WASTEWATER SLUDGE CHARACTERISTICS AND IMPLICATIONS ON
MEMBRANE FOULING

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of

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by

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ABSTRACT

WASTEWATER SLUDGE CHARACTERISTICS AND IMPLICATIONS ON MEMBRANE FOULING

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Wastewater samples from eight membrane biological reactors (MBR) and four activated sludge plants (AS) were taken. Bench scale membrane filtration tests using both a stirred cell and cross flow apparatus were performed. Computational fluid dynamic (CFD) models for both modules were created using FLUENT[®] v6 to accurately characterize module hydrodynamics. Wastewater properties, including dissolved and extracted EPS, were analyzed to identify the most important characteristics influencing membrane fouling. Steady state permeate flux for cross flow and stirred cell tests ranged from 6 to 29 Lm⁻²h⁻¹ and 17 to 115 Lm⁻²h⁻¹ respectively. Total dissolved carbohydrates negatively influenced permeate flux at values below 20 mg/L. In general, MBR samples had lower permeate fluxes compared to AS samples. This was due to larger total dissolved carbohydrate concentrations and increased numbers of particles with average diameters between 1 and 2.6 µm.

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LIST OF SYMBOLS

CA	Cellulose acetate
CFD	Computational fluid dynamics
DSVI	Diluted sludge volume index
EPS	Extracellular polymeric substances
HRT	Hydraulic retention time
MATH	Microbial adhesion to hydrocarbons
MBR	Membrane biological reactor
MF	Microfiltration
MFI	Modified fouling index
NF	Nanofiltration
NFR	Normalized fouling rate
PUM	Phosphate urea magnesium sulfate
PVSK	Potassium polyvinyl sulfate
RO	Reverse osmosis
SCR	Specific cake resistance
SDI	Silt density index
SMP	Soluble microbial products
SRT	Sludge retention time
SVI	Sludge volume index
UF	Ultrafiltration

WTC	Wastewater Technology Centre
WWTP	Wastewater Treatment Plant

.

1 INTRODUCTION

1.1 Statement of the Problem and Significance

Membrane filtration is one of the most promising technologies available for both water and wastewater treatment. Although costs have been significantly reduced in the past 10 years due to advances in membrane manufacturing technology, membrane fouling remains the largest barrier to its widespread application for both water and wastewater treatment. Considerable knowledge has been learned about membrane fouling but there is a great deal of uncertainty about the role of wastewater sludge characteristics in membrane fouling. Thus, this study is directed to use the latest analytical methods to characterize various types of sludge and examine their impact on membrane fouling by conducting both specially designed stirred cell and cross flow membrane filtration tests. Sludge samples were taken from a number of representative full and pilot scale membrane bioreactor (MBR) plants. For comparison purposes, additional samples from conventional activated sludge treatment plants were also examined.

2 LITERATURE REVIEW

2.1 Membranes in Wastewater Treatment

Five main factors have driven the recent rapid development of membrane filtration:

1. Stricter environmental regulations governing both water and wastewater quality,
2. Increased water demand due to world population growth and industrial development,
3. Desire for wastewater reuse,
4. Decreased membrane costs due to advances in membrane manufacturing techniques, and
5. Improvement in membrane technology application.

Originally, membrane filtration was introduced to replace secondary clarifiers, which often control effluent quality. Recently, membrane filtration has been incorporated directly into the activated sludge process for wastewater treatment.

Membrane bioreactor systems have been used to allow complete biological and physical treatment to occur in a single tank. Advantages of this process include (Manem and Sanderson 1996):

1. Ability to independently control the sludge residence time (SRT) and hydraulic residence time (HRT),
2. High effluent quality with chemical oxygen demand (COD), biological oxygen demand (BOD) and suspended solid (SS) removals typically at least 95%, 98% and 99% respectively,
3. Extremely resistant to variable influent quality and hydraulic loading shocks,

4. Increased biomass concentrations in the bioreactor allow for compact designs and more efficient biological degradation, and
5. Lower sludge production rates.

DiGiano *et al.* (2004) have suggested MBR technology will play a central role in wastewater reuse and provide opportunities for decentralized treatment.

2.2 Membrane Fouling

Membrane filtration is essentially a physical separation process using a driving force, typically a pressure gradient, to intercept the solids from water. Membrane processes can be characterized by pore size, transmembrane pressure (TMP), module geometry, operation mode and materials. Microfiltration (MF) and ultrafiltration (UF) processes consist of membrane with pore sizes ranges greater than 0.05 μm and 0.003 to 0.1 μm respectively and are widely used for most water and wastewater treatment applications (Zhou and Smith 2001). Nanofiltration (NF) and reverse osmosis (RO) can reject particles as small as 0.001 and 0.0001 μm respectively. They are typically used in water reuse or desalination applications (Taylor and Jacobs 1996). Figure 2-1 illustrates relative size ranges of membrane processes and common substances found in water.

Size μm	Ionic Range		Molecular Range			Macromolecular Range	Microparticle Range	Macroparticle Range	
	0.001		0.01			0.1	1.0	10	100
Approximate Molecular Weight	100 200		1,000 10,000 20,000			100,000 500,000			
Relative Size of Various Materials in Water	Aqueous salts Metal ions		Viruses Humic acids			Clays Asbestos fibers	Bacteria Algae Cysts Silt	Sand	
Separation Process	Reverse osmosis		Nanofiltration			Ultrafiltration	Microfiltration	Conventional filtration processes	

Figure 2-1 Size ranges of substances in water with separation processes (Jacangelo *et al.* 1989)

Common filtration module configurations used are plate and frame, spiral, tubular and hollow fiber (Aptel and Buckley 1996). Filtration operation conditions are also classified as stirred cell or cross flow with feed flow perpendicular or tangential to the membrane surface respectively.

Membrane fouling is often referred to as “excessive flux decline over time”. Advective transport of dissolved and particulate matter towards the membrane results in the formation of a concentration polarization layer and the accumulation of particles on its surface. While the concentration polarization layer does not provide significant hydraulic resistance, increased concentrations of matter within the layer strongly influence other fouling mechanisms. Fouling mechanisms include cake formation, pore blockage, adsorption, precipitation and biofouling with the first three being the most important short term fouling mechanisms in UF and MF filtration. Cake formation and pore blocking are strongly influenced by particle accumulation near the membrane while adsorptive foulants are mainly organic matter, such as humic acids, that are deposited in the membrane pores. (Weisner and Aptel 1996)

2.2.1 Cake Filtration

The importance of cake resistance in modeling membrane fouling in wastewater treatment is documented extensively (Chang and Judd 2003; Jiang, *et al.* 2003; Shin and Kang 2003). Under the static, dead-end membrane filtration condition, the specific cake resistance (SCR) is related to the cake resistance by the following equation:

$$R_c = \alpha V \frac{C}{A} \quad (2-1)$$

where R_c = cake resistance (m^{-1}), α = specific cake resistance (m/kg), c = dry mass of cake solids in feed (kg/m^3), V = filtered volume (m^3) and A = area of cake (m^2).

Mathematically, specific cake resistance can be quantified using (Lodge *et al.* 2004):

$$\frac{t}{V} = \frac{\mu\alpha c}{2A^2 P} V + \frac{\mu R_m}{AP} \quad (2-2)$$

where V = filtrated volume (m^3), P = transmembrane pressure (Pa), R_m = intrinsic membrane resistance (m^{-1}), μ = viscosity (Pa·s) and t = filtration time (s). Thus, the specific cake resistance can be measured experimentally using a stirred cell membrane filtration apparatus by monitoring the filtrate volume over time at a constant transmembrane pressure.

SCR has been used to evaluate the filtration characteristics of a particular medium. Lee *et al.* (2001) used SCR to compare the filtration characteristics of attached and suspended growth biomass in wastewater treatment systems. Additionally, Lim and Bai (2003) noted that cake filtration is the dominant filtration mechanism, after initial pore blocking, in MBR systems. In contrast, Lodge *et al.* (2004) demonstrated that SCR values estimated for hollow fiber membrane modules using flux versus time data did not explain filtration difference between grey water and sewage matrices. Therefore, while it appears cake filtration theory is useful for filtration of wastewater matrices, no clear relationship between SCR and membrane fouling is apparent in the literature.

Darcy's law, which was developed to describe flow through porous media, has been used to model the filtration behaviour and is given below (Belfort *et al.* 1994):

$$J \equiv \frac{1}{A} \frac{dV}{dt} = \frac{\Delta P}{\eta R_t} \quad (2-3)$$

where J =permeate flux (m/s), A =filtration area (m²), V =filtrate volume (m³), t =filtration time (s), ΔP =TMP (Pa), η =filtrate viscosity (Pa·s), R_t = total filtration resistance (m⁻¹).

The total resistance can be further divided into a series of specific resistances (Lee *et al.* 2002 ; Cho *et al.* 2003; Nagaoka *et al.* 1998; Field *et al.* 1995; Shin and Kang 2002; Jiang *et al.* 2003; Song 1998):

$$R_t = R_m + R_b + R_c + R_{cp} + \dots \quad (2-4)$$

where R_m =membrane resistance (m⁻¹), R_b =pore blocking resistance (m⁻¹), R_c =external cake resistance (m⁻¹), R_{cp} = concentration polarization layer resistance (m⁻¹). The inherent membrane resistance, R_m , mainly depends on the membrane pore size and thickness and can be measured by performing a clean water filtration test and monitoring the permeate flux at a known transmembrane pressure (TMP). It can then be calculated assuming all other resistances are equal to zero. Chang *et al.* (2002) noted the difficulty estimating each resistance component and consequently some authors group all non-membrane resistances into an overall fouling resistance, R_f .

Jiang *et al.* (2003) demonstrated that at higher fluxes, above 52 L/(m²·h), pore blocking dominated filtration during the short term, $t = 0 - 8$ s, followed by a transition period from 8 – 100 s and then by cake filtration after 100 s. The quick termination of pore blocking in less than 100 s agrees with Song (1998) who stated that pore blocking is quick because one layer of particles is sufficient to achieve maximum blocking. At lower fluxes around 18 L/(m²·h), pore blocking was hardly observed. While Jiang *et al.* (2003) did not perform any critical flux studies, a possible explanation for his results is that the fluxes 52 L/(m²·h) and 18 L/(m²·h) fall within two different permeate flux regimes.

Chang *et al.* (2002) noted rapid and slow fouling occurs for permeate fluxes above and below the critical flux respectively. Perhaps pore blocking resistance is the dominant resistance in the Jiang *et al.* (2003) study indicating that the membrane filtration was operated above the critical flux. Critical flux is essentially a permeate flux value below which membrane fouling occurs at a much slower rate compared to fluxes above this value. This concept is further discussed in section 2.2.5.

Particle size has been shown to affect pore blocking. Lim and Bai (2003) observed that smaller particle sizes result in more pore blocking. This agrees with Song (1998) who stated pore blocking tends to increase when particles and pores are of the same magnitude in size and shape. Lim and Bai (2003) also observed that the pore blocking-cake filtration transition occurs at approximately 5 – 30 minutes, longer than those reported by Jiang (2003). This difference may be attributed to different filtration modes since constant flux and pressure filtration modes were employed by Jiang (2003) and Lim and Bai (2003) respectively.

2.2.2 Fouling Assessment Methods

Traditionally, the silt density index (SDI) and modified fouling index (MFI) have been used to quantify the fouling potential of various feed waters (Weisner and Aptel 1996). Both of these methods attempt to use a standard stirred cell membrane filtration apparatus, a 0.45 μm -47 mm diameter Millipore membrane operated at a TMP of 207 kPa, to obtain different measures of fouling tendency. While both methods have primarily been used for low fouling potential waters for nanofiltration and reverse osmosis applications, the MFI is potentially more relevant to high fouling wastewaters

because of it also accounts for cake formation. Lim and Bai (2003) noted cake filtration is the dominant filtration mechanism in MBR systems. Equation 2-5 mathematically describes cake filtration phenomenon applied to fouling assessment models.

$$\frac{t}{V} = \frac{\mu R_f}{\Delta P A} + \frac{\mu V I}{2 \Delta P A^2} \quad (2-5)$$

where t = time (s), V = cumulative permeate volume (m^3), μ = viscosity (Pa.s), A = filtration area (m^2), ΔP = transmembrane pressure (Pa), I =fouling index (m^{-2}).

Equation 2-5 can be simplified to obtain the modified fouling index equation below.

$$\frac{t}{V} = a + MFI \times V \quad (2-6)$$

where MFI = modified fouling index (s/m^6), a = constant for specific test condition.

Boerlage *et al.* (2004) successfully reported a linear relationship between the fouling index and feedwater concentration for low fouling waters such as diluted river water.

Rosenberger and Kraume (2002) compared the following five methods to estimate activated sludge filterability.

1. Time to filter 100 mL of permeate (TTF)
2. Absolute permeate flux after 100 mL filtration volume
3. Sludge resistance after 100 mL filtration volume
4. Permeate flux after 40 min filtration
5. Sludge resistance after 40 min filtration

Methods 1 to 3 were inappropriate because filtration flux after 100 mL was quite variable for samples with good filterability. Methods 4 and 5 were almost equivalent assuming similar fluid viscosities and pressures because membrane resistance is much less than the cake resistance. However, permeate flux is more stable than sludge resistance after

40 min filtration and method 4 was their preferred fouling index. Brauns *et al.* (2002) extended SDI and MFI methods using a two parameter fouling index derived from the resistance in series model. While the method attempts to use bench scale testing in estimating fouling, it is not clear what advantages exist when compared to the traditional resistance model. Zydney and Ho (2002) successfully estimated system capacity with a maximum operation volume, or V_{MAX} , model that considers pore blocking and cake filtration fouling mechanisms. Rabie *et al.* (2001) predicted filtration performance using short term data by adapting constant pressure fouling indices to constant flux operation. They assumed fouling resistance is directly proportional to specific filtration volume.

In summary, several studies have used cake filtration theory to estimate the fouling propensity of water or wastewater sample. Since activated sludge is dominated by cake filtration, most fouling assessment models are based on cake filtration theory such as the MFI. Fouling assessment methods are influenced by filtration operating parameters that affect the cake formation and properties. For example, aeration in MBR's generates shear stresses at the membrane surface which affect particle transport and detachment at the membrane surface. Fouling assessment testing should be carried out at shear stresses similar to those experienced in full scale systems.

2.2.3 Effect of Shear Stress on Fouling

The benefits of shear stress generated by various fluid instabilities on membrane fouling of protein and colloid suspensions are well documented by Belfort *et al* (1994). Membrane shear stress is strongly related to cross flow velocity for cross flow filtration tests. While increases in cross flow velocity generally correspond to higher shear

stresses, exact relationships also depend on the module geometry which can vary greatly between studies.

Shear stress has been shown to reduce activated sludge fouling in a variety of ways. First, Tardieu *et al.* (1999) established that the fouling velocity, or change in resistance over time, is related to the cross flow velocity for velocities between 1 and 5 m/s, which correspond to shear stresses of 20 and 100 Pa. Their results show that at a constant filtration flux, increases in cross flow velocity leads to a decrease in membrane fouling measured as decreased fouling velocity. Second, Defrance and Jaffrin (1999a) showed that the shear stress introduced by the cross flow velocity increased the stabilized flux at 15 min from approximately 20 L/(m²·h) to 130 L/(m²·h) for velocities of 1 and 5 m/s respectively. Finally, Defrance and Jaffrin (1999b) observed that at a threshold shear stress between 33 and 47 Pa, cake resistance was stable. Thus, cake resistance will increase or decrease over time for shear stresses above and below this threshold respectively. In all, shear stress can reduce fouling but actual flux improvements for a given shear stress will depend on the operation flux and wastewater characteristics.

Shear stress also affects the critical flux. Defrance and Jaffrin (1999a) demonstrated that an increase in membrane wall shear stress from 15 to 80 Pa can increase the critical flux defined by Field *et al.* (1995) from approximately 30 L/(m²·h) to 130 L/(m²·h). Nagaoka *et al.* (1998) studied the effect of shear stress on the maximum operation time, defined as the time when TMP reaches a maximum value. It was predicted that only fluxes below 6 L/(m²·h) saw a significant increase in maximum operation time with increasing shear stress. This suggests that for fluxes larger than a

threshold, the operation time to reach the maximum transmembrane pressure is independent of shear stress. In summary, shear stress can increase the critical flux and is not effective in increasing operation time above a certain flux value.

For MBR systems, Chua *et al.* (2002) measured the effect of air flow rate on permeate flux. There was a clear improvement in permeate flux with increasing superficial gas bubble velocity. Shear stress values on the membrane were not specified but increasing gas bubble velocities result in higher shear stress. Therefore, shear stress induced by aeration in MBR systems can increase permeate flux.

In addition to direct effects on permeate flux and fouling, shear stress can also affect the permeate flux by changing wastewater particle size distribution and composition. Wisniewski and Grasmick (1998) analyzed the particle size distribution in a tubular membrane with and without recirculation and found mean particle size reduced from 125 to 20 μm when subjected to shear stresses of 1.3 and 72 Pa respectively. Wilen *et al.* (2003) also documented the shift of sludge particle size distributions under the effect of shear stress by mixing. Therefore, shear stress can have secondary effects of decreasing the average particle size, which will lead to higher fouling or lower permeate flux. A decrease in floc size from excessive shear could also facilitate the release of extracellular polymeric substances (EPS). Kim and Lee (2003) showed shear stress introduced with cross flow filtration pumping equipment leads to floc breakup and EPS release that negatively affects filtration performance.

2.2.4 Effect of Operating Conditions

Ideally, activated sludge plants coupled with membrane filtration would be able to select for desirable EPS characteristics that minimise fouling by changing operating variables such as SRT, HRT, DO and the F/M ratio. Several researchers have examined the changes in EPS by varying these operational parameters. For a submerged MBR operated at SRT's of 20, 40 and 60 days, Lee *et al.* (2003) found the supernatant resistance, which includes EPS and other colloids, was essentially constant while the microbial floc resistance increased from approximately 5×10^{11} to $8 \times 10^{11} \text{ m}^{-1}$ for SRT's of 20 and 60 days respectively. On the contrary, Chang and Lee (1998) found the cake resistance of sludge operated at a SRT of 3 days to be approximately five times higher than the cake resistance operated at 33 days. Thus, while supernatant resistance may be relatively stable from SRT's of 20 to 60, cake resistance and SRT have no conclusive relationship.

Hong *et al.* (2002) examined the effects of operating modes on fouling in a hollow fiber MBR. A significant increase in permeate flux was shown after changing from continuous suction to 45min ON/15 min OFF filtration scheme. Foulants may be more easily removed with suction off since the cake can relax and is still under the influence of shear stress from aeration. While they acknowledged that this operation scheme may be unrealistic for a full scale MBR plant because of decreased productivity caused by significant off time, other combinations of permeate ON/OFF time might yield flux improvements.

2.2.5 Critical Flux

Field *et al.* (1995) first described the critical flux phenomenon with yeast filtration experiments. They defined the critical flux as “... there exists a flux below which a decline in flux with time does not occur.” Recently, this concept has been refined as a transition flux above which increases in TMP occur more rapidly (Le-Clech *et al.* 2003). For MBR systems, Gui *et al.* (2002) found TMP increases sharply when operated above a “critical flux”. Le-Clech *et al.* (2003) reviewed reported values of critical flux for MBR’s under various biological and hydrodynamic conditions. Generally, they reported values between 20 and 130 L/(m²·h) with the majority between 20 and 40 L/(m²·h). Further research work is needed since critical flux values have been measured using varying experimental protocols and, ideally, a standardized procedure such as the flux step method should be used to quantify the actual value (Le-Clech *et al.* 2003; Kwon *et al.* 2000).

2.3 Extracellular Polymeric Substances

Extracellular polymeric substances are essentially biopolymers that exist exterior to cells. EPS can originate through cell metabolism and autolysis or the wastewater itself (Urbain *et al.* 1993). Consistently, Esparza-Soto and Westerhoff (2003) attributed humic acid sorption from bulk wastewater to activated sludge floc EPS. Li and Ganczarczyk (1990) observed that large amounts of EPS in activated sludge flocs can completely surround cells to form a cell-EPS matrix. The most important function of EPS is the provision of a mechanical support system for biofilms and/or activated sludge flocs. EPS can also assist cell adhesion to surfaces, act as a sink for various substances

such as water and nutrients and protect a bacterial colony from surrounding contaminants. (Wingender, J. *et al.* 1999)

Different definitions and classifications of extracellular polymeric substances (EPS) and soluble microbial products (SMP) exist. Both items are commonly thought to consist of biopolymers such as protein, carbohydrates, humic and fulvic acids, DNA and uronic acids. Barker & Stuckey (1999) said SMP are generally regarded as “...the pool organic compounds that are released into solution from substrate metabolism (usually with biomass growth) and biomass decay.” Geesey (1982) defines EPS as “...extracellular polymeric substances of biological origin that participate in the formation of microbial aggregates.”. Therefore, while EPS and SMP are both composed of biopolymers, EPS is considered the “glue” holding microbial cells together while SMP mainly resides in bulk solution.

Bura (2000) further divided EPS into two groups. He classified slime EPS as effluent extracellular polymers and capsular EPS as material which is adhered to the cell. Capsular EPS require extraction procedures to release them from activated sludge flocs or biofilms. Slime EPS are effluent polymers present in the bulk wastewater solution and are probably more appropriately termed SMP. Laspidou and Rittman (2002) also suggested that soluble EPS is more appropriately characterized as SMP. Additionally, they note SMP consists of hydrolysed bound EPS and substrate metabolism products.

2.3.1 EPS Composition and Characteristics

EPS composition is very heterogeneous and affected by the originating physical environment. Different physical environments influence EPS composition by affecting

cell metabolic processes and the supply of external substances, such as humic compounds, that become part of the EPS.

EPS generally consists of protein, carbohydrates, DNA, uronic acids and humic substances. Bura (2000) has also shown lipids to be a major component of EPS. Earlier researchers such as Horan and Eccles (1986) believed carbohydrates to be the dominant component of EPS but later studies by Urbain (1993) and Frolund (1996) show protein amounts are generally greater than carbohydrate amounts. Some early EPS extraction methods intentionally removed protein and DNA from samples because they believed it originated inside cells and should not be considered an EPS constituent. This likely explains the lower reported protein concentrations in early studies (Nielsen and Jahn 1999). This hypothesis is questionable since cell autolysis provides a continuous source of DNA and protein in the EPS matrix.

Gorner, *et al.* (2003) extracted EPS using cationic exchange resin and characterised the protein in two main groups, short and long chain alkyl groups containing 6-8 alkyl chains and 11-12 alkyl chains respectively. Protein molecular weights ranged from 45 and 670 kDa with the majority between 67 and 200 kDa. Polysaccharides present were much smaller with molecular weights less than 1 kDa. Finally, they found a distinct third group of proteins with smaller molecular weights that were associated with polysaccharides. The authors speculated whether this group is important for floc formation but acknowledge much more work must be done.

EPS components are also differentiated as either tightly or loosely bound to microbial cells (Nielsen and Jahn 1999). Slime and capsular EPS are often defined as

loosely and tightly bound respectively. High speed centrifugation can be used to separate slime EPS in the supernatant and capsular EPS in the sludge pellet Bura (2000) analysed the composition of both slime and capsular EPS. He found them to be very similar except for the lipid content. The only difference between slime and capsular EPS was the lipid content; capsular EPS contained lipids whereas slime EPS did not.

2.3.2 EPS Extraction Techniques

Perhaps the biggest inconsistency in the literature is the lack of a standard extraction technique. Consequently, it is difficult to compare results among the previous studies. Much progress has been made in the past few years to compare various techniques and to adopt improved extraction methods (Liu and Fang 2002). Gehr and Henry (1983) list three requirements for an ideal EPS extraction technique:

1. Minimise cell lysis.
2. Do not cause disruption or alteration of biopolymers.
3. Release all EPS.

Presently, no available method can meet all three requirements. Consequently, extraction techniques must be carefully selected and optimised to ensure reliable results.

Nielsen and Jahn (1999) outline four steps common to most EPS extraction techniques. They are sampling and pre-treatment, extraction, purification and analysis. Sampling and pre-treatment procedures attempt to store and prepare the sample to minimize EPS degradation. They suggested that activated sludge could be stored at 0 to 4°C for 1 to 2 days without significant changes in EPS composition. Numerous extraction techniques have been used but all focus on disrupting attractive forces that

make EPS a cohesive substance. Liao et al (2002) listed charge neutralization, hydrophobic interactions, hydrogen bonds, ionic interactions and physical enmeshment as the forces that affect activated sludge floc stability. A common extraction method uses a cationic exchange resin to replace divalent cations that form ionic bridges in the EPS matrix. Frolund *et al.* (1996) showed this method to be very effective in destabilising activated sludge flocs to extract water soluble EPS. Ethanolic extraction developed by Forster and Clarke (1983) must be used to extract the remaining water insoluble EPS, mainly lipids. The lipid source cannot be determined and may derive from the cell wall, in which case they should be excluded from the EPS. However, this is difficult to achieve in the lab. Most EPS extraction studies do not include a purification step because the EPS extracts could be further degraded or modified before analysis is completed.

Finally, extracted EPS is analysed to determine what components are present. Protein, carbohydrate, uronic acid, humic acid and DNA concentrations are usually determined. The total lipid content is determined where the hydrophobic, or water insoluble, fraction was extracted. The reliability of analytical techniques used in determining EPS components is much improved since the 1950's. For most methods, samples are analysed and compared, using a spectrophotometer, to standard solutions such as bovine serum albumin (BSA) or glucose for protein and carbohydrates respectively. Frolund *et al.* (1996) and Horan and Eccles (1986) noted that standards used do not always represent the actual EPS composition in the sample. Additionally, sample analysis may be compromised by the presence of interfering substances.

Liu and Fang (2002) summarized EPS extraction results by extraction method. Listed in Table 2-1 is the average total EPS yield (mg/gVSS) by extraction method. Frolund *et al.* (1996) showed humic acid interference in protein measurements can lead to higher protein values than actually present. Therefore, protein values listed are labelled as protein & humic.

Significant variability is present since no standardized extraction method is used and variables for identical extraction methods differ between studies. Also, since a portion of EPS originates in the wastewater itself, natural variability exists due to different wastewaters used in each study. Generally, as expected, extraction methods using harsh chemicals such as NaOH and H₂SO₄ gave the highest total EPS values. However, due to likely extensive cell lysis, true EPS located in-between cells is contaminated with the release of cell interior contents, leading to higher total EPS values. Centrifugation and homogenization yield the lowest total EPS values. This is reasonable since the methods are purely physical and hardly break up the sludge flocs. The most effective extraction method that balances maximal EPS extraction and minimal cell lysis is the resin or ultrasonication+resin method. The resin method exchanges cations in sludge flocs and decreases cationic bridging forces holding the flocs together (Frolund *et al.* 1996). Physical mixing is also performed in this method, which will ensure greater cationic exchange and increased floc disintegration due to shear stress.

Table 2-1 Average total EPS by extraction method (Liu and Fang 2002)

Extraction Method	Average Total EPS (mg/gVSS)
Centrifugation	54.8
Heating	150.4
Resin	183.4
Ultrasonication	121.0
Ultrasonication+Resin	212.7
Homogenization	38.9
NaOH	275.4
NaOH+Homogenization	98.2
EDTA	103.7
H ₂ SO ₄	363.5

Table 2-2 Average EPS composition by extraction method (Liu and Fang 2002)

Extraction Method	Average Composition						
	Total Carbohydrates	Protein & Humic Acid	Protein	Humic Acid	Uronic Acid	DNA	Unknown
Centrifugation	23%	67%	28%	23%	2%	11%	16%
Heating	23%	59%	26%	24%	2%	7%	35%
Resin	19%	77%	49%	29%	3%	4%	17%
Ultrasonication	23%	59%	26%	24%	2%	7%	35%
Ultrasonication+Resin	12%	80%	75%	16%	3%	20%	0%
Homogenization	33%	67%	59%	28%	0%	0%	0%
NaOH	16%	81%	33%	31%	3%	1%	9%
NaOH+Homogenization	20%	66%	42%	16%	1%	8%	0%
EDTA	16%	67%	59%	40%	1%	3%	37%
H ₂ SO ₄	37%	62%	62%	0%	0%	1%	0%
All Methods	21%	69%	42%	27%	2%	5%	16%

Table 2-2 compares the average composition of extracted EPS by extraction method. Uronic acids, or acidic polysaccharides, compose no more than 2 to 3 % of total EPS and approximately 10 % from the total carbohydrates. DNA is present in small amounts due to continuous cell lysis occurring in the wastewater microbial community. Protein and humic substances are the dominant components of EPS followed by carbohydrates with average percentage compositions of 69 and 21 % respectively. However, protein concentrations are likely overestimated since few studies corrected for humic acid interference in protein analytical methods. While there is considerable variability in the average compositions among the previous studies, the average composition taken from all studies for each extraction method is consistent. Generally, for each extraction method, protein is the largest component of EPS with humic acid and total carbohydrates the next largest with roughly equal concentrations.

2.3.3 EPS & MBR Modeling

Attempts have been made to predict EPS and SMP formation in MBR systems. Nagoaka *et al.* (1998) first attempted to quantify EPS generation as proportional to the mixed liquor suspended solids (MLSS) growth rate and decay using first order kinetics. They found flux, pressure and resistance variations were well explained by their model. Lee *et al.* (2002) incorporated SMP as an additional parameter in Activated Sludge Model No. 1. SMP and inert soluble substances were suggested to be critical in determining effluent quality. Laspidou and Rittman (2002) developed a unified model coupling EPS and SMP formation and degradation that provides a theoretical basis for considering soluble EPS as SMP. Lu *et al.* (2002) incorporated SMP modeling into the

Activated Sludge Model No. 3 and found treatment performance could be predicted for different operating conditions such as SRT and HRT. However, these models require many input parameters and their application are probably applicable only to each specific case. Laspidou and Rittman (2002) emphasized this limitation and suggested much more research is needed to extend results to other systems.

2.4 Sludge Properties Effects on MBR Fouling

2.4.1 Particle Size Distribution

Since membrane filtration physically separates colloidal and particulate matter from feed streams, its performance would be affected by feed stream particle size distribution. One of the most direct effects is to dictate the characteristics of the cake build-up on the membrane surface. As well, it affects the rates of particle transport to the membrane surface. Davis (1992) predicted that there is a minimum flux for spherical particles with diameters approximately between 0.75 to 1.0 μm based on particle transport caused by inertial lift, shear-induced diffusion and Brownian diffusion (see Figure 2-2). Inertial lift, shear-induced diffusion and Brownian diffusion are all physical mechanisms that transport particles away from the membrane surface (Belfort *et al.* 1994)

Figure 2-2 Permeate flux versus particle diameter (Davis 1992)

Choi, *et al.* (2003) discovered particles with a diameter less than 2 μm tended to remain on the membrane surface since backwashing preferentially removed particles larger than 10 μm . Shimizu *et al.* (1997) found that the proportion of particles between 8 to 15 μm effectively controls maximum filtration flux. Lim and Bai (2003) observed significantly lower permeate fluxes with sludge having a smaller particle size and suggested increased pore blocking resistance is responsible. Choi, *et al.* (2003) also found an aerated MBR had lower numbers of smaller particles, less than 2 μm , on the membrane surface when compared to equivalent cross flow filtration tests. They suggested air agitation impeded the movement of smaller particles to the membrane surface particles.

2.4.2 Mixed Liquor Suspended Solids (MLSS)

Lubbecke *et al.* (1995) found that MLSS values up to 30 g/L did not directly affect filtration flux but observed a continuous flux decrease for MLSS concentrations

above 30 g/L. They attributed the effects to increases in viscosity and dissolved matter concentrations. Rosenberger and Kraume (2002) performed filterability batch tests on MBR sludge in the range of 2 to 24 g/L and found MLSS has no effect on sludge filterability. More recently, Le-Clech *et al.* (2003) and Hong *et al.* (2002) found MLSS did not impact critical or permeate flux respectively for values between 4 and 8 g/L. Therefore, it appears MLSS does not directly affect filtration flux but may have deleterious secondary effects attributable to either increased dissolved matter concentration or viscosity.

2.4.3 Sludge Volume Index

The sludge volume index (SVI) estimates sludge settleability by measuring the sludge blanket depth for a 1000 mL sample allowed to settle for 30 min in an Imhoff Cone. While the SVI has been widely used as a measure of settleability, there is little research correlating SVI to membrane fouling. Sponza *et al.* (2003) correlated higher SVI values to higher protein content in EPS but not the total EPS amount. Jin *et al.* (2003) found higher total EPS values were associated with higher SVI values. Similar phenomenon was reported by Wilen *et al.* (2003) and Liao *et al.* (2001). Given the link between SVI and settling, the relationship between SVI and membrane fouling should be examined further.

2.4.4 Hydrophobicity

Several studies have examined the effect of sludge hydrophobicity on membrane fouling. Lee *et al.* (2003) found sludge hydrophobicity correlated positively to

membrane fouling by measuring the hydraulic resistance of sludge flocs. Chang and Lee (1998) found the hydrophobicity of foaming sludge to be up to 40% higher than non-foaming sludge. The hydraulic cake resistance of foaming sludge was found to be two orders of magnitude higher when compared to non-foaming sludge. They suggested the difference in hydrophobicity is responsible for the difference in membrane fouling behaviour.

Wilén *et al.* (2003) provided evidence that the amount and composition of EPS can affect sludge surface properties such as hydrophobicity. Lee *et al.* (2003) suggested that sludge hydrophobicity might be due to EPS composition, which may in turn control membrane fouling. Kerley and Forster (1995) correlated sludge hydrophobicity to the amount of uronic acids in the EPS expressed as a percentage of carbohydrates. In general, increased hydrophobicity may correlate with increased membrane fouling, but other compounds such as EPS may be the true cause.

2.4.5 Surface Charge

While numerous studies examined the relationship between membrane surface charge and fouling, few examined the effects of sludge surface charge on membrane fouling. Lee *et al.* (2003) found increasing sludge surface charge resulted in larger hydraulic resistances of microbial flocs, but found no relation to the supernatant hydraulic resistance, perhaps due to different charges carried by different organic compounds.

2.4.6 EPS

As outlined in section 2.3, EPS composition and concentrations are strongly dependent on extraction method procedures. Methods range from harsh extractions using acid digestions to mild procedures using only physical separation. Conclusions from previous studies are sometimes conflicting since extraction method efficiency and efficacy vary widely in the literature. Nevertheless, many researchers reported the important role of EPS in membrane fouling.

Harada *et al.* (1994) attributed filtration performance decline to increased soluble organic matter concentration, as measured by soluble COD. Similarly, Nagoaka *et al.* (1996) reported increased supernatant TOC is related to increased filtration resistance. Chang *et al.* (2002) concluded that dissolved organic matter negatively affects membrane fouling at higher concentrations. Soluble fractions of COD and TOC can provide an indication of the amount of soluble EPS. Both Wisniewski and Grasmick (1998) and Bouhabila *et al.* (2001) concluded the dissolved (or soluble) fraction in wastewater, approximately less than 0.1 μm , is responsible for between 50 to 75 percent of the total fouling resistance. While Jefferson *et al.* (2004) did not find any relation between dissolved EPS and fouling, dissolved organic matter is likely an important contributor to membrane fouling.

Chang and Lee (1998) stated that EPS was "...the major contributing component to the total membrane resistance..." and suggested using EPS as an index to determine relative fouling tendencies of various wastewaters. Rosenberger and Kraume (2002) found flux declines with increasing total suspended EPS, also called soluble or dissolved

EPS, but found no relation to EPS extracted with cationic exchange resin. Lee *et al.* (2003) attributed increased floc filtration resistance to changes in the EPS protein/carbohydrate ratio and microbial activity. They suggested that the EPS composition is most important because they found no relation between total EPS and fouling. Jefferson *et al.* (2004) and Jarusutthirak *et al.* (2002) also determined EPS composition is likely more important in determining fouling propensity. Jarusutthirak *et al.* (2002) further suggested polysaccharides as most important.

2.4.7 Summary

Table 2-3 and Table 2-4 summarize the effects of various sludge properties and EPS on membrane filtration permeate flux respectively. Relationships are described using a five scale rating system ranging from a strong positive correlation (+ +) to no correlation (0) and strong negative correlation (- -). Permeate flux is decreased for a negative correlation and increased for a positive correlation. Where no direct studies examining the effect of a factor on membrane fouling are present, n.d. is used to represent no data. Additionally, INC, or inconclusive, is used to represent conflicting evidence reported in the literature. Only studies that directly measured the variable of interest and performed wastewater filtration tests are included.

Particle size results have the strongest correlation to permeate flux. However, the strongest relationships reported are limited to the number of small particles (ex. 8 – 15 μm) and flux. Mean particle size did not significantly influence permeate flux. Weak relationships for hydrophobicity and surface charge are reported. Sludge properties widely used in settling and dewatering analysis, SVI and SCR respectively, had

inconclusive conclusions or no direct studies relating to membrane fouling. MLSS has been conclusively shown to have no direct effect on membrane fouling. Total dissolved carbohydrates are the most important EPS component affecting membrane fouling. No clear relationship is present between total EPS and fouling; however, several studies suggest EPS composition is more important than the total amount. Very little research correlating each of the other EPS components and membrane fouling is available.

Table 2-3 Sludge properties effects on membrane fouling

Sludge Property	Correlation	Comments
Particle Size	--	Number of small particles (ex. 8-15 um)
MLSS	0	Valid for TSS < 24 - 30 g/L
SCR	INC	Conflicting evidence
Hydrophobicity	-	Weak evidence likely explained by other variables
SVI	n.d.	No studies examined the effect of SVI and fouling
Surface Charge	-	One study only

Table 2-4 EPS effects on membrane fouling

EPS Constituent	Correlation	Comments
Dissolved		
Total Carbohydrates	--	Both proxy measurements as sCOD and sTOC and direct polysaccharide quantity
Protein	n.d.	
Humic Acid	n.d.	
Acidic Polysaccharides	n.d.	
Total EPS	0	Composition likely more important
Extracted		
Total Carbohydrates	0	
Protein	n.d.	
Humic Acid	n.d.	
Acidic Polysaccharides	n.d.	
Lipids	n.d.	
Total EPS	0	Composition likely more important

3 RESEARCH OBJECTIVES AND SUMMARY OF WORK

The main research objective is to examine the role of sludge properties, particularly including extracellular polymeric substances (EPS), in determining membrane fouling behaviour. EPS is one of the main groups of organic matter that affects the strength and surface properties of biomass flocs (Liao *et al.* 2001).

Prior to the late 1990's most of the wastewater membrane filtration researchers used sidestream operations that operated at permeate fluxes up to 150 L/(m²·h) and required cross flow velocities between 1.5 and 5 m/s to generate sufficient shear stress to reduce fouling (Chang *et al.* 2002). Studies by Defrance and Jaffrin (1999) and Tardieu *et al.* (1999) estimated that these cross flow velocities would generally cause shear stresses in the range of 20 – 120 Pa. However, recent introduction of submerged membrane systems greatly lower the transmembrane pressures thereby reducing shear stress requirements (Cote *et al.* 1998). Chang *et al.* (2002) estimated the equivalent cross-flow velocity due to aeration in submerged MBR systems to be between 0.3 and 0.5 m/s. Therefore, more research is needed at lower shear stresses to examine membrane fouling mechanisms so that the results will become more comparable to the actual operations of submerged MBR systems.

Specific objectives include:

1. to compare short term steady state fluxes using both stirred cell and cross flow filtration tests at different shear and transmembrane pressure conditions,

2. to provide a comprehensive characterization of MBR and conventional activated sludge properties to reveal their roles in membrane fouling behaviour, and
3. to determine relative importance of dissolved and extracted EPS on membrane fouling.

Both modified stirred cell and cross flow filtration tests were conducted with each sludge sample. Shear stress was introduced in the stirred cell test by including a mixing blade near the membrane at the bottom of the vessel. The shear stress at the membrane surface for both the stirred cell and cross flow modules was calculated using the commercial computational fluid dynamics (CFD) software package, FLUENT[®]. Mixing blade speeds in the stirred cell vessel were then chosen to simulate cross flow filtration velocities.

4 METHODS

This section details the methods used to examine sludge properties effects on membrane fouling including sampling and storage procedures, analytical methods, computational fluid dynamics simulations to characterize the hydrodynamics of testing apparatus and finally testing apparatus setup and operating protocol.

4.1 Sludge Sampling and Storage

Twelve samples were taken from various municipal wastewater treatment plants in Southern Ontario consisting of eight MBR and four AS samples respectively. Table 4-1 lists the treatment plant type and location, sample date and SRT operating range.

Table 4-1 Wastewater sample locations

Sample ID	Date	Location	Plant Type	SRT
1	13-Feb-04	WTC, Burlington, ON (WW1)	Submerged MBR pilot plant	30-60
2	23-Feb-04	Creemore, ON	Submerged MBR full scale	80-120
3	15-Mar-04	Port McNicoll, ON	Submerged MBR full scale	15-30
4	22-Mar-04	WTC, Burlington, ON (WW2)	Submerged MBR pilot plant	15-25
5	1-Jun-04	WTC, Burlington, ON (WW2)	Submerged MBR pilot plant	15-25
6	10-Jun-04	Guelph Pilot 1, No Coagulant	Submerged MBR pilot plant	12
7	14-Jun-04	Guelph Pilot 1, No Coagulant	Submerged MBR pilot plant	12
8	17-Jun-04	Guelph Pilot 2, Coagulant	Submerged MBR pilot plant	12
9	26-Jan-04	Guelph, ON	Conventional AS	20-25
10	26-May-04	Ashbridges Bay, Toronto, ON	Conventional AS	2-5
11	7-Jun-04	Burlington, ON	Conventional AS	8-12
12	21-Jun-04	Kitchener, ON	Conventional AS	3-4

Two samples were taken from full-scale submerged MBR wastewater treatment plants at Creemore and Port McNicoll, Ontario. Three samples were taken from the Wastewater Technology Centre (WTC) in Burlington, ON. The first sample was taken from the WW1 pilot plant. The following two were taken from the WW2 pilot plant with the first at a stable SRT operating condition and the second in a transient state approximately 7

days after start-up. Three samples were also taken from the pilot scale MBR's located at the Guelph Wastewater Treatment Plant (WWTP). The first two were taken while the sludge was in a transient state, at days 6 and 10 of an SRT of 12 days respectively. The third sample was taken from another pilot plant at the same location that contained 300 mg/L of NALCO[®] organic polymer coagulant. Approximately 40 L of sludge was taken from the aeration tank for all AS samples and from the submerged membrane tank for all MBR samples respectively.

Sampling and storage protocols recommended by Standard Methods (1992) were followed for all tests. Samples were transported from the treatment plants in a cooler with ice packs and then stored at the University of Guelph at 0 to 4 °C within 2 hours of collection to minimize the potential effects of continuing biodegradation. A portion of the samples were delivered to the Ontario Ministry of Environment Laboratory in Toronto within 1 hour of sample collection and stored at 0 to 4 °C for particle size distribution analysis.

Note that different sampling protocols were used for samples 1, 2, 3, 4, and 9 and the remaining samples. For the first group, two samples were taken from the treatment plant on two separate days. The second sample was always taken two full days after the first sample date. This was necessary because the total analysis time was between 4 and 5 days, which is significantly longer than the maximum storage time of 1 to 2 days suggested by Nielsen and Jahn (1999). They suggested significant EPS degradation can occur in samples stored for a longer time period. Improvements in the filtration

apparatus allowed a reduction in analysis time from 4 to 5 days to 2.5 to 3 days so only one sample was necessary afterwards.

4.2 Sludge Characterization

Soluble COD, total sludge COD, TSS, VSS, sludge volume index (SVI) and specific cake resistance (SCR) were measured according to Standard Methods (1992). However, due to large TSS values for MBR aerobic sludges, a diluted SVI was measured by diluting the original MBR sample to 2.5 g of total solids prior to measurement. Soluble TOC and soluble TN were determined using a SHIMADZU[®] TOC/TN analyzer. Soluble samples were obtained from the bulk wastewater by filtering through a Whatman #41 1.5 µm filter paper.

All EPS extractions were completed on the subsequent day following sample collection and then stored at 0 to 4 °C. Protein, humic substances, total carbohydrates, acidic polysaccharides and lipids analyses were completed no later than the second day after sample collection. Standard curves for these analyses are provided in Appendix D.

4.2.1 EPS Extraction

The DOWEX[®] extraction procedure was adapted from Frolund *et al.* (1996). The conductivity of the first sample, from the Guelph WWTP, was compared to the phosphate extraction buffer recommended by Frolund *et al.* (1996). A modification was to adjust NaCl concentration in the buffer from 9 to 16 mM to ensure the sludge and buffer have similar conductivities and are approximately isoosmotic. The conductivity of other sludge samples was similar so no other adjustments were made to the buffer. Additional modification was made to use the DOWEX[®] Marathon C, Na⁺ form with 20-50 mesh

(Product number 91973-1KG-F) to replace the DOWEX[®] 50 X 8, 20-50 mesh. (Product number Fluka 44445) which was discontinued. The extraction vessel was a square, glass vessel with length, width and height of 0.1 m X 0.1 m X 0.075 m and the mixing blade width and height was 0.076 m X 0.035 m.

1. Concentrate 1000 mL of activated sludge to 8-11 g/L by gravity sedimentation for about 1.5 hours at 4°C and decant supernatant. Measure TSS of original and settled sludge.
2. Prepare a PBS extraction buffer solution containing 2 mM Na₃PO₄, 4 mM NaH₂PO₄, 16 mM NaCl and 1 mM KCl at pH 7.
3. Wash 40 mL of thickened sludge samples with buffer solution twice and centrifuge in 4 X 10 mL HACH test tubes at 2000 g for 15 min at 4 °C to remove EPS in bulk water.
4. Resuspend sludge pellets to their original volume of 40 mL using the extraction buffer solution. Then dilute with approximately 50 to 150 mL of extraction buffer solution and make appropriate corrections for EPS concentrations later.
5. Use 56 g DOWEX[®] resin/g TSS and mix DOWEX[®] Marathon resin, Na⁺ form with extraction buffer solution for 1 hour.
6. Rinse with Milli-Q[®] water and filter using a Buchner funnel apparatus.
7. Transfer dry, washed resin to a square extraction vessel and then mix with sludge-buffer suspension.
8. Keep the extraction vessel at 4°C while stirring at 900 rpm for 2 hours.

9. Transfer the DOWEX[®]/sludge mixture to 2 X 30 mL test tubes and centrifuge once at 12 000g for 1 min to remove the DOWEX[®].
10. Transfer the supernatant to another centrifuge tube and centrifuge again for 15 min at 12 000g (12,372 rpm) and 4°C to remove floc components. Repeat once.
11. Collect the supernatant from the centrifuge tube for extracted EPS determination.

Dissolved EPS was also extracted by directly transferring the sludge sample to centrifuge tubes and centrifuged twice for 15 min at 12 000 g. The supernatant was collected for the analysis of different EPS constituents including carbohydrates, protein, humic acid and acidic polysaccharides.

4.2.2 Ethanolic Extraction

Ethanol extraction was used to extract non-water soluble lipids according to Forster and Clarke (1983). Denatured ethanol from Fisher Scientific was used as a substitution for ethanol due to the availability of chemical reagents. The detailed extraction procedure includes the following.

1. Pipette 10 mL of original sludge to 2 X 10 mL HACH test tubes.
2. Wash sludge twice with Milli-Q[®] water by centrifuging at 2000g for 15 min and decanting supernatant.
3. Bring to original volume by adding ethanol and resuspend sludge pellet
4. Cap the test tube and store at ambient temperature for 24 hours.
5. Centrifuge the samples at 2000g for 15 min.
6. Collect the supernatant for lipid analysis.

4.2.3 Total Carbohydrates Analysis

The anthrone method, adapted from Bura (2000) and first described by Gaudy (1962), was used to determine the total carbohydrate value using pure glucose as a standard. The detailed procedure is listed below.

1. Dissolve 0.1 g anthrone in 50 mL of 96% sulphuric acid. This solution must be made fresh each day and at least 2 hours before use.
2. Prepare 4 glucose standard solutions from 5 to 50 mg/L and store at 4°C for not more than 2 weeks.
3. Add 2 mL of sample to 10 mL glass HACH test tubes.
4. Add 5 mL of anthrone reagent to each test tube. Include a blind tube containing sample and only 96% sulphuric acid.
5. Cap tubes and mix with a vortex mixer for a few seconds.
6. Place tubes in a boiling water bath for 14 min.
7. Cool down to room temperature using a cool water bath for 5 min.
8. Measure the absorbance at 625 nm using 1 cm cuvettes.
9. Calculate the total carbohydrate concentration (glucose equivalent) from the standard curve after subtracting the blind absorbance from the sample absorbance.
10. Convert into mg/g VSS using the biomass concentration for the EPS extraction.

4.2.4 Protein and Humic Acid Analysis

Protein and humic acid were measured by adapting the procedures given by Frolund *et al.* (1995) who modified the Lowry (1951) method to measure protein in

activated sludge samples in order to correct humic acid interference. Detailed steps includes of the method are given below.

1. Prepare bovine serum albumin (BSA) and humic acid standard solutions with concentrations between 20 and 400 mg/L, 10 and 100 mg/L respectively.
2. Prepare 1L of Reagent A with 143 mM NaOH and 270 mM Na_2CO_3 .
3. Prepare 250 mL of Reagent B with 57mM CuSO_4 .
4. Prepare 250 mL of Reagent C with 124 mM sodium tartrate.
5. Prepare Reagent D by mixing Reagents A, B and C with a ratio of 100:1:1 just before use.
6. Prepare Reagent E by mixing reagents A and C with a ration of 100:1. This will be used for the blind sample test without CuSO_4 .
7. Add 2.5mL of blank, standards and EPS sample to 10mL HACH glass tubes.
8. Dilute stock 2 N Folin reagent (1:1) (v/v) with distilled water.
9. Add 3.5 mL of Reagent D to the tubes and mix with a vortex mixer. Keep the solution for 10 min at room temperature.
10. For the blind, add 3.5 mL of reagent E and mix well. This will be the sample without CuSO_4 addition to correct for humic acid interference.
11. Add 0.5 mL of diluted Folin reagent to each of the test tubes, mix immediately with vortex mixer and keep for 45 min at room temperature to develop color.
12. Measure absorbance at 735 nm using 1 cm cuvettes.
13. Calculate protein and humic acid absorbance by following Frolund *et al.* (1996).

14. Calculate protein and humic acid concentrations from the standard curves and convert into mg (BSA equivalent or humic acid equivalent) / g VSS.

4.2.5 Acidic Polysaccharides Analysis

Acidic polysaccharides were measured according to Filisetti-Cozzi and Carpita (1991) modified by Bura (2000). Detailed procedure is listed below.

1. Prepare D-glucuronic acid solution as a standard with concentrations between 5 and 140 mg/L.
2. Prepare 0.15% (w/v) m-hydroxydiphenyl in 0.5% (w/v) NaOH and store in darkness at 4°C for no more than 2 weeks.
3. Prepare the sulfamic acid-potassium sulfamate solution by vigorously stirring sulfamic acid in one-half final volume of water. Saturated KOH was added dropwise until the sulfamic acid was dissolved.
4. After the sulfamate solution had cooled, adjust the pH to 1.6 with NaOH and bring to 4 M with water. Store at ambient temperature.
5. Prepare 75 mM sodium tetraborate solution by adding analytical grade H_2SO_4 (96%) and stirring overnight.
6. Use 0.8 mL blank, standard and sample solutions in three 10 mL HACH glass tubes respectively. Record tube with no m-hydroxydiphenyl addition as blind EPS measurement.
7. Add 80 μL of 4M sulfamic acid-potassium sulfamate (pH adjusted to 1.6 with NaOH) and mix with a vortex mixer.
8. Add 4.8 mL of H_2SO_4 -sodium tetraborate solution and then mix using a vortex mixer.

9. Cap the test tubes and heat in a boiling water bath for 20 min.
10. Cool to room temperature using an ice water bath for 5 min.
11. Add 160 μ L of 0.15%(w/v) m-hydroxydiphenyl solution and mix with a vortex mixer.
12. Keep the sample tubes for 5 to 10 minutes to develop color.
13. Measure the adsorbance at 525 nm using 1 cm cuvettes.
14. Calculate the acidic polysaccharide concentration from the standard curve and convert to mg (glucuronic acid equivalent) / g VSS.

4.2.6 Lipids Analysis

Lipids were only measured in sample supernatant after ethanol extraction. The method described by Bura (2000) was used which was based on the original method described by Frings and Dunn (1970). The method below replaces the pure ethanol originally used to make olive oil standards with denatured 85 % ethanol. Details of the method are given below.

1. Prepare olive oil standards between 35 and 450 mg/L in denatured 85% ethanol.
Standard solutions should be stable for at least 1 month at 4°C.
2. Prepare the phospho-vanillin reagent by combining 100 mL of 0.6% w/v vanillin with 400 mL concentrated phosphoric acid in a 500mL volumetric flask. Store the solution in a brown bottle at room temperature and it should be stable for at least 6 weeks.
3. Mix a 1 mL sample with 2 mL of 96% sulphuric acid in 10 mL glass test tubes and digest for 10 min in a 100°C water bath.
4. Cool the tubes in a cold water bath for 5 min.

5. Mix with 5 mL of phospho-vanillin reagent.
6. Incubate all tubes at 37°C for 15 min and then cool at room temperature for 5 min.
7. Measure the absorbance at 528 nm using 1 cm cuvettes. The color is stable for at least 10 min.
8. Convert into mg/g VSS using the biomass concentration for the EPS extraction.

4.2.7 Surface Charge Analysis

Sludge surface charge was measured by the colloid titration technique according to Morgan *et al.* (1990). The detailed procedure is listed below.

1. Use polybrene (0.001 N) and potassium polyvinyl sulphate (PVSK) (0.001 N) as the cationic and anionic standards respectively.
2. Adjust polybrene and PVSK solutions to neutral pH using dilute solutions of NaOH and HCl.
3. Measure 1 mL of sludge sample and dilute to 100 mL.
4. Add 2mL of polybrene into the diluted sample and blank while swirling around for approximately 10 s.
5. Titrate against polybrene with the PVSK standard using 3-4 drops of 0.1% toluidine blue as the indicator.
6. Calculate the charge in meq/L.

4.2.8 MATH Analysis

Cell surface hydrophobicity was measured using the microbial adhesion to hydrocarbons test (MATH) first described by Rosenberg (1980). The detailed procedure is given below.

1. Prepare phosphate urea magnesium sulfate (PUM) buffer solution at pH 7.1 with 22.2 g $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$, 7.26 g KH_2PO_4 , 1.8 g urea, 0.2 g $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ with distilled water to 1L.
2. Add 0.5 mL of sludge and 4.5 mL of buffer solution to each of four 10 mL HACH test tubes.
3. Wash and resuspend the sludge sample in PUM buffer solution.
4. Adjust absorbance to approximately 1.5 at 400 nm with buffer solution.
5. Add 0.5 mL of n-hexadecane to each tube and mix for 2 min using a vortex mixer.
6. Transfer contents to 60 mL separation funnel and allow 15 min for the cells to partition.
7. Take aqueous layer and measure the absorbance at 400 nm using a 1 cm cuvette.
8. Calculate the hydrophobicity using the relative percentage of bacteria removed from the aqueous phase.

4.2.9 Particle Size Analysis

Sludge particle size distribution was measured using the laser diffraction method with a Coulter LS particle size analyzer having a measurement range between 0.1 and 1000 μm . Sludge was added to a water reservoir containing Milli-Q[®] water using a dropper until the analyzer indicated an obscuration value of at least 50 %. The total

sludge volume added varied between samples but was generally between 10 and 50 mL. The Fraunhofer optical model filter was used to convert raw data to a size distribution based on volume percentage. All samples were analyzed twice for quality control.

4.3 Membrane Filtration Setup and Operation

4.3.1 Experimental Apparatus Setup

A modified stirred cell apparatus, with an interior diameter and height of 88 and 304 mm respectively, was constructed using transparent plexiglass (See Figure 4-1). The membrane and permeate outlet are located at the bottom of the vessel. Pressurized air and wastewater inlets are located through the vessel walls near the top. The permeate outlet leads to a beaker on an electronic balance which is connected to a personal computer for automated permeate flux measurement. A rectangular mixing blade, with a width and height of 76 and 25 mm respectively, is located near the membrane surface. The clear gap between the mixing blade and membrane surface was 10 mm. A CAFRAMO[®] overhead mixer with digital speed control and display was positioned above the filtration vessel. A MINEX[®] SA-46/6 permanent magnetic coupling manufactured by KTR was used to connect the mixer drive shaft and mixing blade. The coupling allowed mixing shaft rotation to occur while the vessel interior was pressurized for each filtration test. Detailed dimensional sketches and photographs of the stirred cell apparatus are provided in Appendix A. Only a narrow ringed area between radii 25 and 35 mm was used for filtration to minimize shear stress variation along the radius (See Figure 4-2). The remaining membrane area was made impermeable by gluing thin teflon sheet to the membrane surface.

Figure 4-1 Modified stirred cell apparatus

Figure 4-2 Stirred cell membrane effective filtration area

Figure 4-3 Cross flow testing apparatus

Figure 4-3 provides details of the cross flow membrane filtration testing unit. Three membrane units can be operated in parallel with valves to allow independent pressure and flow control for each unit. Each unit has a width, length and height of 50, 120 and 1.727 mm respectively. Wastewater sample enters the port on the right lower surface and leaves the port on the left lower surface. The membrane is located on the top of each unit and permeate is collected through 21 X 1 mm diameter holes on the top plate. Automated flux measurement is accomplished by the same computerized data acquisition system used for the stirred cell apparatus. Detailed dimensional sketches are provided in Appendix B.

All membranes used were cellulose acetate (CA) membranes with a pore size of 0.22 μm . A large flat sheet ($0.3 \times 3 \text{ m}^2$) was purchased from OSMONICS® and cut into rectangular $55 \times 120 \text{ mm}^2$ units for cross flow tests or circular units with a diameter of 110 mm for stirred cell tests.

4.3.2 Apparatus Operating Procedure

Both the stirred cell and cross flow systems were operated at a constant pressure to measure the permeate flux decline over time. Clean water filtration tests were first conducted for both dead and cross flow systems to ensure membrane permeability did not significantly decrease between membrane tests. For the stirred cell system, the permeate tubing was full with clean water from the clean water test and wastewater was then pumped into the filtration vessel. This allowed a quick permeate response at the start of the wastewater filtration. For the cross flow system, permeate tubing did not remain completely full because the pump was turned off when switching the water source from

clean water to wastewater. Therefore, permeate response was not immediately measured at the start of filtration but developed in approximately 1 to 2 minutes.

For the stirred cell system, approximately 1.5 to 2 L of wastewater sample was pumped into the vessel. The system was then pressurized to the operating pressure using the air supply system available in the lab. The mixer was then operated at the desired operation speed. The permeate valve was then opened and the filtration test commenced.

Approximately 10 L of wastewater was transferred to a container for each of the cross flow filtration tests. The centrifugal pump was turned on and pressure and flow control valves were adjusted to ensure the system operated at the required cross flow velocity and operating pressure. A computer controlled solenoid valve was used to alternately direct permeate from each unit to an electronic balance for permeate flux measurements. Permeate not collected in the beaker, along with remaining wastewater, was returned to the container and recirculated throughout the filtration test.

4.3.3 Experimental Condition Selection and Arrangement

The maximum filtration time for each testing condition was 45 min. Rosenberger and Kraume (2002) suggested 40 min filtration time was sufficient to characterize permeate flux decline for activated sludge samples. Additionally, since Lim and Bai (2003) noted that cake filtration is the dominant filtration mechanism for activated samples, the maximum filtration time should be large enough to allow the cake filtration regime to develop. Jiang *et al.* (2003) suggested that at fluxes above $52 \text{ L}/(\text{m}^2\cdot\text{h})$, cake filtration dominates after approximately 100 s of filtration. Initial activated sludge

filtration tests established that the permeate flux is initially much larger than $52 \text{ L}/(\text{m}^2 \cdot \text{h})$ and a 45 min filtration time is sufficient for cake filtration to develop.

Operating pressure conditions of 69 and 207 kPa were used for both cross flow and stirred cell tests respectively. Previous fouling indices such as the silt density index (SDI) and modified fouling index (MFI) perform filtration tests at 207 kPa (Weisner and Aptel 1996; Taylor and Jacobs 1996). Fouling behaviour at 69 kPa was characterized because the pressure is similar to full-scale submerged MBR systems that operate between 20 and 50 kPa (Judd 2004).

At each operating pressure, two stirred cell and cross flow tests were performed at a high and low shear conditions to investigate the effect shear stress has on membrane fouling. Shear stresses ranged from approximately 0.60 to 3.0 Pa which correspond to maximum fluid velocities between 0.20 and 0.60 m/s for cross flow and 0.30 and 1.0 m/s for stirred cell respectively. The test velocities are comparable to equivalent cross flow velocities between 0.3 and 0.5 m/s for submerged MBR systems with aeration as confirmed by CFD simulation presented later.

4.3.4 Quality Control/ Quality Assurance

All wastewater samples were stored at 0 to 4 °C until filtration. Approximately 80 % of dead-end and cross flow filtration tests were completed within 2 days of sample collection and the remaining no later than 3 days. Wastewater temperature was measured at the start and end of each test in order to adjust permeate flux values. Finally, a set of four membranes were pre-soaked in Milli-Q[®] water for four hours before use and cleaned by immersion in a 250 ppm NaClO solution for 12 – 24 hours after use.

4.4 CFD Characterization of Shear Stress on Membrane Surface

Recently, commercial software packages such as FLUENT[®] allowed researchers to simulate the hydrodynamic performance of their applications based on the principles of computational fluid dynamics (CFD). This section will give some background on the use of CFD in membrane applications and describe how simulations were performed for both dead-end and cross flow systems. CFD software discretizes a system into a number of finite volumes using a mesh, or grid. Governing fluid dynamics equations applicable to the problem of interest are then solved for each finite volume. Results are then post processed for presentation in the desired format. A detailed discussion of numerical solution procedures can be found in the FLUENT[®] user manual. (FLUENT[®] 2003)

Due to the recent development of easily accessible commercially available CFD software programs, few researchers were reported using CFD to simulate the hydrodynamic characteristics of membrane systems. Schwinge *et al.* (2002) and Li *et al.* (2002) successfully used the CFD software CFX v4.3 to simulate flow patterns in membrane spacers. Schwinge *et al.* (2002) simulated unsteady flow patterns for various geometric spacer configurations. They compared their unsteady simulation results to theoretical and reported values in the literature and good agreement was found. Li *et al.* (2002) found good agreement between simulated and observed mass transfer and power consumption. Taha and Cui (2002) used FLUENT[®] to simulate the shear stress when a Taylor air bubble propagates inside a hollow fiber membrane. While no comparison to experimental data was given, they predicted the permeate flux with errors

less than 20 %, and the wall shear stress was identified as a critical variable affecting the permeate flux.

4.4.1 Stirred Cell Simulation

The stirred cell membrane filtration system, described in section 4.3, was studied to estimate the shear stress experienced at the membrane surface located at the bottom of the cylinder. A three dimensional wire frame model of the stirred cell system was created using GAMBIT[®] v2.1, a pre-processor included with the FLUENT[®] v6 software package. Next, all 2D wire frame surfaces were meshed using triangular and quadrilateral elements. The 3D tetrahedral mesh was then generated from the base 2D mesh. The mesh generated from GAMBIT[®] is included in Appendix A.

Increased velocity gradients were expected in the region close to the mixing blade so the fluid volume mesh was divided into two regions with different mesh densities. This was done to limit the maximum mesh velocity gradients that can lead to increased numerical inaccuracy. The two mesh volumes were separated 40 mm from the bottom of the vessel and the bottom and top fluid volumes consist of 29,117 and 41,283 elements respectively. The software package allowed for a smooth transition between the two mesh sizes to minimize any inaccuracy related to abrupt changes in mesh geometry. Finally, mesh skewness was checked against the minimum skewness of 0.6 and the software iteratively performed a smoothing procedure until all elements satisfied the minimum skewness. Good agreement between total mesh and real vessel volumes was observed with values of $1.8317 \times 10^{-3} \text{ m}^3$ and $1.8490 \times 10^{-3} \text{ m}^3$ respectively.

Boundary conditions used in the simulation are discussed below. The vessel was considered a closed system completely full of pure water at 20°C. Atmospheric pressure was introduced at the membrane surface. Surfaces were considered smooth with no roughness and the no-slip condition was used at all solid-fluid interfaces. Membrane permeate flow was not modelled since its effect on membrane shear stress should be small compared to the shear stress generated by the mixing blade.

The governing equations were continuity, Navier-Stokes and k- ϵ turbulence. The complete flow simulation was solved in steps, as recommended in the FLUENT[®] (2003) manual. First, a solution was obtained for the steady state laminar condition with the turbulence disabled. Next, laminar solution values were used as initial guesses for the turbulence model and the steady state solution was solved again. This procedure reduces turbulence solution uncertainty because solution accuracy can depend on initial estimates for values (FLUENT[®] 2003). Finally, once convergence for the steady state turbulence model is established, the unsteady state simulation is completed.

FLUENT[®] allows two different types of velocity formulations to be used in solving the governing equations, namely relative and absolute velocity respectively. The relative velocity formulation reduces errors in problems where fluid is moving at high velocities, but the change in velocity between mesh elements is small or follows a pattern. The relative velocity formulation was used since it is anticipated that the fluid velocity is strongly correlated to the radial distance from the centre of the mixing blade.

In the actual stirred cell apparatus, the mixing blade is rotated at a constant angular speed while the vessel is stationary. While a steady state solution with a rotating

blade was possible with FLUENT[®], the software was unable to produce time dependent shear stress variation at the membrane surface. In order to obtain transient shear stress behaviour the inverse problem was considered. Specifically, the mixing blade was considered stationary while both the fluid and cylinder were moving at a constant angular speed equal to the mixing blade speed in the real system. A moving mesh solution procedure was used consisting of a moving fluid mesh rotating at an angular speed equal to the mixing blade angular speed. The vessel walls were also rotating at the same angular speed. Node numbers and co-ordinates changed with each time step and results were interpreted based on the global Cartesian co-ordinate system.

Time steps were iteratively estimated using the guidelines in the FLUENT[®] (2003) manual. The guidelines state that during each time step all residuals should decrease monotonically toward the convergence criteria in a relatively low number of iterations, preferably ranging between 10 and 20. Additionally, it was anticipated that larger time steps would be needed for simulations with larger mixing blade angular speeds. Solution convergence was defined using the program default of less than 0.01 % change in successive values of continuity, velocity and turbulence parameters. While convergence robustness can be affected by initial parameter estimates, confidence in solution convergence is increased when residuals continue to decrease to values with decreasing orders or magnitude.

FLUENT[®] did not provide any option to summarize detailed data such as shear stress and fluid velocities for each time step in the unsteady simulation. Therefore, velocity, shear stress and position vectors were exported to a comma separated text file

after solution of time step. Microsoft Excel was then used to import and manipulate the text files for each simulation case (ex. different angular velocities).

4.4.2 Cross Flow Simulation

FLUENT[®] v6.0 and GAMBIT[®] v2.1 were also used for hydrodynamic simulations of the cross flow apparatus. A 3D quadrilateral mesh was used because it closely resembles the filtration module geometry. Maximum mesh spacing of 0.5 mm was governed by the smallest dimension, the module height of 1.727 mm. Total mesh and real apparatus volumes were identical at $1.0362 \times 10^{-5} \text{ m}^3$.

Boundary conditions are specified below. The fluid was defined as water at 20 °C and a reference pressure of 101 kPa was introduced at the bottom surface. Steel and membrane roughness values of 1.14×10^{-3} and 5×10^{-6} mm respectively were used. The fluid inlet and outlet ports were modeled as a constant velocity source and outlet respectively with velocity components perpendicular to the inlet and outlet surface only. Permeation through the membrane was not considered for the same reason as discussed in section 4.4.1.

Governing equations solved were continuity, Navier-Stokes and k- ϵ turbulence. The simulation was solved as a steady state solution, i.e. – no change with time, since the shear stress at the membrane surface is constant for a constant inlet velocity. Laminar flow equations were solved first and then turbulence equations were initialized and solved. Only one simulation was needed for each different crossflow velocity. All convergence criteria were identical to those presented in section 4.4.1. Results were exported from FLUENT[®] in a text file and then imported into Microsoft Excel.

5 RESULTS AND DISCUSSION

5.1 Introduction

Membrane fouling results are organized into three main sections: CFD simulation, membrane fouling evaluation and sludge properties effects on fouling. CFD results are first presented to allow comparison of the hydrodynamics of the cross flow and stirred cell systems. Membrane fouling evaluation presents filtration data consisting of flux vs. time and steady state flux values after 45 minutes filtration for stirred cell and cross flow filtration tests. The final section examines the relationship between membrane fouling evaluation data and sludge properties.

5.2 CFD Simulations

5.2.1 Stirred Cell Membrane Module

Simulations were performed using mixing blade – membrane clear gaps of 5 mm and 10 mm respectively and blade rotational speeds between 100 and 500 rpm. All results presented in this section are for the 10 mm gap unless otherwise stated. The 10 mm gap was chosen to minimize shear stress uncertainty caused by measurement inaccuracies when placing the mixing blade near the membrane surface.

Steady state continuity, velocity and turbulence residuals for the 100 rpm 10 mm gap simulation are illustrated in Figure 5-1. Residual plots for all other simulations are similar and not included. All residuals decrease monotonically towards the default convergence criteria of 0.01 %. Simulation results are compared to theoretical solution values later because the converged solution may be different from the true solution. For the 100 rpm - 10 mm gap unsteady simulations, convergence for each discrete time step

occurred after 10 and 20 iterations. This agrees with the time step estimation criteria suggested in the FLUENT[®] (2003) manual. In initial simulations, solution convergence problems were encountered with the default k- ϵ turbulence model. Turbulence residuals decreased to values near the convergence criterion of 0.01 % but did not continue to decrease with further iterations. FLUENT[®] (2003) provided another numerical solution option called the RNG approach that reduces errors for swirl dominated flow situations with high degrees of rotational velocity. Stirred cell hydrodynamics can be characterized as similar to a swirling flow and consistent convergence for all rotational speeds was obtained with turbulence residuals monotonically decreasing to values near 0.000001 %. All stirred cell simulation results presented use the RNG numerical approach.

Time steps were decreased for simulations at increasing blade rotational speeds. Conceptually, this is reasonable since convergence depends on maximum allowable velocity gradients and tolerances in mesh geometry. For example, the time step for the 200 rpm solution should be no greater than one half of the 100 rpm solution time step. Time steps used for all 10 mm gap simulations are given in Table 5-1. Simulation time needed to simulate real system time increases with blade angular velocity due to larger velocity gradients and smaller time steps to ensure solution stability and convergence.

Figure 5-1 Simulation residuals for 100 rpm, 10 mm gap

Table 5-1 Time steps and simulation time for varying blade angular velocities

10 mm Blade-Membrane Gap				
Angular Velocity	Time Step	Total	Real System Time	Simulation Time
(rpm)	(s)	Steps	(s)	(hours)
100	0.002	1445	2.890	15.2
200	0.001	1224	1.224	15.3
300	0.0005	1245	0.623	15.4
400	0.0005	1113	0.557	15.3
500	0.0002	1352	0.270	15.3

Results for each time step were exported to a text file and manipulated using Microsoft Excel. Since shear stress at the membrane surface is the main variable of interest, only results at particular points were exported to keep file sizes manageable. Figure 5-2 illustrates the results section located on the membrane surface. Shear stress values at the membrane surface depend on the fluid velocity gradient, which is related to the distance from the centre of the mixing blade. The linear velocity at the blade tip is related to the radial distance by Equation 5-1.

$$v = \frac{\omega \cdot 2\pi \cdot r}{60} \quad (5-1)$$

where v = linear velocity (m/s); r = radius (m); ω = angular velocity (rev/minute).

Shear stress variation with time at a fixed point located at radial distances of 10, 30 and 40 mm from the vessel centre are plotted in Figures 5-3 to 5-5 respectively. The rotational speed and membrane blade gap were 100 rpm and 10 mm respectively.

Maximum shear stress increases with increasing radius, which qualitatively agrees with equation 5-1. Shear stress at 40 mm is slightly smaller than shear at 30 mm due to the effect of the cylinder wall at a radius of 44 mm. Shear stress temporal variation follows a sinusoidal pattern with the peak shear stress occurring when the blade passes over the results section. Results at a radius of 30 mm are included in Appendix C for all rotational speeds and both 5 and 10 mm blade gaps.

Figure 5-2 CFD results section at membrane surface

Figure 5-3 Shear stress at membrane surface at 10 mm radius

Figure 5-4 Shear stress at membrane surface at 30 mm radius

Figure 5-5 Shear stress at membrane surface at 40 mm radius

Since all shear stress plots exhibit some variation with time, a long term simulation was performed to ensure uncertainties did not accumulate over a larger time frame. The 10 mm gap – 100 rpm case was simulated for approximately 3900 time steps that is equivalent to a real system time of 7.80 s. Area weighted average shear stress between radii of 25 and 35 mm are plotted in Figure 5-6 and no significant long term variation is evident.

Average maximum shear stresses at a radius of 30 mm for both 5 and 10 mm gaps are presented in Figure 5-7. Maximum shear stress values for both gaps follow a power law relationship for blade rotational speeds between 100 and 500 rpm. In addition, maximum shear stress values for the 5 mm gap are not appreciably larger than the 10 mm gap for the blade rotational speeds studied.

5.2.2 Cross Flow Membrane Module

Six steady state simulations were performed at varying cross flow velocities between 0.25 and 1.5 m/s for the cross flow apparatus presented in Section 4.3. Continuity, velocity and turbulence residuals for the 0.5 m/s simulation are illustrated in Figure 5-8. Residuals decreased monotonically to the convergence criterion of 0.01 % in approximately 500 iterations. Similar residual and convergence plots were obtained for all other cross flow simulations.

Velocity and shear stress results at a line located on the membrane surface at one-half the module length are presented in Figure 5-9. Shear stress is relatively constant across the complete cross section for each crossflow velocity. Shear stress also increases

with increasing cross flow velocities. Figure 5-10 summarizes the relationship between average shear stress at the results section and cross flow velocity.

Figure 5-6 Long term simulation average shear stress

Figure 5-7 Maximum shear stress at varying blade velocities

Figure 5-8 Simulation residuals for cross flow velocity of 0.5 m/s

Figure 5-9 Cross flow shear stress at varying cross flow velocities

Figure 5-10 Shear stress at varying cross flow velocities

5.3 Membrane Fouling Evaluation

5.3.1 Filtration Module Hydrodynamic Characterization

Four stirred cell and crossflow filtration tests were performed at different shear and pressure conditions for each sample. Table 5-2 provides a legend that identifies each test and their corresponding shear and pressure conditions.

Maximum shear for stirred cell and cross flow modules was estimated using the relationship established in Figure 5-7. Actual maximum shear stress values corresponding to the blade rotational speeds and crossflow velocities used in the filtration tests are given in Table 5-3. For the stirred cell module, the maximum shear at a radius of 30 mm was used to characterize the average shear conditions during the test. This radius was chosen because it is located in the middle of the effective filtration area. In addition, while CFD estimated shear stress temporal variations, maximum shear was used because it best characterized maximum particle transport away from membrane surface that limits filtration flux. Cross flow shear stress was estimated using the relationship established in Figure 5-10.

Filtration tests were conducted at high and low pressure conditions of 69 and 207 kPa respectively. All stirred cell and crossflow tests at 207 kPa were performed at shear stress conditions of 1.0 and 2.9 Pa respectively. Shear stress conditions for tests at 69 kPa varied and are listed in Table 5-4. The crossflow velocity, and consequently shear stress, was increased after the first two filtration tests due to frequent apparatus clogging. Reliable operation of the cross flow apparatus was difficult at low cross flow velocities

and did not occur at the higher velocities. The same problem was not encountered at 207 kPa because the increased driving pressure inhibited small particle clogging by increasing the fluid recirculation velocity.

Cross flow and stirred cell flux values were temperature corrected by adjusting the water viscosity, according to Roorda and van der Graaf (2001), using the following equation:

$$\frac{\eta_{20}}{\eta_T} = \frac{(T + 42.5)^{1.5}}{(20 + 42.5)^{1.5}} \quad (5-2)$$

where η_{20} = water viscosity at 20°C, η_T = water viscosity at wastewater test temperature (°C), T = wastewater test temperature (°C). The adjusted filtration flux at 20°C, J_{20} , was obtained by multiplying the measured permeate flux, J_T , by the reciprocal of the left hand side of Equation 5-2.

5.3.2 Stirred Cell Membrane Filtration Tests

Stirred cell permeate flux decline curves with time for sample 12 are illustrated in Figures 5-11 to 5-12 for filtration times of 500 and 2700 s respectively. Rapid permeate flux decline occurs from 1600 to 100 L/(m²h) during the first 100 s of filtration time. Permeate flux then gradually decreases from approximately 100 L/(m²h) to between 30 and 50 L/(m²h) during the remaining 2600 s. Similar flux decline patterns were observed for all other stirred cell filtration tests.

Steady state permeate flux after 45 min (2700 s) filtration time were used to measure the relative fouling potential of different samples. This procedure is similar to the fouling assessment method suggested by Rosenberger and Kraume (2002) who used

permeate flux after 40 min filtration time. They evaluated five different fouling indices, three of which measured variables after a defined permeate flux volume (ex. 100 mL) while the remaining two measured permeate flux and sludge resistance after 40 min filtration time. Permeate flux after 40 min was chosen as a preferred fouling index because the permeate flux volume beyond which filtration was stable varied greatly for low and high filterability sludges. Table 5-5 summarizes steady state flux for all samples and testing conditions. MBR sample ID's are from 1 to 8 inclusive while all others are activated sludge samples. Steady state fluxes ranged from 17 to 115 L/m²h, which are comparable to permeability values summarized by Chang *et al.* (2002) of approximately 60 to 80 L/m²h/bar for tests on activated sludge at similar shear conditions. Average steady state fluxes for MBR and AS wastewaters were 42 and 71 L/m²h respectively and is perhaps due to higher soluble organic compound concentrations, which is further discussed in section 5.4.

Figure 5-13 illustrates steady state fluxes were generally independent of transmembrane pressure for the range of shear stresses in this study. Data points are presented on the x-axis in order of sample date, not consecutive sample ID. Higher transmembrane pressures did not significantly increase steady state flux. Defrance and Jaffrin (1999a) similarly reported that at a cross flow velocity of 1 m/s, flux stabilized at approximately 20 L/m²h when transmembrane pressure was increased beyond 20 kPa. Since both cross flow and stirred cell filtration tests operated at constant pressure, initial permeate flux was much higher than the critical flux for all tests. Therefore, the pressure independent behaviour of steady state fluxes observed was due to operation above the

critical flux since by definition, increases in transmembrane pressure will not correlate to increases in permeate flux for fluxes above the critical flux.

5.3.2.1 *Specific Cake Resistance*

Specific cake resistance (SCR) values were estimated by plotting t/V vs. V obtained from both stirred cell and Buchner Funnel (BF) filtration tests. The slope of the linear portion after initial filtration is used to estimate the SCR using Equation 2-2. Linear regressions were used to obtain slope estimates for all 48 stirred cell tests using Excel. Figure 5-14 illustrates the procedure for sample ID 9. Permeate volume was multiplied by actual sample MLSS concentrations to estimate the dry mass of cake solids, c , in Equation 2-2. The transmembrane pressure was estimated as approximately equal to the filtration test operating pressure since direct pressure measurements on the permeate tubing were not available. However, during the cake filtration phase, permeate velocities were not greater than 0.01 m/s, which approximately correspond to pressure heads less than 0.1 Pa.

Table 5-2 Filtration test condition legend

Filtration Test Legend			
		Dead End	Crossflow
69 kPa	low shear	DE1	XF1
	high shear	DE2	XF2
207 kPa	low shear	DE3	XF3
	high shear	DE4	XF4

Table 5-3 Actual maximum shear values for cross flow and stirred cell tests

Dead End	
Blade Speed	Shear Stress
(rpm)	(Pa)
126	0.59
170	0.96
178	1.03
230	1.58
285	2.29
328	2.92
Crossflow	
Crossflow Velocity	Shear Stress
(m/s)	(Pa)
0.19	0.58
0.29	1.03
0.39	1.59
0.50	2.32
0.58	2.93

Table 5-4 Shear stress conditions for 69 kPa filtration tests

Sample ID	Description	Shear Stress (Pa)			
		DE1	DE2	XF1	XF2
1	WTC, Burlington, ON (WW1)	0.6	1.6	0.6	1.6
2	Creemore, ON	0.6	1.6	1.0	2.2
3	Port McNicoll, ON	0.6	1.6	1.0	2.2
4	WTC, Burlington, ON (WW2)	0.6	1.6	0.9	2.3
5	WTC, Burlington, ON (WW2)	1.0	2.3	0.9	2.3
6	Guelph Pilot 1, No Coagulant	1.0	2.3	0.9	2.3
7	Guelph Pilot 1, No Coagulant	1.0	2.3	0.9	2.3
8	Guelph Pilot 2, Coagulant	1.0	2.3	0.9	2.3
9	Guelph, ON	0.6	1.6	0.6	1.6
10	Ashbridges Bay, Toronto, ON	1.0	2.3	0.9	2.3
11	Burlington, ON	1.0	2.3	0.9	2.3
12	Kitchener, ON	1.0	2.3	0.9	2.3

Figure 5-11 Initial permeate flux decline versus time for sample 12 stirred cell tests

Figure 5-12 Permeate flux decline versus time for sample 12 stirred cell tests

Table 5-5 Steady state filtration flux after 45 min filtration time for stirred cell tests

Sample ID	DE1	DE2	DE3	DE4
1	42	38	52	57
2	49	47	57	57
3	64	52	57	66
4	57	63	72	75
5	30	41	28	52
6	19	23	17	27
7	18	25	22	32
8	22	28	18	27
9	68	73	73	87
10	65	69	54	79
11	95	93	115	95
12	32	50	40	55

Figure 5-13 Steady state flux at varying sample ID for stirred cell tests

Figure 5-14 Specific cake resistance calculation procedure

Figure 5-15 Specific cake resistance by sample ID

Figure 5-16 Permeate flux decline versus time for sample 12 cross flow tests

Table 5-6 Steady state filtration flux after 45 min filtration time for cross flow tests

Sample ID	XF1	XF2	XF3	XF4
1	15	29	16	24
2	15	29	16	23
3	16	20	12	14
4	14	27	18	24
5	7	16	16	17
6	6	16	7	11
7	9	11	8	12
8	7	8	8	12
9	15	17	15	23
10	14	20	14	14
11	9	13	17	18
12	8	9	7	10

Figure 5-17 Steady state flux at varying sample ID for cross flow tests

Specific cake resistance for all samples were plotted in Figure 5-15. SCR data obtained by the Buchner Funnel (BF) method (Standard Methods 1992), with no membrane shear stress and a 1.5 μm pore size, is included for comparison. SCR values for all stirred cell filtration tests range from approximately 2×10^{12} to 2×10^{14} m/kg. This compares to values reported by Lee *et al.* (2001) of approximately 10^{11} to 10^{14} m/kg for MBR sludge and membrane pore size of 0.1 μm . In general, SCR from BF tests were lower than those obtained from stirred cell membrane filtration tests because of the effects of mixing. This was particularly true for samples 5, 6, 7, 8, 9 and 11 which had SCR values between one and two orders of magnitude lower than corresponding stirred cell SCR values.

5.3.3 Crossflow Membrane Filtration Tests

Flux decline curves versus time are shown in Figure 5-16 for sample ID 12. Similar plots were obtained for other samples. Note that initial rapid flux decline is not observed because permeate tubing could not be pre-filled, as discussed in section 4.3. Specific cake resistance estimates could not be accurately obtained because permeate flux for each unit was measured alternately for each of the two operating units. Thus, total cumulative filtration volume data was not available. Theoretically, the cross flow flux decline curve could be integrated to obtain total cumulative filtration volume for each test. However, cross flow flux decline behaviour was not stable and integration of the flux decline curve would not result in accurate cumulative filtration volume estimates. Table 5-6 lists steady state flux values for all cross flow filtration tests. Steady state flux values range from 6 to 29 L/m²h. For sidestream filtration module configurations

operating at similar transmembrane pressures, reported permeate flux varies widely from 8 to 150 L/m²h (Chang *et al.* 2003). Thus, cross flow fluxes measured agree with the lower range of fluxes reported in the literature. Figure 5-17 presents steady state flux by sample ID. Increasing transmembrane pressures do not correspond to increased permeate fluxes, suggesting that the pressure independent behaviour of permeate flux observed in the stirred cell tests is also valid for cross flow filtration tests.

5.3.4 Comparison of Stirred Cell and Cross Flow Systems

Steady state flux is plotted against shear stress for both filtration modules in Figures 5-18 and 5-19 for MBR and AS samples together. Cross flow permeate fluxes were consistently lower than stirred cell permeate fluxes with values between 6-29 L/m²h and 17-115 L/m²h respectively. The major difference between the two modules is the behaviour of shear stress at the membrane surface. Shear in the stirred cell module approximates a sinusoidal variation while cross flow shear stress is constant. Since the stirred cell and cross flow maximum shear stresses are equal, the variation in shear is likely more important in limiting permeate flux than the maximum value. Hong *et al.* (2002) observed a similar phenomenon whereby cake relaxation, by alternating filtration ON and OFF durations, significantly reduces membrane fouling compared to a system that operates continuously. Permeate flux was continuous for both systems studied but the shear variation would subject the cake to varying pressure gradients reduce fouling. The filtration cake on the membrane surface is more likely to consolidate and stabilize when subjected to constant shear stress. Thus, the cake thickness will

constantly adjust when subjected to varying shear stress, resulting in a lower porosity cake that leads higher permeate fluxes.

Based on Figures 5-18 and 5-19, there is no constant relationship between cross flow and stirred cell fluxes applicable to all samples. Since no unifying relationship between cross flow and stirred cell steady state fluxes exists, results will now be compared for each specific sample. Table 5-7 presents the ratio of stirred cell and cross flow steady state fluxes for each test condition. While results are not conclusive, it appears more likely that there may be a relationship between stirred cell and cross flow fluxes when examining a particular sample. For instance, ratios appear to be constant for 207 kPa tests for samples 4 and 9-12. Filtration tests at 69 kPa exhibit increased variability and no relationship between stirred cell and cross flow fluxes are evident for any samples. This suggests that sample characteristics are the most important variable in determining steady state flux values.

Figure 5-18 Steady state permeate flux at 69 kPa transmembrane pressure

Figure 5-19 Steady state permeate flux at 207 kPa transmembrane pressure

Table 5-7 Ratio of stirred cell and cross flow fluxes at varying test conditions

Sample ID	69 kPa		207 kPa	
	low shear	high shear	low shear	high shear
1	3.4	1.6	3.6	2.4
2	3.9	2.6	4.9	4.8
3	3.9	2.4	4.0	3.1
4	4.3	2.6	1.7	3.1
5	1.9	2.3	2.8	2.6
6	4.7	4.2	5.0	3.7
7	4.6	3.4	3.8	5.8
8	10.4	7.2	6.8	5.4
9	2.9	1.3	3.3	2.4
10	3.2	1.5	2.5	2.5
11	3.1	3.5	2.3	2.3
12	3.9	5.6	5.5	5.7

5.4 Effects of Mixed Liquor Characteristics on Membrane Fouling

Mixed liquor characteristics for MBR and AS samples are presented in this section. As well, since steady state fluxes were little affected by the transmembrane pressure as compared to shear stress, low and high pressure steady state permeate fluxes were pooled together using identical symbols in the following flux plots.

5.4.1 Sludge Solids

Sludge characterization parameters are given in Table 5-8. Soluble variables were obtained by performing the respective analytical procedures on wastewater filtered through a 1.5 μm filter paper. MBR samples had much higher TSS, VSS and COD than AS samples. This is reasonable since MBR's commonly operate at higher SRT conditions leading to higher TSS values. No significant difference was present for either sCOD or sTOC. This is important since the higher TSS values did not correspond to larger soluble organic matter concentrations.

Figures 5-20 and 5-21 compare steady state flux at different VSS values. Plots of flux and TSS were similar and not included. Additionally, Pearson product moment correlations, using the statistical software package S-PLUS v6.2, were performed and are presented in Table 5-9. No significant correlation exists between flux and either TSS or VSS. These conclusions are in agreement with results reported by Lubbecke *et al.* (1995); Rosenberger and Kraume (2002); Le-Clech *et al.* (2003) and Hong *et al.* (2002). Therefore, the higher TSS values present in most MBR systems do not directly contribute to higher membrane fouling.

Figures 5-22 to 5-25 present flux versus two measures of soluble organic matter, sCOD and sTOC, and Pearson product moment correlations are given in Table 5-10. A suspected outlier with sCOD of 169 mg/L for both stirred cell and cross flow tests was omitted from the correlation. At a significance level of 0.05, sCOD and steady state flux for all stirred cell tests have an average negative correlation of 0.78 while no significant correlation exists for cross flow test. Additionally, sTOC is negatively correlated to steady state stirred cell flux at a similar level (0.80) while only two of four cross flow tests exhibit significant relationships (0.77). Therefore, soluble organic matter, as measured by TOC and COD, negatively affects steady state filtration flux. Harada, *et al.* (1994) and Nagoaka *et al.* (1996) also reported increased membrane fouling with increases in sCOD and sTOC respectively. Significant negative correlations were obtained for all 8 stirred cell tests and only 2 of 8 cross flow tests. Thus, modified stirred cell experiments better characterize membrane fouling caused by soluble organic compounds such as sCOD and sTOC, compared to cross flow filtration.

Table 5-8 Wastewater sample characterization

Sample ID	TSS	VSS	sCOD	COD	sTOC	TN
	(g/L)	(g/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
1	14.0	9.6	169	18400	26	9
2	19.1	13.0			11	
3	16.5	10.3	15	15800	11	4
4	12.9	8.5	53	12200	26	6
5	10.7	7.3	102	6400	67	26
6	11.8	7.7			76	35
7	8.7	5.6	112	8400	57	44
8	9.9	6.5	101	10000	62	30
9	3.1	2.4	51		27	12
10	1.1	0.8	60	1100	17	31
11	2.2	1.8	26	3100	7	17
12	3.4	2.5	50	3150	34	33

Figure 5-20 Steady state flux versus VSS for stirred cell

Figure 5-21 Steady state flux versus VSS for cross flow

Table 5-9 Flux correlations with TSS and VSS

	TSS (g/L)		VSS (g/L)	
	r	p	r	p
DE1	-0.30	0.342	-0.29	0.355
DE2	-0.51	0.090	0.36	0.355
DE3	-0.27	0.401	-0.25	-0.248
DE4	-0.40	0.197	-0.39	0.216
XF1	0.40	0.401	0.26	0.255
XF2	0.57	0.572	0.60	0.598
XF3	0.57	0.572	0.18	0.585
XF4	0.57	0.572	0.31	0.329

Figure 5-22 Steady state flux versus sCOD for stirred cell

Figure 5-23 Steady state flux versus sCOD for cross flow

Figure 5-24 Steady state flux versus sTOC for stirred cell

Figure 5-25 Steady state flux versus sTOC for cross flow

Table 5-10 Flux correlations with sCOD and sTOC

	sCOD (mg/L)		sTOC (mg/L)	
	r	p	r	p
DE1	-0.82	0.006	-0.84	0.001
DE2	-0.76	0.019	-0.75	0.005
DE3	-0.78	0.013	-0.82	0.001
DE4	-0.77	0.015	-0.80	0.002
XF1	-0.62	0.076	-0.78	0.003
XF2	-0.41	0.278	-0.50	0.101
XF3	-0.65	0.060	-0.76	0.004
XF4	-0.39	0.295	-0.57	0.052

Table 5-11 Surface properties for all samples

Sample ID	Hydrophobicity	Surface Charge	Surface Charge
	(%)	(meq/gVSS)	(meq/L)
1	40%	-0.90	-8.63
2	56%	-0.42	-5.49
3	13%	-0.96	-9.94
4	47%	-0.87	-7.37
5	45%	-1.02	-7.41
6	34%	-1.14	-8.80
7	47%	-1.49	-8.38
8	34%	-1.51	-9.81
9	72%	-0.37	-0.88
10	46%	-2.84	-2.36
11	39%	-1.78	-3.20
12	39%	-3.00	-7.36

5.4.2 Sludge Surface Properties

Sludge hydrophobicity and surface charge results for MBR and AS samples are shown in Table 5-11 below. Surface charge results are expressed in meq/gVSS and meq/L. There is no significant difference between MBR and AS samples, using the t-test, for hydrophobicity and surface charge expressed as meq/gVSS. Significant statistical differences exist between MBR and AS samples when surface charge is expressed as meq/L because MBR samples contained much higher VSS solids.

Steady state flux is plotted against surface charge, both in meq/L and meq/gVSS, and hydrophobicity for all samples in Figures 26-31. Additionally, Pearson product moment correlations are given in Table 5-12. At a significance level of 0.05, stirred cell steady state flux has an average positive correlation of 0.71 to surface charge expressed in meq/L. In other words, the steady state flux tends to increase with increasing sludge surface charge. Previous research by Lee *et al.* (2003) contradicts this finding since they determined that filtration resistance increases, or flux decreases, with increasing sludge surface charge. Choi *et al.* (2003) also demonstrated larger absolute surface charges result in higher permeate fluxes. While the research by Choi *et al.* (2003) was with pure microsphere suspensions in water, larger surface charges should increase repulsive forces in the cake and therefore lead to higher permeate fluxes. On the other hand, larger surface charges stabilize the particle suspension in water. It is well known that smaller particles could cause more membrane fouling as compared to large ones. The phenomena of higher permeate flux with smaller surface charge observed in this study is likely explained by the reduced concentrations of small particles at low surface charges.

The same correlation was not observed when cross flow fluxes were compared to surface charge, both in meq/L and meq/gVSS, again suggesting stirred cell tests are more sensitive to sludge characteristics compared to cross flow tests. Hydrophobicity is not related to steady state flux for either of the modules and therefore not useful for characterizing sludge filtration performance.

Figure 5-26 Steady state flux versus hydrophobicity for stirred cell

Figure 5-27 Steady state flux versus hydrophobicity for cross flow

Figure 5-28 Steady state flux versus surface charge in meq/L for stirred cell

Figure 5-29 Steady state flux versus surface charge in meq/L for cross flow

Figure 5-30 Steady state flux versus surface charge in meq/gVSS for stirred cell

Figure 5-31 Steady state flux versus surface charge in meq/gVSS for cross flow

Table 5-12 Flux correlations with surface properties

	Surface Charge (meq/L)		Surface Charge (meq/gVSS)		Hydrophobicity	
	r	p	r	p	r	p
DE1	0.67	0.017	0.02	0.945	0.12	0.711
DE2	0.78	0.003	-0.14	0.674	0.27	0.393
DE3	0.62	0.031	0.08	0.810	0.20	0.539
DE4	0.75	0.005	-0.02	0.954	0.30	0.345
XF1	0.29	0.362	0.32	0.318	0.15	0.652
XF2	0.09	0.781	0.52	0.085	0.17	0.590
XF3	0.39	0.215	0.41	0.191	0.27	0.390
XF4	0.37	0.237	0.61	0.037	0.51	0.092

Table 5-13 SVI and Buchner funnel SCR for all samples

Sample ID	SVI	SCR
	(mL/g)	(m/kg)
1	111	4.3E+12
2	63	2.6E+12
3	97	4.8E+12
4	100	2.6E+12
5	94	3.0E+12
6	72	8.4E+12
7	88	8.1E+12
8	101	7.1E+12
9	54	2.9E+11
10	162	3.6E+13
11	81	2.3E+11
12	258	5.3E+13

Figure 5-32 Steady state flux versus SVI for stirred cell

Figure 5-33 Steady state flux versus SVI for cross flow

Figure 5-34 Steady state flux versus Buchner funnel SCR for stirred cell

Figure 5-35 Steady state flux versus Buchner funnel SCR for cross flow

Table 5-14 Flux correlations for SVI and Buchner funnel SCR

	SVI (mL/g)		SCR (m/kg)	
	r	p	r	p
DE1	-0.14	0.662	-0.06	0.853
DE2	0.03	0.930	0.02	0.944
DE3	-0.15	0.649	-0.23	0.470
DE4	-0.01	0.980	0.00	0.988
XF1	-0.13	0.679	0.03	0.937
XF2	-0.29	0.355	-0.14	0.657
XF3	-0.33	0.291	-0.37	0.239
XF4	-0.43	0.164	-0.42	0.172

5.4.3 SVI and SCR

Sludge volume index, SVI and specific cake resistance data are presented in Table 5-13. Figures 5-32 to 5-35 compare steady state flux to SVI and SCR. Detailed correlation coefficients and associated p-values are given in Table 5-14. There is no significant correlation between any steady state fluxes and either SVI or SCR values. While SVI has been widely used to predict sludge settling efficiency, it is of limited value for predicting permeate flux for these modules. This is because SVI measures sludge settlement in the absence of a driving pressure. Specific cake resistance, as measured by the Buchner Funnel method, does not provide any predictive value for permeate flux since cake formation and compaction with and without shear stress are not comparable.

5.4.4 Particle Size Distribution

Particle size distribution results are presented as volume percentage by particle diameter. Figures 5-36 and 5-37 and Table 5-15 present particle size distribution results for MBR and AS samples separately. In general, MBR samples had smaller average particle sizes due to higher TSS concentrations except for sample 12, which had a median size of 35 μm , much smaller than the average of samples 9, 10 and 11.

MBR samples are composed of a larger proportion of smaller particles compared to AS samples. In particular, the 10th percentile particle size for six of seven MBR samples is approximately 10 μm , while for AS samples it ranges from 10 to 40 μm . A smaller 10th percentile particle diameter correlates to larger numbers of small particles present in the wastewater matrix.

Flux was plotted against median, average and 10th percentile particle size and no significant relationship was evident. Pearson product moment correlations were calculated and given in Table 5-16 . Surprisingly, only stirred cell filtration tests two and four were significantly correlated to wastewater particle size at with values between 0.60 to 0.65. A positive correlation between particle size and permeate flux is reasonable since cake porosity is increased with increasing average particle size. Previous research has suggested smaller particles may disproportionately negatively affect filtration, or permeate flux. Specifically, Shimizu *et al.* (1997) found particles between 8 and 15 μm had a greater affect on filtration than average particle size. Also, Choi *et al.* (2003) found particle diameters close to 2 μm tended to remain near the membrane surface after backwashing due to preferential removal of particles greater than 10 μm .

Flux was plotted against several particle size ranges to examine relationships between flux and the volume percentage of small particle sizes, or particles less than 21.1 μm for this analysis. Particle size ranges examined were between 0.1 and 1.0 μm , 1.0 and 2.6 μm , 0.1 and 2.6 μm , 0.1 and 21.1 μm and finally 7.5 and 14.9 μm . Suspected outliers, the minimum and maximum percentage values, were deleted before performing the correlation. No relationships were found between any particle size range and cross flow flux. The clearest relationship between flux and particle size are evident in Figure 5-38 and Table 5-17 and correspond to particles between 1 and 2.6 μm . Increasing proportions of smaller particles correlated to lower steady state permeate fluxes. This is reasonable since an increased number of small particles similar to the membrane pore

size of 0.22 μm will increase both specific cake resistance and pore clogging (Song 1998).

Figure 5-36 Particle size distributions for AS samples

Figure 5-37 Particle size distributions for MBR samples

Table 5-15 Particle size parameters for all samples

Sample ID	Mean	Median	Mode	Std. Dev.	% less than			
					10	25	75	90
1	57	31	35	124	11	19	48	79
2	46	25	29	107	9	15	38	56
3	36	19	19	81	8	12	30	52
5	90	55	55	158	18	32	92	155
6	45	33	38	62	10	19	52	79
7	41	32	38	42	10	18	52	78
8	37	32	38	28	10	19	48	69
9	149	144	185	91	40	85	197	249
10	98	67	71	149	21	41	105	161
11	79	67	73	63	19	44	101	141
12	46	35	38	37	10	19	61	99

Table 5-16 Flux correlations for particle size parameters

	Mean		Median		Mode		10 th Percentile	
	r	p	r	p	r	p	r	p
DE1	0.50	0.119	0.478	0.137	0.436	0.181	0.50	0.114
DE2	0.62	0.041	0.610	0.046	0.556	0.076	0.62	0.040
DE3	0.44	0.175	0.452	0.163	0.418	0.201	0.46	0.153
DE4	0.67	0.024	0.624	0.040	0.575	0.065	0.65	0.029
XF1	0.24	0.470	0.180	0.596	0.198	0.560	0.23	0.497
XF2	0.08	0.809	-0.077	0.821	-0.072	0.833	-0.02	0.954
XF3	0.27	0.426	0.278	0.408	0.288	0.390	0.29	0.383
XF4	0.37	0.256	0.408	0.272	0.397	0.227	0.38	0.248
	25 th Perc.		75 th Perc.		90 th Perc.			
	r	p	r	p	r	p		
DE1	0.53	0.094	0.469	0.146	0.446	0.169		
DE2	0.65	0.030	0.620	0.042	0.616	0.044		
DE3	0.50	0.114	0.437	0.179	0.402	0.220		
DE4	0.66	0.026	0.629	0.038	0.630	0.038		
XF1	0.20	0.562	0.135	0.692	0.093	0.785		
XF2	-0.06	0.865	-0.108	0.752	-0.108	0.751		
XF3	0.32	0.333	0.223	0.509	0.145	0.670		
XF4	0.39	0.242	0.301	0.368	0.222	0.513

Figure 5-38 Steady state flux versus particle size volume percentage between 1 and 2.6 μm

Table 5-17 Flux correlations for particle sizes between 1 and 2.6 μm

	1 μm <x<2.6 μm (%)	
	r	p
DE1	-0.68	0.045
DE2	-0.74	0.024
DE3	-0.58	0.103
DE4	-0.83	0.006

5.4.5 EPS

Standard curves for total carbohydrates, acidic polysaccharides, protein, humic acid and lipids analysis are presented in Appendix D. Tables 5-18 and 5-19 present the total amounts of extracted and dissolved EPS respectively. Extracted and dissolved activated sludge EPS levels, expressed in mg/gVSS, are not significantly different from MBR samples with the exception of higher lipid levels in the AS samples. Lipids are omitted from total extracted EPS to allow for comparison between dissolved EPS and previously reported EPS results.

EPS extraction data for MBR and AS samples are compared to averages obtained from Liu and Fang (2003) in Table 5-20. Reported MBR and AS EPS concentrations are averages of measured data in this study. The DOWEX[®] and Centrif. averages are based on the review by Liu and Fang (2003). Total extractable EPS from MBR and AS samples are less than the reported average. However, two large extraction values in Liu and Fang (2003), 373 mg/gVSS and 629 mg/gVSS, positively skewed the average. Median total EPS from Liu and Fang (2003) is 114 mg/gVSS and is comparable to 92 mg/gVSS and 75 mg/gVSS for AS and MBR samples respectively. Total dissolved EPS was 17.2 mg/gVSS and 9.1 mg/gVSS for AS and MBR samples respectively and represents approximately 10 – 20 % of total EPS values. Median dissolved EPS from Liu and Fang (2003) is 19.5 mg/gVSS and is comparable to results obtained from this study.

Table 5-18 Extracted EPS in mg/gVSS

Sample ID	Carbs.	Protein	Humic	Acidic Poly.	Lipids	Total EPS
1	8.7	31.0	10.4	3.0	24.4	53.1
2	11.6	43.2	15.6	2.4	30.5	72.8
3	6.1	41.4	12.6	2.4	27.3	62.5
4	10.3	53.9	19.7	3.9	33.0	87.8
5	7.3	49.4	15.8	5.5	37.5	78.0
6	10.7	25.0	40.2	2.5	33.7	78.3
7	16.6	46.0	21.6	0.0	21.4	84.2
8	12.6	52.9	17.0	2.9	34.8	85.5
9	14.5	57.5	38.2	4.0	68.3	114.3
10	10.4	72.1	15.3	0.0	62.9	97.8
11	21.2	44.7	13.0	1.8	39.9	80.8
12	15.4	47.1	12.6	0.0	47.7	75.0

Table 5-19 Dissolved EPS in mg/gVSS

Sample ID	Carbs.	Protein	Humic	Acidic Poly.	Total EPS
1	0.7	1.1	1.9	0.0	3.7
2	0.5	0.0	2.6	0.0	3.1
3	0.0	2.2	1.6	0.3	4.2
4	0.9	1.5	3.9	0.2	6.4
5	1.8	5.0	3.8	0.2	10.8
6	3.6	2.5	9.1	0.0	15.1
7	7.5	9.1	1.8	0.0	18.4
8	3.4	0.0	7.2	0.5	11.0
9	0.0	2.3	7.3	0.2	9.8
10	1.3	2.8	5.9	0.0	10.0
11	4.2	12.9	6.6	1.4	25.1
12	2.4	2.6	18.4	0.5	23.8

Table 5-20 Extraction efficiency comparison between results and reported values (Averages from Liu and Fang (2003))

Sample Type	Carbs	Protein	Humic	Acidic Poly.	Lipids	Total EPS
Extracted EPS						
AS	15.4	55.4	19.8	1.5	54.7	92.0
MBR	10.5	42.8	19.1	2.8	30.3	75.3
DOWEX Average	34.8	89.0	52.6	5.0	-	181.3
Dissolved EPS						
AS	2.0	5.2	9.5	0.5	-	17.2
MBR	2.3	2.7	4.0	0.1	-	9.1
Centrif. Average	4.5	5.5	4.6	0.4	-	19.5

Table 5-21 EPS composition comparison between results and reported values (Averages from Liu and Fang (2003))

Sample Type	Carbs	Protein	Humic	Acidic Poly.
Extracted EPS				
AS	17%	60%	21%	2%
MBR	14%	57%	25%	4%
DOWEX Average	19%	49%	29%	3%
Dissolved EPS				
AS	11%	30%	56%	3%
MBR	25%	29%	44%	2%
Centrif. Average	23%	28%	23%	2%

Average extractable EPS compositions for MBR and AS samples obtained in this study are similar to average reported compositions for the DOWEX[®] extraction method from Liu and Fang (2003) (See Table 5-21). Protein was the largest component followed by humic acid, carbohydrates and acidic polysaccharides respectively. For dissolved EPS, both AS and MBR samples have an average protein content around 30 %. However, AS samples have lower total carbohydrate compositions, expressed as mg/gVSS, compared to MBR samples. Humic acid averages around 50 % of dissolved EPS for both MBR and AS samples, which is much larger than the reported 23 %. However, only one study (Liu and Fang 2002) used centrifugation and also quantified humic acid concentrations.

Steady state flux for stirred cell and cross flow tests are plotted against total carbohydrates for dissolved EPS in Figures 5-40 and 5-41. Figure 5-40 suggests that total dissolved carbohydrates negatively affects steady state permeate flux. Tables 5-24 and 5-25 summarize pearson correlations between all dissolved and extracted EPS constituents and steady state flux. Data points corresponding to 17.7 mg/L of total carbohydrates, sample ID 11, are suspected outliers since all other data fit the same trend. Therefore, sample 11 was omitted from the correlations in Tables 5-22 and 5-23. Increasing total carbohydrate concentrations negatively affect steady state permeate flux for all flux tests with a clearer relationship evident for stirred cell filtration tests having an average negative correlation of 0.84. In particular, steady state flux decreases approximately 70 % for total carbohydrate concentrations from 0 to 20 mg/L for stirred cell filtration tests. Flux above 20 mg/L is independent of carbohydrate concentrations.

Harada *et al.* (1994) and Nagoaka *et al.* (1996) also reported increases in filtration resistance (decreasing flux) due to increasing organic carbon fraction expressed as soluble COD and supernatant TOC values respectively. Additionally, Jarusutthirak *et al.* (2002) observed polysaccharides played an important role in UF and NF fouling.

Flux versus dissolved protein is plotted for stirred cell tests in Figure 5-39. No relation was evident for dissolved protein and cross flow flux as well as both extracted protein plots. For the stirred cell tests, a peak in permeate flux may be evident at approximately 20 mg/L protein concentration but results are not conclusive. No statistically significant correlations exist for dissolved protein and stirred cell tests. Lee *et al.* (2003) postulated floc hydraulic resistance is increased with changes in the protein to carbohydrate ratio. As is evident from Figures 5-42 and 5-43, no such relationship exists for samples in this study for either dissolved or extracted protein/carbohydrate ratios. However, Lee *et al.* (2003) also suggested that EPS composition is more important than the total amount. Results show that the flux relationship to carbohydrates, but not to protein, confirms that EPS composition is important in membrane fouling.

Figure 5-39 Steady state flux versus dissolved protein for stirred cell

Figure 5-40 Steady state flux versus dissolved total carbohydrates for stirred cell

Figure 5-41 Steady state flux versus dissolved total carbohydrates for cross flow

Table 5-22 Flux correlations for extracted EPS expressed as mg/L

	Carbohydrates		Protein		Humic	
	r	p	r	p	r	p
DE1	-0.31	0.359	0.03	0.932	-0.32	0.330
DE2	-0.48	0.131	-0.17	0.613	-0.48	0.133
DE3	-0.11	0.744	0.14	0.678	-0.24	0.470
DE4	-0.43	0.186	-0.11	0.753	-0.45	0.165
XF1	0.02	0.949	0.24	0.469	-0.22	0.510
XF2	0.38	0.251	0.50	0.120	0.22	0.525
XF3	0.32	0.341	0.41	0.211	0.05	0.879
XF4	0.36	0.275	0.38	0.243	0.10	0.765
	Acidic Poly.		Lipids		Total EPS	
	r	p	r	p	r	p
DE1	-0.16	0.651	0.50	0.114	0.05	0.874
DE2	-0.34	0.339	0.46	0.157	-0.14	0.676
DE3	-0.03	0.926	0.59	0.054	0.19	0.566
DE4	-0.20	0.580	0.49	0.128	-0.08	0.822
XF1	0.03	0.931	0.41	0.213	0.21	0.534
XF2	0.50	0.144	0.43	0.186	0.54	0.085
XF3	0.26	0.473	0.53	0.090	0.47	0.149
XF4	0.33	0.358	0.64	0.034	0.51	0.110

Table 5-23 Flux correlations for dissolved EPS expressed as mg/L

	Carbohydrates		Protein		Humic	
	r	p	r	p	r	p
DE1	-0.87	0.001	-0.32	0.345	-0.22	0.509
DE2	-0.81	0.002	-0.32	0.341	0.07	0.846
DE3	-0.81	0.002	-0.33	0.324	-0.18	0.591
DE4	-0.85	0.001	-0.24	0.475	-0.08	0.822
XF1	-0.71	0.014	-0.23	0.491	-0.47	0.145
XF2	-0.55	0.077	-0.25	0.462	-0.57	0.069
XF3	-0.57	0.068	-0.37	0.260	-0.41	0.205
XF4	-0.50	0.113	-0.33	0.327	-0.42	0.195
	Acidic Poly.		Total EPS			
	r	p	r	p		
DE1	0.18	0.603	-0.50	0.113		
DE2	0.12	0.716	-0.42	0.195		
DE3	0.08	0.819	-0.45	0.161		
DE4	0.07	0.842	-0.42	0.203		
XF1	0.04	0.903	-0.35	0.294		
XF2	-0.30	0.371	-0.48	0.134		
XF3	-0.06	0.859	-0.42	0.199		
XF4	-0.17	0.624	-0.39	0.239

Figure 5-42 Steady state flux versus dissolved protein/carb. ratio for stirred cell

Figure 5-43 Steady state flux versus extracted protein/carb. ratio for stirred cell

Flux and humic acid concentrations, both dissolved and extracted, are plotted in Figures 5-44 to 5-46. No relationship between extracted humic acid and cross flow steady state flux is present. Referring to Tables 5-22 and 5-23, weak negative correlations with an average p value of 0.21 are present for the dissolved humic and cross flow tests and the extracted humic and stirred cell tests. This suggests increased humic acid concentrations may lead to decreased permeate flux but the relationship is not conclusive. Since no published studies have examined humic acid EPS concentration and membrane fouling, further work is necessary to confirm whether a relationship exists.

There is no relationship between steady state flux and either dissolved or extracted acidic polysaccharide concentrations in this study. No published studies examining the relationship between acidic polysaccharides and fouling have been available to date.

Figures 5-47 and 5-48 compare steady state flux and lipids concentration. Increasing amounts of extracted lipids in sludge samples is positively correlated with higher steady state flux values. The average correlation coefficient for stirred cell and cross flow tests combined is 0.50 with an average significance level of 0.122. Three of eight filtration tests have p values above the 90 % significance level. Bura (2000) established that lipids are a main component of EPS and no published studies are known to have examined the effects lipid EPS concentrations have on membrane fouling.

Total dissolved EPS and extracted EPS, without lipids, is plotted against steady state flux in Figures 5-49 to 5-51. Stirred cell tests and extracted EPS are not shown since no relationship is evident in Table 5-22. For both stirred cell and cross flow tests, a

weak negative correlation exists between total dissolved EPS and flux. Similar results were reported by Rosenberger and Kraume (2002) who found increasing suspended EPS, analogous to dissolved, resulted in lower filtration flux. This finding is reasonable and is probably due to increased amounts of dissolved total carbohydrate which would likely increase with higher dissolved EPS levels. No relationship was found between total extracted EPS and steady state flux using stirred cell test data but two of four cross flow tests showed significant correlations with p values of 0.085 and 0.110. No explanation can be given for this observation.

In summary, tables 5-24 and 5-25 summarize the effects sludge properties and EPS constituents have on membrane fouling. Relationships reported in the literature are included for comparison. The rating system is identical to the one used in section 2.4.7.

Figure 5-44 Steady state flux versus dissolved humic acid for stirred cell

Figure 5-45 Steady state flux versus dissolved humic acid for cross flow

Figure 5-46 Steady state flux versus extracted humic acid for stirred cell

Figure 5-47 Steady state flux versus extracted lipids for stirred cell

Figure 5-48 Steady state flux versus extracted lipids for cross flow

Figure 5-49 Steady state flux versus total dissolved EPS for stirred cell

Figure 5-50 Steady state flux versus total dissolved EPS for cross flow

Figure 5-51 Steady state flux versus total extracted EPS for stirred cell

Table 5-24 Comparison of sludge properties effects on membrane fouling between literature and thesis results

Sludge Property	Correlation		Comments
	Literature	Thesis	
Particle Size	--	--	# of small particles (ex. 8-15 um or 1-2.5 um)
MLSS	0	0	Valid for TSS < 24 - 30 g/L
SCR	INC	0	Based on Buchner Funnel tests
Hydrophobicity	-	0	No direct correlation evident, previous results probably a proxy of some other mechanism, ex. EPS concentration
SVI	n.d.	0	No relationship evident, therefore sludge settling and filtration due to different mechanisms
Surface Charge	-	+	Only one study

Table 5-25 Comparison of EPS effects on membrane fouling between literature and thesis results

EPS Constituent	Correlation		Comments
	Literature	Thesis	
Dissolved			
Total Carbohydrates	--	--	Direct measurement of total carbohydrates in solution
Protein	n.d.	0 to +	Subset of data suggests positive correlation but not conculsive
Humic Acid	n.d.	0 to +	Similar to protein data
Acidic Polysaccharides	n.d.	0	Small amounts and not important
Total EPS	0	-	Weak negative correlation but results not conclusive, EPS composition likely more important
Extracted			
Total Carbohydrates	0	0	
Protein	n.d.	0	
Humic Acid	n.d.	0 to -	Results not conclusive
Acidic Polysaccharides	n.d.	0	Small amounts and not important
Lipids	n.d.	0 to +	Possibly most important extractable EPS component but results not conclusive
Total EPS	0	0	No effect on flux

6 GENERAL CONCLUSIONS AND RECOMMENDATIONS

Both modified stirred cell and cross flow membrane filtration tests have been conducted at different shear and pressure conditions for four conventional AS samples and eight MBR samples. Their sludge properties were examined by measuring EPS composition, hydrophobicity, particle size and other wastewater characterization parameters. In addition, the flow hydrodynamics of both testing apparatus were simulated using the CFD approach. Specific conclusions can be drawn and are summarized below.

1. CFD can effectively simulate shear stress in the modified stirred cell and cross flow membrane filtration modules.
2. Cross flow fluxes are lower than modified stirred cell fluxes at similar shear and pressure conditions. This may be due to either shear stress variability in the stirred cell module or smaller particle sizes, due to shear introduced at the centrifugal pump, in the cross flow module.
3. Steady state fluxes are more sensitive to shear stress than transmembrane pressure under the experimental conditions examined. Sludge sample characteristics were more important than shear stress and transmembrane pressure in determining membrane fouling behaviour.
4. There is no consistent relationship, valid for all samples, between membrane fouling behaviour for stirred cell and cross flow filtration tests.

5. Membrane fouling in the stirred cell system is more sensitive to wastewater characteristics compared to cross flow system.
6. Dissolved EPS is more important than extracted EPS in determining membrane fouling behaviour. Further, EPS composition, rather than the total amount, is more important for membrane fouling. Soluble total carbohydrates was identified as the most important EPS component to affect fouling while other measures of soluble organic matter, sTOC and sCOD, also strongly influenced membrane fouling behaviour. Extracted lipids may be the most important extracted EPS component since higher lipid concentrations may be correlated to higher permeate flux but further work is needed to confirm this.
7. MBR and AS wastewaters have significant differences that influence membrane fouling behaviour. MBR wastewaters have increased concentrations of smaller particles, which are correlated to lower permeate fluxes. Also, MBR wastewaters have higher total dissolved carbohydrate EPS concentrations compared to AS, which also leads to increased fouling. Extracted EPS amounts for MBR samples are not different from AS samples expressed as mg/gVSS, but actual EPS concentrations in mg/L will be much higher due to higher VSS levels. Therefore, fouling is not caused by higher VSS concentrations in MBR samples, but by higher EPS levels, particularly total dissolved carbohydrates.

- **Recommendations**

This work demonstrated stirred cell and cross flow membrane modules have different filtration behaviour. Future research directions are suggested below.

1. Extend CFD work to predict membrane shear stress in hollow fiber membrane systems that use aeration to generate shear stress, which are widely used in full-scale MBR installations.
2. Modify or create a stirred cell apparatus that provides a constant shear stress at the membrane surface, perhaps by varying the blade to membrane gap along the blade radius. Further experiments can then be completed with this apparatus at different shear and pressure conditions to develop a bench scale system capable of rapidly assessing membrane fouling behaviour.
3. Modify cross flow and stirred cell systems so they can be operated at constant flux operating modes. Relationships between fouling behaviour and critical flux can then be more easily investigated.
4. Further characterize soluble organic matter in the wastewater into different fractions, such as molecular weight, so the key compounds that cause fouling can be identified and possibly minimized or treated.
5. Identify the composition and concentrations of particles with diameters similar to the membrane pore size that may disproportionately affect membrane fouling.
6. Examine relationships between MBR operating parameters, such as SRT, HRT and F/M, and fouling in well-controlled pilot plants using real wastewater so operational control strategies can be developed in real systems.

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Appendices

A. Stirred Cell Dimensional Sketches, Photograph and Mesh

Stirred cell dimensions with mixing blade, Front View

Stirred cell dimensions with mixing blade, Side View

Data collection system

FLUENT® Wireframe, Stirred Cell

FLUENT[®] Surface Mesh, Stirred Cell

Stirred Cell, Bottom of Cylinder

Stirred cell apparatus with mixer above cylinder

B. Crossflow Dimensional Sketches, Photographs and Mesh

Cross flow cell dimensions, top view

Cross flow filtration unit with three filtration cells

Cross flow filtration apparatus, one unit

C Shear stress results at radius of 30 mm at all blade rotational speeds for both 5 and
10 mm blade gaps
10 mm - 200 rpm

10 mm – 300 rpm

10 mm – 400 rpm

10 mm – 500 rpm

5 mm – 100 rpm

5 mm – 200 rpm

5 mm – 300 rpm

5 mm – 400 rpm

5 mm – 500 rpm

D. Standard curves for EPS analyses

Total Carbohydrates

Protein

Humic

Acidic Polysaccharides

Lipids