$ is function of the raw water characteristics ($\mu$) and the membrane module characteristics ($\tau L$, $n$). Recall that both the raw water composition and the membrane module configuration were constant during the different experiments. Therefore, in the present study, $K_1''$ was expected to be constant for all experiments. The parameter $K_3$ describes the extent to which material adsorbs on the inside of a membrane pore. Considering that the adsorption of concern occurs within the pores themselves, $K_3$ is not expected to be affected by the hydrodynamic conditions outside of the pores (e.g. bulk cross-flow velocity). However, adsorption is expected to be affected by the hydrodynamic conditions within the pores themselves, and these conditions are governed by the permeate flow rate (i.e. operating permeate flux). Adsorption is also expected to be affected by the raw water matrix. Considering that all experiments were performed with the same raw water, $K_3$ was therefore expected to be affected only by the permeate flux for all experiments.

By using regression wizard in Sigmaplot software, the relationship presented in Equation 5.8 was fitted to the experimental data, and $K_1''$, $K_3$ values could be subsequently estimated. Table 5.1 shows the estimated $K_1''$, $K_3$ values and $R^2$ for the regression.
Table 5.1 $R^2$ for regression of model 1 and estimated $K_1''$, $K_3$ values

<table>
<thead>
<tr>
<th>Operating permeate flux (L/m²h)</th>
<th>Cross-flow Velocity (m/s)</th>
<th>Membrane module</th>
<th>$R^2$</th>
<th>$K_1''$ values (Nm⁴h/L)</th>
<th>$K_3$ values (1/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>0.2</td>
<td>1#</td>
<td>0.993</td>
<td>2.617E-29±2.906E-32</td>
<td>1.136E-14±.744E-18</td>
</tr>
<tr>
<td>40</td>
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<td>0.966</td>
<td>2.835E-29±6.830E-32</td>
<td>9.608E-15±1.543E-17</td>
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<tr>
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<td>3#</td>
<td>0.972</td>
<td>3.226E-29±9.249E-32</td>
<td>1.550E-14±3.369E-17</td>
</tr>
<tr>
<td>60</td>
<td>0.3</td>
<td>3#</td>
<td>0.974</td>
<td>3.422E-29±6.879E-32</td>
<td>1.439E-14±2.614E-17</td>
</tr>
<tr>
<td>60</td>
<td>0.4</td>
<td>3#</td>
<td>0.905</td>
<td>3.750E-29±1.283E-31</td>
<td>1.085E-14±4.759E-17</td>
</tr>
<tr>
<td>60</td>
<td>0.4</td>
<td>3#</td>
<td>0.948</td>
<td>3.813E-29±1.201E-31</td>
<td>1.373E-14±4.226E-17</td>
</tr>
</tbody>
</table>

± values are based on 90% confidence interval of the estimated parameters

The fit of Equation 5.8 to the data was consistently good (i.e. $R^2$ typically greater than 0.9). As expected, for a given membrane module, the parameter $K_1''$ was relatively constant for all experiments (Table 5.1). Recall that the parameter $K_1''$ corresponds to the raw water viscosity and clean membrane characteristics (see Equation 5.8), which are not expected to change over
time. However, as shown in Figure 5.2, the parameter $K_3$ was impacted by not only the operating flux, but the bulk cross-flow velocity (i.e. hydrodynamic conditions outside of the membrane pores) as well. As previously discussed, parameters $K_3$ was not expected to be impacted by the bulk cross-flow velocity.

![Graphs showing $K_3$ vs $J_v$ at different cross-flow velocities](image)

Figure 5.2 $K_3$ vs $J_v$ at different cross-flow velocities

Scanning Electron Microscope (SEM) images were taken of clean and fouled membrane surfaces to provide additional insight into the fouling mechanisms at the membrane surface. Presented in Figure 5.3 are 3 SEM images: Figure 5.3 a shows a clean membrane; Figure 5.3 b shows an intermediate fouled membrane (i.e. trans-membrane pressure reached 17.5 kPa); Figure 5.3 c shows an extensively fouled membrane (i.e. trans-membrane pressure reached 35 kPa).
As presented, in Figure 5.3 b, there was no surface fouling for conditions representative of an intermediate amount of fouling. For these conditions, fouling appeared to be due mainly to the constriction of the pore structure. However, surface fouling was observed for conditions representative of extensive fouling (see Figure 5.3 c). As previously discussed, surface fouling is impacted by the bulk cross-flow velocity. Therefore, the parameter $K_3$ is likely not impacted by the bulk cross-flow velocity, but rather, the bulk cross-flow velocity likely impacts surface fouling, which is not considered in Equation 5.8.

![SEM images for clean and fouled membranes](image_url)

Figure 5.3 SEM images for clean and fouled membranes

As previously discussed, when the operating permeate flux in a membrane system is less than the critical permeate flux, the extent of surface fouling (i.e. cake fouling and/or intermediate/complete blocking) is expected to be minimal (Field et al., 1995). However, as presented in Figure 5.3, even though all of the operating permeate fluxes utilized in the present study were below critical permeate flux conditions, surface fouling was observed, for extensively fouled membranes.
5.1.2 Model 2: Irreversible fouling is due to internal fouling + surface fouling

To account for the observed surface fouling, the relationship presented in Equation 5.8 was modified. A new model incorporating both internal fouling and surface fouling was developed.

Derivation of Model 2

For a given membrane module, the number of pores \( n \) (i.e. the active membrane surface area) was assumed to become smaller when a given volume of liquid had been filtered as illustrated in Figure 5.3.

![Diagram of active surface areas of clean membrane and after filtering unit volume of liquid](image)

(a) Area of clean membrane

(b) Active surface area after filtering a unit volume of liquid

Figure 5.4 Active surface areas of clean membrane and after filtering unit volume of liquid

(where \( A_0 \) is the initial active surface area of a given membrane module)

The reduction in the active surface area could be related to the volume of water filtered. The greater the volume of water filtered, the greater the amount of surface fouling (i.e. reduction in active surface area). For a specific membrane, \( S_v \) was defined (see Equation 5.9) as the ratio of the area impacted by surface fouling to the volume of liquid filtered through the membrane.

\[
S_v = \left[ \frac{\text{Area impacted by surface fouling}}{\text{Volume of liquid filtered through membrane}} \right]
\]  

(5.9)

Based on this assumption, the change in the active surface area with respect to the
volume of permeate filtered could be expressed using Equation 5.10.

\[
\text{Active area} = A_0 - S_v V
\]  \hspace{1cm} (5.10)

Where \( A_0 \): membrane initial active surface area = 0.0023 m\(^2\) in the present study

Renaming \( S_v \) as \( K_2 \), for consistency in terminology, substituting Equation 5.10 for the number of filtration pores \( n \) in Equation 1, and applying a similar development as presented in Equation 5.2 to 5.8 yields Equation 5.11 (i.e. Model 2)

\[
\Delta P = \frac{J v K_1}{(A_0 - K_2 V)(r_0^2 - K_3 V)^2}
\]  \hspace{1cm} (5.11)

Where \( K_1 = \frac{8\mu L}{\pi \times 10^{-3}} \) represents all constants in Equation 5.7 [Nm\(^6\)h/L]

\( K_2 \): rate of pore number reduction (i.e. rate of surface fouling) [1/m]
\( K_3 \): rate of pore radius reduction (i.e. rate of internal fouling) [1/m]

**Significance of coefficients**

Model 2 represents irreversible fouling comprehensively, by combining surface fouling and internal fouling together. Again, the parameter \( K_1 \) was not expected to be affected by the experimental conditions investigated in the present study, and \( K_3 \) was not expected to be affected by the bulk cross-flow velocity, but rather by the permeate flux. The parameter \( K_2 \) describes the extent of surface fouling, and its value was expected to be related to the difference between the rate of mass transfer away from the membrane surface and the rate of mass transfer toward the membrane surface. The rate of mass transfer away from a membrane surface is governed by the hydrodynamic conditions (i.e. cross-flow velocity) and system configuration (Malleviale et al., 1996), while the rate of mass transfer toward a membrane surface is governed by the operating permeate flux. Therefore, the parameter \( K_2 \) was expected to be affected by the bulk cross-flow velocity and the operating permeate flux.
5.2 Data Analysis and Parameter Estimation of Irreversible Fouling Model

Since Model 2 was a mathematically complex model, the regression software (i.e. Sigmaplot) could not be used to compute the parameters $K_1$, $K_2$ and $K_3$ directly for Model 2.

5.2.1 Approach 1: Combining numerical approaches to estimate $K_1$, $K_2$ and $K_3$

Initially, a combination of analytic software: Matlab, Excel and regression software: Sigmaplot, was used to attempt to estimate parameters $K_1$, $K_2$ and $K_3$.

The first step consisted of inverting both sides of Equation 5.11 yielding Equation 5.12

$$\frac{1}{\Delta P} = \frac{A_0 r_0^4}{JvK_i} + \frac{(-2 A_0 r_0^2 K_3 - K_2 r_0^4)}{JvK_i} \gamma + \frac{A_0 K_3^2 + 2 r_0^2 K_2 K_3}{JvK_i} \gamma^2 + \frac{(-K_2 K_3^2)}{JvK_i} \gamma^3$$

(5.12)

Equation 5.12 can be simplified by adopting the definitions presented in Equations 5.13 to 5.18.

$$Y = \Delta P$$

(5.13)

$$X = \gamma$$

(5.14)

$$Y_0 = \frac{A_0 r_0^4}{JvK_i}$$

(5.15)

$$a = \frac{(-2 A_0 r_0^2 K_3 - K_2 r_0^4)}{JvK_i}$$

(5.16)

$$b = \frac{A_0 K_3^2 + 2 r_0^2 K_2 K_3}{JvK_i}$$

(5.17)

$$c = \frac{-K_2 K_3^2}{JvK_i}$$

(5.18)
With the above definition, Equation 5.12 could be rewritten as presented in Equation 5.19 for which the transition coefficients $y_0$, $a$, $b$, $c$, could be solved using polynomial equation fitting in regression wizard of Sigmaplot.

$$Y = Y_0 + aX + bX^2 + cX^3$$  \hspace{1cm} (5.19)

The second step consisted of using Matlab (see Appendix A for the editing code) to compute parameters $K_1$, $K_2$ and $K_3$ from the coefficients $y_0$, $a$, $b$, $c$ obtained using Sigmaplot. Unfortunately, due to the high dependency between parameters $K_2$ and $K_3$, their values calculated from the coefficients obtained from Sigmaplot were not real numbers, but rather complex numbers. When using Matlab to solve $K_1$, $K_2$ and $K_3$, the imaginary part was not taken into account, leading to significant errors in the estimation of $K_2$ and $K_3$ values. In addition, it was also not possible to obtain the standard errors of the estimated parameters $K_2$ and $K_3$ using this approach. It was concluded that a more robust approach was needed to estimate the parameters $K_1$, $K_2$ and $K_3$.

5.2.2 Approach 2: Estimate $K_1$, $K_2$ and $K_3$ separately

A more robust approach was developed where by the relationship presented in Equation 5.11 was separated into two parts as presented in Equation 5.20.

$$\Delta P = \frac{K_1}{(A_0 - K_3 V)} \times \frac{JV K_1}{(V_0^2 - K_3 V)} \hspace{1cm} (5.20)$$

Where $K_1 = K_1' K_1''$ \hspace{1cm} (5.21)

$K_1'$: a constant related to membrane module and raw water characteristics [m²]

In Equation 5.20, Part A represented surface fouling and Part B represented internal fouling. This more robust approach enabled the highly dependent parameters $K_2$ and $K_3$ to be estimated. Details of the estimation procedure are presented below.
Step 1 Estimating the parameters $K_1''$ and $K_3$

The first step consisted of rewriting Equation 5.8 which is similar to Part B of Equation 5.20, as presented in Equation 5.22.

$$\sqrt{\Delta P} = \frac{\sqrt{JvK_1''}}{r_0^2} \left( 1 + \left( \frac{K_3}{r_0^2} \right)^2 \right)$$

(5.22)

Equation 5.22 can be simplified by adopting the definitions presented in Equations 5.23 to 5.26.

$$Y = \sqrt{\Delta P}$$

(5.23)

$$X = V$$

(5.24)

$$a = \frac{\sqrt{JvK_1''}}{r_0^2}$$

(5.25)

$$b = -\frac{K_3}{r_0^2}$$

(5.26)

Combining Equations 5.23 to 5.26 yields Equation 5.27

$$Y = \frac{a}{1 + bX}$$

(5.27)

Where $a, b$ could be solved using rational equation fitting in regression wizard of SigmaPlot. Then parameters $K_1''$ and $K_3$ can be computed using Excel. Note that with this approach, the standard error of the estimates for the parameters $K_1''$ and $K_3$ could be obtained.

Equation 5.27 was fitted (i.e. using rational equation in regression wizard of SigmaPlot) to the experimental data obtained when operating the membrane system with a high bulk cross-flow velocity (0.4 m/s). At a high bulk cross-flow velocity, the impact of surface fouling was expected to be minimal (Field et al., 1995). This was confirmed using SEM images (i.e. for
bulk cross-flow velocities of 0.4 m/s, no surface fouling was observed).

The estimated $K_1''$ and $K_3$ values for the different experiments conducted with a bulk cross-flow velocity of 0.4 m/s are presented in Table 5.2.

Table 5.2 Estimated $K_1''$ and $K_3$ values at a bulk cross-flow velocity of 0.4 m/s

<table>
<thead>
<tr>
<th>Operating permeate flux (L/m$^2$·h)</th>
<th>Cross-flow Velocity (m/s)</th>
<th>Membrane module</th>
<th>$K_1''$ values (Nm$^4$·h/L)</th>
<th>$K_3$ values (1/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>0.4</td>
<td>1#</td>
<td>2.279E-29±2.433E-32</td>
<td>7.248E-15±4.212E-18</td>
</tr>
<tr>
<td>40</td>
<td>0.4</td>
<td>4#</td>
<td>2.462E-29±2.888E-32</td>
<td>5.124E-15±3.307E-18</td>
</tr>
<tr>
<td>50</td>
<td>0.4</td>
<td>3#</td>
<td>3.177E-29±6.253E-32</td>
<td>7.640E-15±1.244E-17</td>
</tr>
<tr>
<td>50</td>
<td>0.4</td>
<td>3#</td>
<td>3.242E-29±9.841E-32</td>
<td>8.752E-15±2.388E-17</td>
</tr>
<tr>
<td>60</td>
<td>0.4</td>
<td>3#</td>
<td>3.750E-29±1.283E-31</td>
<td>1.085E-14±4.759E-17</td>
</tr>
<tr>
<td>60</td>
<td>0.4</td>
<td>3#</td>
<td>3.813E-29±1.201E-31</td>
<td>1.373E-14±4.226E-17</td>
</tr>
</tbody>
</table>

± values are based on 90% confidence interval of the estimated parameters

Table 5.2 shows that $K_1''$ values are relatively constant for a given membrane module (e.g. #3). Table 5.2 also shows that for a given operating permeate flux, $K_3$ values are relatively constant as expected (see Section 5.1.1).

**Step 2 Estimating the parameters $K_1'$ and $K_2$**

The second step consisted of estimating parameters $K_1'$ and $K_2$ from the residuals obtained from fitting Equation 5.8, with the parameters ($K_1''$ and $K_3$) obtained from step 1, to all of the experimental data as presented in Equation 5.28.

$$
\frac{\Delta P_{\text{experimental}}}{Jv K_1''} = \frac{K_1'}{A_0 - K_2 V} \frac{1}{(r_0^2 - K_3 V)^2} 
$$

(5.28)
Where $\Delta P_{\text{experimental}}$: the increase of trans-membrane pressure values from experimental data

$K_1''$ and $K_3$ were estimated from step 1

Equation 5.28 can be modified as presented in Equation 5.29

$$\frac{\Delta P_{\text{experimental}}}{JvK_1''} = \frac{K_1'}{A_0} \frac{(r_0^2 - K_3V)^2}{1 + (\frac{K_3}{A_0})V} \quad (5.29)$$

Equation 5.29 can be simplified by adopting the definitions presented in Equations 5.30 to 5.33.

$$Y = \frac{\Delta P_{\text{experimental}}}{JvK_1''} \frac{(r_0^2 - K_3V)^2}{(r_0^2 - K_3V)^2} \quad (5.30)$$

$$a' = \frac{K_1'}{A_0} \quad (5.31)$$

$$b' = \frac{-K_3}{A_0} \quad (5.32)$$

$$X = V \quad (5.33)$$

Combining Equations 5.30 to 5.33 yields Equation 5.34

$$Y = \frac{a'}{1 + b'X} \quad (5.34)$$

Where $a'$, $b'$ can be estimated using rational equation fitting in regression wizard of Sigmaplot. The parameters $K_1'$ and $K_2$ could be subsequently calculated. The standard error of the estimates for the parameters $K_1'$ and $K_2$ could also be obtained.
The estimated $K'_1$ and $K_2$ values from different experiments conducted are presented in Table 5.3.

Table 5.3 Estimated $K'_1$ and $K_2$ values

<table>
<thead>
<tr>
<th>Operating permeate flux (L/m$^2$h)</th>
<th>Cross-flow Velocity (m/s)</th>
<th>Membrane module</th>
<th>$K'_1$ values (m$^2$)</th>
<th>$K_2$ values (1/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>0.2</td>
<td>1#</td>
<td>2.102E-03±1.635E-06</td>
<td>6.914E-02±4.315E-05</td>
</tr>
<tr>
<td>40</td>
<td>0.2</td>
<td>4#</td>
<td>2.277E-03±4.368E-06</td>
<td>4.963E-02±1.142E-04</td>
</tr>
<tr>
<td>40</td>
<td>0.3</td>
<td>3#</td>
<td>2.300E-03±3.356E-06</td>
<td>1.935E-02±1.207E-04</td>
</tr>
<tr>
<td>40</td>
<td>0.3</td>
<td>3#</td>
<td>2.413E-03±4.760E-06</td>
<td>2.231E-02±1.559E-04</td>
</tr>
<tr>
<td>50</td>
<td>0.2</td>
<td>4#</td>
<td>2.192E-03±2.552E-06</td>
<td>7.728E-02±1.073E-04</td>
</tr>
<tr>
<td>50</td>
<td>0.2</td>
<td>4#</td>
<td>2.088E-03±1.330E-06</td>
<td>6.941E-02±6.130E-05</td>
</tr>
<tr>
<td>*50</td>
<td>0.3</td>
<td>3#</td>
<td>3.229E-03±5.296E-06</td>
<td>5.131E-02±2.315E-04</td>
</tr>
<tr>
<td>60</td>
<td>0.2</td>
<td>3#</td>
<td>2.477E-03±7.280E-06</td>
<td>1.528E-01±4.685E-04</td>
</tr>
<tr>
<td>60</td>
<td>0.2</td>
<td>3#</td>
<td>2.914E-03±1.097E-05</td>
<td>1.085E-01±6.990E-04</td>
</tr>
<tr>
<td>60</td>
<td>0.3</td>
<td>3#</td>
<td>2.445E-03±6.194E-06</td>
<td>6.682E-02±4.394E-04</td>
</tr>
<tr>
<td>60</td>
<td>0.3</td>
<td>3#</td>
<td>2.673E-03±5.779E-06</td>
<td>4.398E-02±4.560E-04</td>
</tr>
</tbody>
</table>

± values are based on 90% confidence interval of the estimated values

*The results of $K'_1$ and $K_2$ from one of the experiments with a cross-flow velocity of 0.3 m/s and an operating permeate flux of 50 L/m$^2$h were discarded because the model did not fit the experiment data ($R^2 = 0.202$ from Sigmaplot regression)

It should be noted that there are no results for $K'_1$ and $K_2$ for a cross-flow velocity of 0.4 m/s, since at this cross-flow velocity, the extent of surface fouling was assumed to be minimal as discussed in Step 1.

Table 5.3 shows that $K'_1$ values are relatively constant for the same membrane module,
and all the $K_1'$ values from different membrane modules are similar. Table 5.3 also shows that for a given operating permeate flux and cross-flow velocity, $K_2$ values are relatively constant as expected (see Section 5.1.2).

**Step 3 Combining Steps 1 and 2 to yield $K_1$.**

$$K_1 = K_1' K_1''$$  \hspace{1cm} (5.35)

The product of $K_1''$ and $K_1'$ (i.e. $K_1 = K_1' K_1''$) was relatively constant for all the experiments. This was expected since the parameter $K_1$ is only a function of the membrane module and the raw water characteristics, both of which were constant through the study. Thus the average values of $K_1''$ and $K_1'$ were used to estimate parameter $K_1$. The resulting $K_1$ was $7.080E-32 \pm 2.745E-37$ for the membrane module and raw water used in the present study.

### 5.3 Model Parameter Quantification and Discussion

#### 5.3.1 Quantification of $K_1$

As discussed previously, $K_1$ is only a function of the characteristics of the specific membrane module used and the raw water characteristics. As expected, the parameter $K_1$ was relatively constant for a given membrane module. Recall that the parameter $K_1$ corresponds to the raw water viscosity and clean membrane characteristics (see Equation 5.20), which are not expected to change over time. Since the same length and material of membrane modules were used for all experiments and the same raw water was used throughout the study, $K_1$ values should be constant for a given membrane module. Thus the average value of $K_1$ could be presented as $K_1$ for the membrane module and raw water used in the present study. As shown in Step 3 in 5.2.2, the average $K_1$ was estimated to be $K_1 = 7.080E-32 \pm 2.745E-37$. 
5.3.2 Quantification of $K_2$ and the impact of operating permeate flux and bulk cross-flow velocity on the extent of surface fouling

Surface fouling is governed by both the mass transfer towards and away from the membrane surface. The rate of mass transfer towards the membrane surface is largely governed by the operating permeate flux, while the rate of mass transfer away from the membrane surface is largely governed by the bulk cross-flow velocity. Therefore, the extent of surface fouling, which is described using the parameter $K_2$ was expected to be a function of both the operating permeate flux and the bulk cross-flow velocity.

The relationship between the parameter $K_2$ and the operating flux as well as the bulk cross-flow velocity is presented in Figure 5.5. An empirical relationship was developed in Sigmaplot to describe the impact of cross-flow velocity and operating permeate flux on $K_2$ as presented in Equation 5.36. Equation 5.36 could be used to accurately estimate the parameter $K_2$ from the cross-flow velocity and operating permeate flux (i.e. $R^2 = 0.865$ for the exponential relationship was the highest $R^2$ among all the regressions).

$$K_2 = 133.0 \exp\left(-0.5 \times \left[ \left( \frac{v - 387.1}{87.73} \right)^2 + \left( \frac{CFV - 0.2}{0.08004} \right)^2 \right] \right)$$

Where $CFV$: cross-flow velocity applied to the membrane system [m/s]
As expected, increasing the cross-flow velocity decreases the rate of surface fouling, defined based on the parameter $K_2$. Higher cross-flow velocities create stronger shear force along a membrane surface, and remove and/or prevent the accumulation of material on the membrane surface, thus reducing surface fouling.

In addition, increasing the operating permeate flux increases the rate of surface fouling $K_2$. At higher operating flux, the mass transfer of material towards the membrane surface is higher, and therefore, more material is likely to accumulate on the membrane surface. Surface fouling occurs more quickly at higher operating flux.

It should be noted that the empirical relationship developed to estimate the parameter $K_2$ (Equation 5.36) is only valid for conditions relatively similar to those used in the present study. More specifically, Equation 5.36 cannot be used to estimate the parameter $K_2$ when the...
cross-flow velocity is less than 0.2 m/s and when the operating permeate flux is greater than 387.1 L/m²h. Additional research is required to develop a mechanistic relationship that can be used to model the experimental results presented in Figure 5.4.

5.3.3 Quantification of $K_3$ and the impact of the operating permeate flux on the extent of internal fouling

Internal fouling is governed by the hydrodynamic conditions inside the membrane pores, which in turn is determined by the permeate flow rate (i.e. operating permeate flux). Therefore, the parameter $K_3$ is only expected to be affected by the operating permeate flux.

**Linear relationship between $K_3$ and $J_v$**

A relatively linear relationship was observed between the parameter $K_3$ and the operating permeate flux ($J_v$) from the experimental data as illustrated in Figure 5.6. As expected, even for operation below the critical flux, increasing the operating permeate flux ($J_v$) increases the rate of internal fouling.

![Figure 5.6 Linear relationship between $K_3$ and $J_v$](image)
The fit of $K_3$ values to the linear relationship (i.e. $K_3 = (3.051 \times 10^{-16})J_v - 6.365 \times 10^{-15}$) was good ($R^2 = 0.8147$). However, this linear relationship was only effective over the range of experiments performed in this study. Theoretically, the rate of internal fouling $K_3$ should be minimal when there is no flux. But according to the above relationship, when operating at a low permeate flux (e.g. $J_v = 20$ L/m$^2$h), the value associated with $K_3$ would be negative. Thus the linear relationship is not fully compatible with the definition of $K_3$.

**Non-linear relationship between $K_3$ and $J_v$**

For model development purpose, it was assumed that $K_3$ should be zero at an operating permeate flux of zero. Based on this assumption, a non-linear regression was conducted to reveal the relationship between $K_3$ and the operating permeate flux. A non-linear relationship was observed between $K_3$ and the operating permeate flux as presented in Figure 5.6. The quadratic polynomial relationship presented in Equation 5.37 could be used to accurately estimate the parameter $K_3$ from the operating permeate flux (i.e. $R^2 = 0.9311$).

\[ K_3 = 2.727 \times 10^{-18} J_v^2 + 3.769 \times 10^{-17} J_v \quad (5.37) \]

![Figure 5.7 Non-linear relationship between $K_3$ and $J_v$ (forcing intercept = 0)](Image)
Non-linear relationship and adsorption kinetics

The non-linear relationship between $K_3$ and operating permeate flux is consistent with the hypothesis that internal pore fouling occurs due to adsorption of foulants to the pore surface. The rate of adsorption is greatest when the concentration gradient of the material being adsorbed at the surface of the adsorbent is high. Increasing the operating permeate flux (i.e. liquid flow through the pore), increases the concentration gradient at the surface of the adsorbent (i.e. membrane surface).

The results from the present study appear to contradict those reported by Bolton et al. (2006b). Based on their data analysis, they reported that membrane capacity could increase with increasing flow rate (i.e. extent of fouling decreases with increasing flow rate). However, their estimate of capacity was based on the volume of permeate filtered after a given time. When considering the extent of fouling (i.e. pressure increase) based on a given volume of permeate filtered, the extent of fouling increased with increasing flow rate, contradicting their conclusion that membrane capacity can increase with increasing flow rate.

Further research is required to comprehensively investigate adsorption kinetics within membrane pores. Nonetheless, the results from the present study, and those from other studies (Bolton et al. 2006b) confirm that for a given volume of permeate filtered, increasing the operating permeate flux increases the extent of fouling.

5.3.4 Relative contribution of internal fouling and surface fouling to irreversible fouling

It should be noted that the model developed in the present study (Equation 5.11) is only valid when $K_2V$ is less than $A_0$ and $K_3V$ is less than $r_0^2$. Equation 5.11 can be rewritten as presented in Equation 5.38:

$$\Delta P = JvK_1 \left( \frac{1}{A_0 - K_2V} \right) \left( \frac{1}{(r_0^2 - K_3V)^2} \right) \quad \text{(5.38)}$$
Where Part $C = \frac{1}{A_0 - K_2 V}$, and Part $D = \frac{1}{(r_0^2 - K_3 V)^2}$

For a given membrane module, Part C represents surface fouling, which is impacted by cross-flow velocity as well as operating permeate flux, while Part D represents internal fouling, which is impacted by operating permeate flux. Both surface fouling and internal fouling contribute to the increase of trans-membrane pressure. However, the part that changes the most when filtering a given volume of water has a greater impact on the increase of trans-membrane pressure. Taking conditions of cross-flow velocity of 0.3 m/s and operating permeate flux 50 L/m$^2$h as an example, the changes of surface fouling and internal fouling (i.e. Parts C and D) over time are presented in Figure 5.8 and 5.9.

![Figure 5. 8 The change of surface fouling over volume of water filtered](image-url)
Figure 5.9 The change of internal fouling over volume of water filtered

Figure 5.8 shows that the magnitude of Part C increases less than 100% over the volume of water V filtered, while Figure 5.9 shows that the magnitude of Part D increases more than 200% over the volume of water V filtered. These results indicate that internal fouling has a much bigger effect on fouling. This also indicates that for operation below the critical flux, even though surface fouling and internal fouling both contribute to the extent of fouling, internal fouling plays a much more important role than surface fouling. Extensive internal fouling occurs along with small amount of surface fouling over the volume of water filtered, when operating the system at less than critical flux.

5.4 Comparison of Model Predictions and Experimental Data

By quantifying the parameters $K_1$, $K_2$ and $K_3$ in model 2 (i.e. Equation 5.11), trans-membrane pressure over time can be predicted. Figures 5.10 to 5.12 present a comparison between the modeled and measured trans-membrane pressure values for the different experiments performed with operating permeate fluxes of 40 L/m$^2$h, 50 L/m$^2$h and 60 L/m$^2$h respectively. To model the evolution of the trans-membrane pressure over time, the parameter $K_1$ was estimated to be $K_1 = 7.080E-32$, and the parameters $K_2$ and $K_3$ were estimated from Equations 5.36 and 5.37, respectively. In these figures, data points that are located directly on the
dotted line correspond to conditions under which the measured trans-membrane pressure was identical to the modeled trans-membrane pressure.

5.4.1 Conditions for which model agrees with experimental trans-membrane pressure data

For an operating permeate flux of 40 L/m²h, as presented in Figure 5.10, the model predictions were typically in relatively close agreement with the experimental measurements. For experiment 24-T-D (Figure 5.10 f), the measured trans-membrane pressure was consistently and substantially less than the modeled trans-membrane pressure. However, it should be noted that experiments 24-T-D (Figure 5.10 f) and 2-T-D (Figure 5.10 e) were performed under similar experimental conditions (i.e. cross-flow velocity 0.4 m/s and operating permeate flux of 40 L/m²h), and that the measured and modeled trans-membrane pressures for experiment 2-T-D (Figure 5.10 e) were in relatively close agreement. The discrepancies observed between the modeled and measured values presented in Figures 5.10 f are likely due to non-controllable experimental variations (i.e. experimental error).

For an operating permeate flux of 50 L/m²h, as presented in Figure 5.11, the model predictions were typically in relatively close agreement with the experimental measurements. For experiment 24-T-H (Figure 5.11 d), the measured trans-membrane pressure was consistently and substantially less than the model predicted trans-membrane pressure. However, it should be noted that experiments 24-T-H (Figure 5.11 d) and 2-T-G (Figure 5.11 c) were performed under similar experimental conditions (i.e. cross-flow velocity 0.3 m/s and operating permeate flux of 50 L/m²h), and that the measured and modeled trans-membrane pressure for experiment 2-T-G (Figure 5.10 c) were in relatively close agreement. The discrepancies observed between the modeled and measured values presented in Figures 5.11 d are likely due to non-controllable experimental variations (i.e. experimental error). In addition, the model predicted trans-membrane pressures of experiments 24-T-B (Figure 5.11 b) and 2-T-J (Figure 5.11 e) were more than the measured trans-membrane pressure after certain amount of water had been filtered. However, for experiments 2-T-H (Figure 5.11 a) and 2-T-K (Figure 5.11 f), which were
conducted under the similar conditions as experiments 24-T-B and 2-T-J respectively, the model predictions were in relatively close agreements with the measured trans-membrane pressures. Again, the discrepancies observed between the modeled and experimental values presented in Figures 5.11 c and d, as well as Figure 5.11 b and e, are likely due to non-controllable experimental variations (i.e. experimental error).
Figure 5. 10 Predicated against measured data for 40 L/m$^2$h operating permeate flux
Figure 5. 11 Predicated against measured data for 50 L/m^2h operating permeate flux
Figure 5.12 Predicted against measured data for 60 L/m²h operating permeate flux
For an operating permeate flux of 60 L/m$^2$h, as presented in Figure 5.12, the model predictions were typically in relatively close agreement with the experimental measurements. For experiment 2-T-I (Figure 5.12 f), the measured trans-membrane pressure was consistently and substantially less than the model predicted trans-membrane pressure. However, it should be noted that experiments 2-T-I (Figure 5.12 f) and 2-T-E' (Figure 5.12 e) were performed under similar experimental conditions (i.e. cross-flow velocity 0.4m/s and operating permeate flux of 60 L/m$^2$h), and that the measured and modeled trans-membrane pressure for experiment 2-T-E' (Figure 5.12 e) were in relatively close agreement. In addition, the model predicted trans-membrane pressures of experiments 2-T-F (Figure 5.12 a) were less than the measured trans-membrane pressure after certain amount of water had been filtered. However, for experiments 2-T-F' (Figure 5.12 b), which was conducted under the similar conditions as experiments 2-T-F (Figure 5.12 a), the model predictions were in relatively close agreements with the measured trans-membrane pressures. Therefore the discrepancies observed between the model predicted and measured values presented in Figure 5.12 f and e, as well as Figure 5.12 a and b, are likely due to non-controllable experimental variations (i.e. experimental error).

5.4.2 Conditions when model overestimates trans-membrane pressure data

For all experiments, the model predictions were greater than the experimental measurements at low trans-membrane pressure. Low trans-membrane pressures occur at the start of filtration cycles when the membrane is not extensively fouled. It is not clear why this discrepancy was observed. It could be hypothesized that as foulants adhere to membrane material, the effective characteristics of the membrane surface change. As a result, a partially fouled membrane could subsequently foul more easily than a clean membrane. Evidence for such behavior was also provided by the SEM images (Figure 5.3). For partially fouled membranes, no surface fouling was visually observed, while for heavily fouled membranes, extensive surface fouling was observed. Further studies are required to investigate this hypothesis.
CHAPTER 6 CONCLUSIONS AND SIGNIFICANCE TO ENGINEERING

6.1 Conclusions

1. Even though all experiments were performed with an operating flux that was less than the critical flux in this study, a substantial amount of fouling was observed when filtering over extended periods of time.

2. The extent of fouling was observed to be related to both the operating permeate flux and the system hydrodynamic conditions (i.e. the cross-flow velocity).

3. Irreversible fouling observed in this study was due to both extensive internal/pore fouling and surface/cake fouling. Internal fouling was the predominant mechanism that governed irreversible fouling.

4. A semi-empirical relationship (see Equation 6.1) was developed to model the extent of fouling when filtering over an extended period of time for conditions under which the operating permeate flux is less than the critical flux. The relationship is based on three parameters $K_1$, $K_2$ and $K_3$ which correspond to the membrane characteristics, the extent of surface/cake fouling and the extent of internal/pore fouling, respectively.

   \[ \Delta P = \frac{JvK_1}{(A_0 - K_2 V)(r_0^2 - K_3 V)^2} \]  

   Where

   - $K_1$: a constant related to membrane module and raw water characteristics [Nm$^6$h/L]
   - $K_2$: rate of pore number reduction (i.e. rate of surface fouling) [1/m]
   - $K_3$: rate of pore radius reduction (i.e. rate of internal fouling) [1/m]

5. The extent of surface/cake fouling was determined to be governed by the operating permeate
flux and the system hydrodynamic conditions (i.e. the cross-flow velocity) as presented in Equation 6.2.

\[ K_2 = 133.0 \exp \left\{ -0.5 \times \left[ \left( \frac{Jv - 387.1}{87.73} \right)^2 + \left( \frac{CFV - 0.2}{0.08004} \right)^2 \right] \right\} \]  

(6.2)

Where CFV: cross-flow velocity applied to the membrane system [m/s]

Jv: the operating permeate flux [L/m²h]

6. The extent of internal/pore fouling was determined to be governed only by the operating permeate flux as presented in Equation 6.3.

\[ K_3 = 2.7268E-18 Jv^2 + 3.769E-17 Jv \]  

(6.3)

7. The study indicated that when operating a membrane filtration system below critical flux conditions, for a given volume of permeate filtered, the extent of irreversible fouling increases as the operating permeate flux increases and decreases as the cross-flow velocity increases.

6.2 Significance to Engineering

As concluded in Section 6.1, when operating the membrane filtration system below the critical flux conditions, increasing the operating permeate flux can increase the extent of fouling. Also, increasing the cross-flow velocity to the system can decrease the extent of fouling. Therefore, for the design and operation of membrane filtration system, high air sparging intensity and low operating permeate flux can be applied to the systems operated below critical flux to control the extent of fouling.

However, high air sparging intensity can increase the operating cost of a membrane system. In addition, operating at a lower operating flux, can increase the membrane surface area.
needed to maintain a given permeate flux, and therefore can increase the capital cost of a membrane system. An engineering economic analysis would have to be performed to establish the optimal air sparging intensities and operating permeate flux to minimize the cost associated with membrane systems.
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APPENDIX A: CODES FOR MATLAB CALCULATION

function f = computeKs(y0,a,b,c,Jv)

A0=2.3e-3;
R=2e-8;
%Jv=3.83e-8;
%Jv=3.19e-8
%Jv=2.56e-8;

k1=A0*R^4/(Jv*y0);

if ((a*k1*Jv)^2-3*A0*b*R^4*k1*Jv)>=0
k3_1=(-a*k1*Jv+sqrt((a*k1*Jv)^2-3*A0*b*R^4*k1*Jv))/(3*A0*R^2);
k3_2=(-a*k1*Jv-sqrt((a*k1*Jv)^2-3*A0*b*R^4*k1*Jv))/(3*A0*R^2);

k2_1=-(a*Jv*k1+2*A0*k3_1*R^2)/R^4;
k2_2=-(a*Jv*k1+2*A0*k3_2*R^2)/R^4;

k3_11=c*Jv*k1/k3_1^2;
k3_12=c*Jv*k1/k3_2^2;

fprintf('Group 1: 
');
fprintf('k1= %d
', k1);
fprintf('k2_1= %d
', k2_1);
fprintf('k3_1= %d
', k3_1);

fprintf('Group 2: 
');
fprintf('k1= %d
', k1);
fprintf('k2_2= %d
', k2_2);
fprintf('k3_2= %d
', k3_2);

%else
% fprintf('b^2-4ac<0, no resolution! Jv= %d
', Jv);
%end

clear all;

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