Investigation of the Effects of Coagulation on Membrane Filtration of Moving Bed Biofilm Reactor Effluent

by

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A thesis

presented to the University of Waterloo

in fulfillment of the

thesis requirement for the degree of

Master of Applied Science

in

Civil Engineering

Waterloo, Ontario, Canada, 2010

AUTHOR'S DECLARATION

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

Atehna Pervissian

Abstract

The combination of moving bed biofilm reactors and membrane bioreactors (MBBR-MR) can compensate for the drawbacks of both of these systems and further increase their acceptance and application in wastewater treatment industries. Despite the potential benefits of a MBBR-MR technology there has only been limited study of this configuration. The present study consisted of an overall assessment of the performance of a combined MBBR-MR system under high and low loading rates. Since colloidal matter in mixed liquor suspended solid (MLSS) is considered as one of the important contributors to membrane fouling, pre-treatment of membrane feed by coagulation was investigated for improving membrane performance. The performance of the MBBR-MR was assessed based on its chemical oxygen demand (COD) removal efficiency and membrane fouling mechanisms.

The study was carried out using pilot-scale MBBR and bench-scale batch membrane filtration setups (Millipore Inc. Bedford, MA). The pilot MBBR had a working volume of 1.8 m^3 and a 30% carrier fill fraction. The MBBR was operated with loading rates of 160 ± 44 $g/m^2/d$ (hydraulic residence time (HRT) of 4.6 h) and 223 $g/m^2/d$ (HRT of 2.6 h). The MBBR feed was obtained from a starch recovery line in a potato chip processing factory. The carriers were mixed by coarse bubble aeration and the dissolved oxygen (DO) was maintained above 2 mg/l.

Preliminary jar test trials (based on turbidity removal) were performed in order to obtain an optimal dosage of coagulants for subsequent ultrafiltration (UF) tests. The efficiency of three coagulants (alum, ferric chloride, and a blend of polyaluminum chloride and polyamine) was evaluated. The membranes were composed of polyethersulfone (PES) and had a pore size of 0.05 microns.

The results of this study indicate that the combination of MBBR with membrane filtration can be operated at relatively high loading rates to yield a constant high quality permeate that is suitable for water reuse purposes. Fouling of the membrane by the wastewater was found to be substantially reduced by treatment with the MBBR. The reversible and irreversible fouling of the MBBR effluent were 56 and 63%, respectively, of that observed with the raw wastewater. The MBBR Loading-rate was found to affect treatment efficiency of the MBBR-MR and membrane performance. Operation under the elevated loading-rate conditions HRT = 2.6 hours) resulted in an increase in the irreversible fouling of the membranes (60% on average). The addition of all the coagulants in this study was found to decrease the fouling of the membrane. However, the extent of the pre-coagulation effect on membrane fouling was found to strongly depend on the type and dosage of the coagulant and the MBBR effluent characteristics. All the coagulants were effective in decreasing membrane fouling at their optimal dosages which was determined in preliminary jar tests. Ferric chloride performed the best as a pretreatment coagulant compared to alum (Aluminum sulfate) and the coagulant blend with reductions in both reversible and irreversible fouling (43-86% and 51-71%, respectively) and increased consistency (in decreasing fouling) as compared to the other coagulants. Alum had no effect on irreversible fouling and the coagulant blend significantly increased irreversible fouling in some trials (up to 196% or by a factor of 3 when overdosed). Additionally, alum and the blend were, on average, 29% and 7%, less effective than ferric chloride in reducing reversible fouling under the conditions and dosages tested.

Acknowledgements

The completion of this thesis would definitely not have been possible without the help, support and motivation of several important individuals and institutions.

First and foremost, I would like to sincerely thank my supervisors, Dr. Wayne Parker and Dr. Raymond Legge, for the opportunity that they have given me, for their support and guidance, and for their inspiration throughout my thesis work. I feel very privileged for having spent the last two years working with these two enlightened individuals.

A special thank-you goes to Terry Ridgway and Mark Sobon who were two of the vital components during my studies in the University of Waterloo. I could not have accomplished this project without their assistance and extensive experience in countless occasions. They made every difficult situation look easy.

I would like to thank Headworks Bio Canada Inc. for providing the moving bed biofilm reactor and for their support of this project. In particular, I would like to thank Siva Angappan for sharing his experience.

I would like to thank Dr. Sigrid Peldszus for lending me two Amicon-cell membranes; this was a great help as it expedited my experiments.

Thanks to Bernard Segal from Northland Chemical Inc., who provided me with all of the coagulant samples, and for his advice along the way.

I would also like to extend a heartfelt thanks to my lab-mates—and friends—Mirzaman Zamanzadeh, WeiWei Du, and Peiman Kianmehr who patiently showed me the way when I first came to the lab and were always willing to answer my questions. I truly enjoyed working and spending time with them in the lab.

A special Thanks to my friend, Amin Rajabzadeh, who helped me like a big brother in every possible way in countless occasions.

I would like to thank my assistant Michael Bielawski. He was a very quick learner and was very dedicated to his job. I am sure he has a bright future ahead.

Dedication

To my sister, Pantea, who was an endless source of motivation and moral support and was always there for me. I am very lucky to have such a sister.

To my parents, Afsaneh and Khosrow Pervissian, who have supported me in every possible way. I owe not only this degree but everything I have to them.

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List of Abbreviations

µ	Dynamic viscosity
a	Slope
AGST	Attached growth total solids
BOD	Biological Oxygen Demand
CFV	Cross flow velocity
DBP	Disinfection byproduct
DO	Dissolved oxygen
DOC	Dissolved organic matter
EPS	Extracellular polymeric substances
FCOD	Filtered COD, SCOD
FFCOD	Flocculated filtered chemical oxygen demand
Flux	Flows through a unit area per unit time
HRT	Hydraulic retention time
J	Filtration flux
LMH	Flux unit (L/m^{2}h)
MBBR	Moving bed biofilm reactor
MBBR-MR	Combined moving bed biofilm reactor and membrane bioreactor
MBR	Membrane bioreactor
MF	Micro-filtration
MLSS	Mixed Liquor Suspended Solids
PAC	powdered activated carbon
PACl	Poly-aluminium chloride
PES	Polyethersulfone
PSD	Particle size distribution
Q	Permeate flow
R	Resistance
R_f	Fouling resistance
R_{irr}	Irreversible fouling resistance, $R_{irreversible}$
R_m	Clean membrane resistance
R_{rev}	Reversible fouling resistance, $R_{reversible}$
R_t	Total resistance of the membrane including clean membrane resistance and fouling resistance
SCOD	Soluble chemical oxygen demand, FCOD

SMP	Soluble microbial products
SP	Soluble phosphorous
SRT	Solids retention time
SS	Suspended solids
TCOD	Total chemical oxygen demand
TKN	Total Kjeldahl nitrogen
TMP	Trans membrane pressure
TOC	Total Organic Carbon
TP	Total phosphorous
TS	Total solid
TSS	Total suspended solids
UF	Ultra-filtration
VSS	Volatile Suspended Solids

Chapter 1

INTRODUCTION

1.1 INTRODUCTION TO MBBR-MRS

The application of membrane bioreactors (MBR) as reliable and compact systems for wastewater treatment has increased in the past decade. This is due to advances in their design and operation that decrease membrane fouling and correspondingly capital and operational costs. As compared to conventional activated sludge, MBRs have higher solids retention times, absolute solids separation, permeate disinfection, and lower sludge production without bulking problems [1-3]; however, membrane fouling remains as the most important barrier to MBR application.

All mixed liquor constituents contribute to membrane fouling and the extent of their effect depends on their relative contribution in the sludge and the process operating conditions. Tak and Bae (2005) [4] found that the suspended solids contributed the most to membrane fouling (72-83%) and cake formation represented 90% of the total fouling. The sludge in their study was cultivated in a submerged MBR from a synthetic substrate with a composition that was typical of municipal wastewater. Defrance *et al.* (2000) [2] studied an MBR which was fed with raw municipal wastewater from a treatment plant and also found that suspended solids were the most significant contributor (65%) to membrane fouling. An alternative to conventional MBRs is to integrate MBBR processes with a membrane technology (MBBR-MR).

MBBRs have significantly lower suspended solids production and hence the membrane will be exposed to lower solids concentrations leading to reduced fouling potential. Additionally, the readily biodegradable component of COD will be removed in the MBBR and hence biological activity on the membrane surface will be reduced. MBBRs are more compact than conventional activated sludge processes and due to the attached biomass on carriers they operate with high concentrations of active biomass [5]. MBBR-MRs can be operated at relatively low HRTs or high organic loading rates since the readily biodegradable (or soluble biodegradable) matter is removed in the MBBR and the particulate matter (from the influent and the biomass produced in the MBBR) is separated by the membrane. Therefore, MBBR-MRs may be more compact than MBRs. Despite the potential benefits of a MBBR-MR technology there has only been limited study of this configuration. More research is required to assess various operational conditions for this system in order to develop this process and increase its acceptance for wastewater treatment.

The following section introduces important concepts related to the membrane bioreactors and membrane fouling, moving bed biofilm reactors (MBBR), and the combination of MBBRs and processes membrane separation processes. The important operational factors for MBBRs and MBRs which can affect the MBBR-MR system and are related to this research are presented. It should be noted that there are relatively few references to MBBR-MR technology and for treatment of industrial wastewater with this system; therefore, studies with different wastewater types have been included in this review and the types of wastewaters employed in each study have been included for clarity.

1.2 BACKGROUND ON MEMBRANE AND MEMBRANE BIOREACTORS (MBR)

The application of membranes in water and waste water treatment has accelerated in the past decade mainly due to membrane improvements and reduced costs. Low pressure membranes, in particular, are becoming more popular due to their lower fouling and are used widely at full scale. Their installed capacity has increased to 3,500 million gallons per day (13,249 L/day) in 2006 and 85% of this was for drinking water treatment and wastewater reuse [6].

A recent study by the Freedonia Group (an industry research firm) forecasted that membrane demand will increase 8.6% each year through to 2012 and it will exceed 15 billion dollars in 2012 [7]. There are several reasons behind the growth of membrane demand in water and wastewater treatment depending on the regions of the world. Reasons include increasing attention towards water quality, industrial waste, food and beverage safety regulations and environmental concerns especially due to water scarcity in many regions in the world. Another reason is the high cost of raw water and waste disposal which is increasing every year. Therefore, membrane–based separation processes which have a small footprint, produce consistent high quality and reusable water, and can reduce waste disposal have become an interesting alternative for wastewater treatment. North America had one third of the membrane sales in the world in 2007 and will continue to be the largest regional market for membranes with a projected 8.3% annual increase through 2012. It is expected that the US will have the largest share in the membrane industry around the world. The membrane market in Canada is not as large as in US, however, it will benefit from the developments in US. The main reasons driving membrane demand in the USA are the demand for upgrading existing water and wastewater treatment facilities to meet the high water quality regulations, usage of resources with low water quality in water stressed regions and industrial use for water reuse and decreased waste disposal [7].

Membrane bioreactors (MBR) were commercialized 30 years ago and their application in wastewater treatment has increased over the past decade. MBRs are becoming known as reliable and compact systems due to developments in their design and operation which has resulted in decreased membrane fouling and corresponding operational costs. These developments have made MBRs an interesting alternative to activated sludge systems. Some of the advantages of MBR systems over the activated sludge processes are the smaller foot print due to reduced bioreactor volumes that result from the ability to operate at higher biomass concentrations (up to 30 g/l) and the lack of a need for a settling tank, absolute solids separation, and permeate disinfection, lower sludge production with no bulking problems [1,2]. MBRs have been found to provide higher COD removal efficiencies and consistent high quality permeate which can be reused [1,2]. The influent quality and operational conditions typically have an insignificant influence on the permeate quality [1]. On the other hand, the efficiency of the activated sludge process is constrained by settling tank performance and depends on the settleability of its flocs. These systems cannot be operated with biomass concentrations higher than 5 g/l and require a large footprint for their settling tank; their higher sludge production represents additional treatment costs for excess sludge disposal [2].

1.3 MEMBRANE PRINCIPLES

Membrane performance is typically evaluated on the basis of efficiency of contaminant removal and fouling. A membrane’s performance can be affected by various physical and chemical factors which are interrelated. Low pressure membranes include ultra-filtration and micro-filtration with pore sizes in the range of 0.01-0.1 micron and 0.1-1 micron, respectively [19] and are usually operated with trans membrane pressures (TMP) of 1-2 bars (100-200 kPa). Judd (2006) [19] described membranes simply as a material which allows some components to pass through more readily than others and rejects some other components depending on its pore size. Contaminants may either be adsorbed to or repelled from the fouled membrane by colloids depending on the interaction forces between the fouled membrane and contaminants. The removal efficiency of soluble/low molecular weight contaminants smaller than the membrane pores depends on membrane characteristics such as hydrophobicity and surface charge and the membrane feed chemistry. In general low pressure membranes are not reliable for soluble matter removal [6]. Larger particles such as pathogens and turbidity are effectively removed whereas soluble matter may remain in the permeate [6].

1.4 MEMBRANE FOULING

The most important barrier to MBR application in wastewater treatment is membrane fouling. During filtration, fouling increases due to accumulation and penetration of MLSS constituents onto and into the membrane pores which decreases the membrane permeability. Hence, in order to maintain a constant flux a higher transmembrane pressure is required.

Fouling tends to result in increased capital (since a higher membrane surface is required) and operational costs since higher membrane maintenance requirements requires more frequent backwashing, higher aeration, chemical cleaning, and eventually membrane replacement in a shorter period of time [1,8]. Over the past 10 to 15 years many studies have investigated different operational conditions and the corresponding fouling mechanisms and have proposed various solutions and techniques in order to minimize and control fouling.

Membrane fouling is caused by various organic and inorganic, soluble and particulate substances. Each of these substances has various effects on membranes depending on their concentration and the operating conditions. Hence, membrane performance depends on fouling mechanisms which are interrelated and can be affected by physical, chemical or biological processes [8].

1.4.1 Fouling mechanisms

The main fouling mechanisms include deposition of solids on the membrane surface that forms a cake or biofilm layer, pore blocking or clogging by colloidal matter, and adsorption of soluble matter (macromolecules) into the pores of the membrane [1]. Micro-organisms including bacteria can also stick to the membrane surface and grow causing biological fouling. However, this type of fouling is typically not observed in full-scale systems, probably due to the periodic chemical cleaning of the membrane which prevents bacterial growth [6]. The development of cake layer and loose deposition is referred to as reversible fouling and can easily be removed, while the other forms of fouling are referred to as irreversible and require chemical cleaning. Fouling mechanisms are complex and often related to one another. Changes in one mechanism can affect the development of the other. Many studies have attempted to determine the dominating fouling mechanism in order to reduce fouling [8].

1.4.2 Factors affecting membrane fouling

Factors that can affect membrane fouling can be categorized and summarized into three different groups including the membrane, MLSS constituents (and their concentrations) and operating conditions. Figure 1-1 [10] shows the connection between each of these factors and membrane fouling and their interrelations. The effect of these factors on fouling is a very broad subject in the literature, and will be discussed briefly with a focus on the mechanisms that are more related to the issues associated with this research project. Aside from the factors shown in Figure 1-1, feed characteristics may also affect membrane fouling [9].

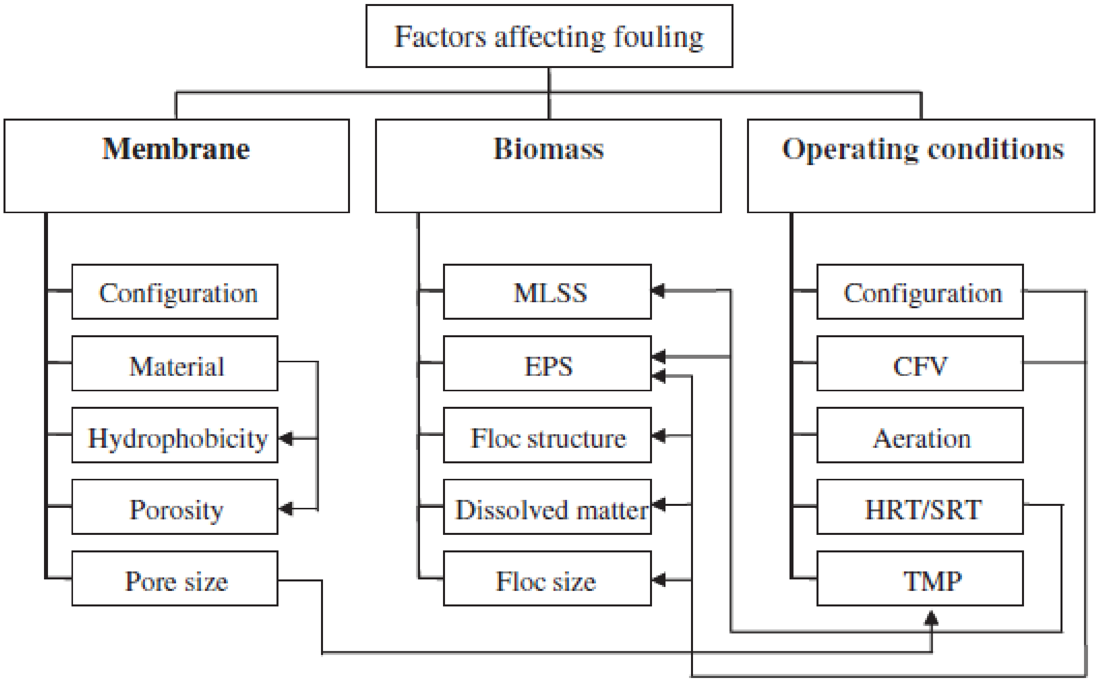


Figure 1-1 Factors influencing fouling of the membrane fouling in MBRs (From Chang *et al.* (2002) [10]), Permission conveyed through Copyright Clearance Center)

1.4.2.1 Membranes

Membranes used in wastewater treatment have various pores sizes, materials of construction and configurations and all of these can affect the fouling rate and mechanism. Membranes may be porous or non-porous, made from polymer or ceramic material and have different degrees of hydrophilicity [6]. Usually, polymeric membranes are optimized to obtain an optimal degree of hydrophilicity in order to reduce the fouling by hydrophobic substances found in MLSS [11]. Ceramic membranes have longer life cycle (due to their higher hydraulic, thermal, and chemical resistance) than polymeric membranes, however, they are more expensive and their application is therefore, limited [19].

Membrane pore size: Depending on the membrane pore size relative to the size of the colloids in the membrane feed, colloidal matter can contribute to different types of fouling mechanisms. For example, if the membrane pore size is close to the size of the colloids pore blockage can occur and if the membrane pore size is smaller than the colloids size then cake formation on the surface of membrane can occur. The latter fouling mechanism is usually easier to remove than the more severe fouling caused by pore blockage [6]. This illustrates the importance of choosing a proper membrane pore size for each application.

Tak and Bae (2005) [4] studied the effect of 4 different pore sizes in the UF range of pore sizes (35-300 kDa) on membrane performance and their effect on fouling mechanisms (The sludge in their study was cultivated in a submerged MBR from a synthetic substrate with a composition that was typical of municipal wastewater). Their results showed that with increasing pore size, cake layer resistance increased. The higher permeability of membranes with larger pore sizes caused higher deposition of solids on the membrane surface. Since the cake layer is known to act as a barrier to irreversible fouling (caused by pore clogging and adsorption of fine particles and soluble matter on the UF membrane), an increase in cake layer resistance limited irreversible fouling. In brief, larger pore sizes caused greater cake layer resistance and lower irreversible fouling. As a result in their study, the total fouling increased by increasing the pore size. It is worth to noting that under different circumstances, such as different pore size ranges and operating conditions, increasing the pore size may have different effects on membrane fouling as a result of different fouling mechanisms. For example, higher irreversible fouling may occur since pore sizes are equal or larger than the colloidal matter and the colloidal matter clogs the membrane pores more readily.

Membrane configurations: Membranes may be operated at different pressures which categorizes them as high pressure or low pressure membranes. In addition, membranes may be installed in two different configurations including side-stream (cross flow) where the membrane is installed external to a bioreactor and submerged configurations in which the membrane is immersed in the bioreactor (or in an external tank) [11]. Figure 1-2 shows a simple schematic of these configurations. Side-stream membranes were used in earlier generation of MBRs since the early 1970s, while the submerged configuration are a more recent development in MBR processes and have been used since 1990 [11]. Compared to the side-stream configuration, submerged processes have lower energy demand, work with lower fluxes, have lower hydraulic resistance, and require higher aeration and membrane area. In addition to aeration and chemical cleaning, submerged membranes typically employ short back wash cycles so that they can operate at a sustainable flux. Cross flow membranes require high energy to generate a high flow velocity across the membrane surface for membrane scouring [11].

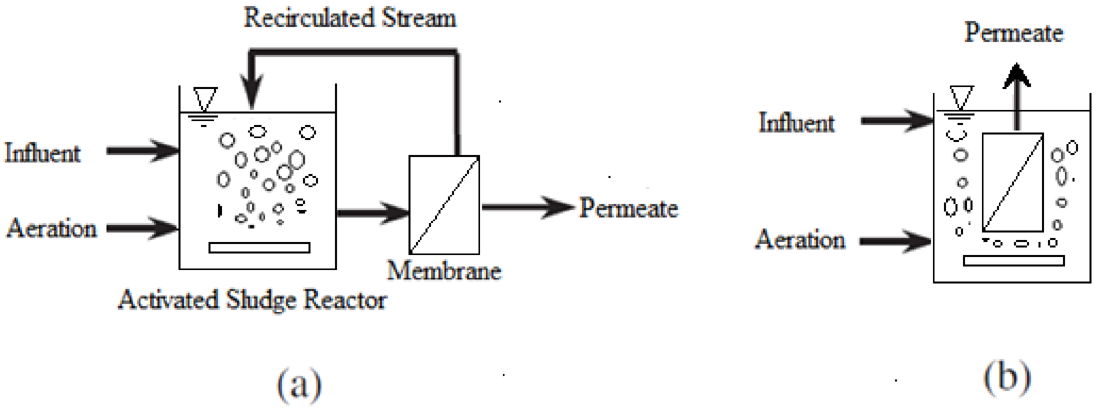


Figure 1-2 (a) Side-stream and (b) submerged membrane bioreactors (adapted from Judd (2004) [11]).

Hollow fiber, tubular (often used in side-stream configuration), or flat plate membranes are the modules most commonly used in MBR processes. Changes in operating conditions have different effects on the performance of each of these membrane configurations. For example, a slight decrease of aeration rate can result in a greater decrease in the permeability of a hollow fiber membrane as compared to flat plate membranes due to their different hydrodynamics [11]. On the other hand, side-stream configurations may have a higher shear stress which can cause higher breakage of flocs and consequently, release of extra cellular polymeric substances (EPS) (which is known to be an important foulant and hence, cause higher fouling) [11].

1.4.2.2 Foulants

The composition of the mixed liquor suspended solids (MLSS) with respect to constituents and concentrations is known to have a significant effect on membrane fouling propensity and is correlated with design of MBR and operational conditions. All MLSS constituents contribute to membrane fouling in different forms, however, the extent of their effect depends on their presence in the MLSS [4]. Membrane fouling by inorganic constituents has not so far been adequately investigated; however, they may cause severe fouling especially for industrial wastewater treatment. Inorganic fouling is usually due to substances such as calcium carbonate that can cause scaling [11]. Other constituents of MLSS include suspended solids and dissolved organic matter (DOC). From largest to smallest, the DOC of MLSS mainly includes biopolymers such as EPS which are bacterial products mainly made of protein and polysaccharides, humic substances, low-molecular weight acids and low molecular weight neutrals [12]. MLSS also includes residual DOC from the feed water [12].

During batch filtration under constant pressure, rate of flux decrease declines due to changes in contribution of each MLSS fraction to fouling. Fouling mechanisms change during the filtration period mostly due to the changes in permeation drag forces and back transport forces. Permeation drag forces cause deposition and attachment of MLSS fractions on the membrane by moving them toward the membrane surface which depends on membrane pore size since it can change the membrane permeability and flux. These fractions are detached by back transport forces (which includes Brownian diffusion, inertial lift, shear induced migration/ diffusion, and electrostatic repulsion) [4, 13]. Figure 1-3 shows a schematic of flux decline versus filtration time under constant TMP. Tak and Bae (2005) [4] defined three different zones/phases based on the fouling mechanism and fouling rate in each zone.

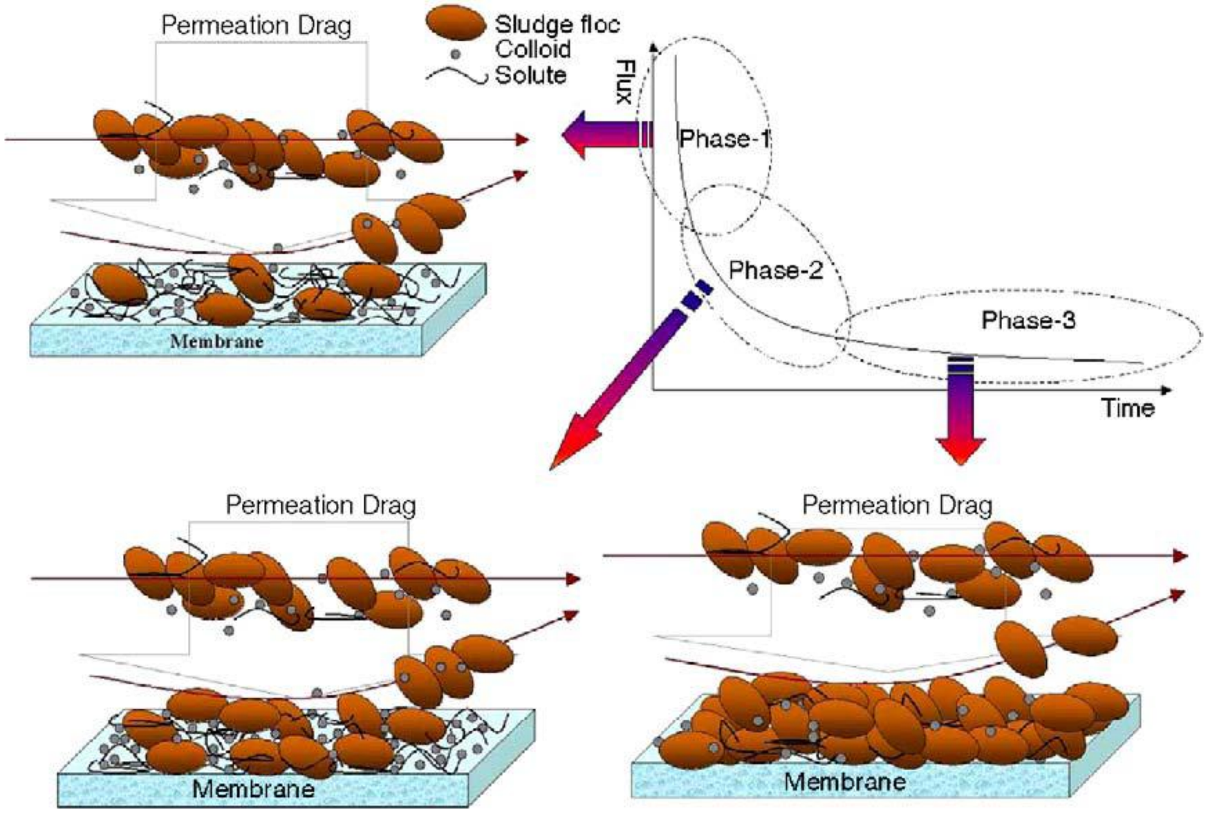


Figure 1-3 Fouling phases and flux diagram for operation under constant pressure (From Tak and Bae (2005) [4], Permission conveyed through Copyright Clearance Center)

At the beginning of the filtration, all MLSS components deposit on the membrane, however, larger flocs can be removed by cross flow forces. Soluble matter contributes the most to membrane fouling and deposits onto the membrane surface and into the pores to cause irreversible fouling. Colloidal matter contributes the least to membrane fouling at this point due to their lower fraction/concentration in MLSS as compared to the suspended solids and also because some of the deposited colloids are removed by cross flow. At this stage membrane flux decreases rapidly since all the MLSS components contribute to membrane fouling [3,4].

During the second phase, the flux decreases at a lower rate as compared to phase one since the fouling in the first phase has decreased the flux and hence the drag permeation forces. The irreversible resistance due to soluble matter reaches steady state at the beginning of this stage since back transport and permeation drag of this fraction become equal. The fouling rate by colloidal matter decreases at this stage until its resistance also reaches steady state at the end of this stage. However, solids continue to deposit on the membrane surface and as a result, the fouling formed at this stage is mainly reversible [3,4].

During the third stage, the flux decline rate decreases further until a sustainable flux is obtained. Fouling is caused by two mechanisms: deposition of larger particles which occurs in the beginning of this stage until permeation forces and back transport forces reach equilibrium; the second fouling mechanism is the compaction of the cake layer due to the trans membrane pressure which increases the resistance of the cake layer. This mechanism becomes more significant at this stage since the cake layer has a greater particle concentration as compared to the previous phases [4]. Juang *et al.* (2007) [3] reported that in the first 10 minutes of filtration in UF membranes the dominant fouling mechanism is pore blockage by the colloidal matter which is slightly different from Tak and Bae (2005) [4] who stated that in the first stage all fractions contribute to membrane fouling with the soluble fraction having the highest contribution. However, both of these studies found that during the final stage suspended solids are the main contributor to membrane fouling.

A number of studies have fractionated the MLSS into three different fractions including suspended solids, colloidal matter, and soluble matter [2,4,14,15]. In these studies, the fractions were separated and filtered individually to quantify the contribution of each fraction to membrane fouling. The results indicated which fraction contributed the most to membrane fouling, and consequently the dominant fouling mechanism was determined.

Tak and Bae (2005) [4] found that suspended solids contributed the most to membrane fouling (72-83%) due to their high fraction in MLSS. Cake formation represented 90% of total fouling and was identified as the dominate mechanism. It is worth noting that these results were obtained from a bench scale dead-end cell operated at a relatively low cross flow velocity (1.2 m/s) and high TMP (100 kPa). Therefore, the permeation drag forces were higher and back transport velocity was lower than in what would be found in commercial membrane configurations and therefore, the contribution of each MLSS fraction to membrane fouling and correspondingly their fouling mechanisms may differ from full scale installations. Tak and Bae (2005) [4] performed another dead-end filtration trial with a lower TMP (20 kPa) and higher cross flow velocity obtained using a high mixing speed (600 RPM) to assess the effect of TMP and cross flow velocity on the fouling mechanisms. The cake layer formation and its resistance decreased allowing for higher solute deposition on the membrane. As a result solutes became the main contributors to membrane fouling and contributed 67% of the total fouling resistance while suspended solids and colloidal matter contributed only 24% and 6% of total resistances, respectively. These results show the effect of different operating conditions and the importance of hydrodynamics of the filtration on the fouling mechanism.

Defrance *et al.* (2000) [2] found that suspended solids had the highest contribution to membrane fouling. Suspended solids, colloids and solutes contributed 65%, 30% and 5% of the total membrane fouling resistance, respectively. They also observed that the sum of resistances found from filtration of each MLSS fraction was higher than the total resistance due to the filtration of MLSS compliment. Filtration of colloidal and suspended solids separately caused individual cake layer resistances whereas in MLSS these fractions were mixed and the cake layer was made of their combination which decreased their individual contribution to cake resistance. Defrance *et al.* (2000) [2] concluded the ratios obtained by this method were not perfectly representative of each the components contribution to fouling. A more general explanation is that the effect of each of these components on membrane fouling are interrelated and correlated, illustrating a drawback to these experiments. A summary of the results of these studies is presented in Table 1-1. Table 1-1 provides a summary of the results of the four studies that evaluated the contribution of each of the MLSS components to fouling. From Table 1-1 it can be observed that the contribution of each MLSS fraction to fouling differed between the studies. The variation in their results was likely due to differences in several factors including the fractionation methods employed, the nature of the MBR influent (synthetic, municipal and industrial), the system hydrodynamics, the filtration time (back transport and permeation drag forces), system configurations and operating conditions (aeration and back washing or cross flow), the physiological properties of the biomass, membrane material and pore size and the concentration of DOC fractions (such as polysaccharide, phospholipid, protein) [4,14,15]. These factors can change the biomass characteristics and composition and particle size distribution in the MLSS. The effects of these parameters on fouling should be considered when analyzing the results of membrane filtration.

Table 1-1 Contribution of MLSS fractions to total fouling

Fractions	Tak and Bae (2005) [4]		Defrance *et al.* (2000) [2]	Wisniewski *et al.* (1998) [15]	Bouhabila *et al.* (2001) [14]
	High flux & low cross flow	Low flux & high cross flow			
Suspended solids (%)	72 – 83	67	65	24	24
Colloids (%)	4 – 14	9	30	24	50
Solutes (%)	13 – 14	24	5	52	26

Table 1-1 also shows that all of MLSS fractions contributed to membrane fouling (to different degrees). However, it is unclear whether decreases in the concentration of each of these components would result in a decrease in membrane fouling. In the literature conflicting results regarding the relationship of membrane fouling and MLSS fractions exists. For example, Defrance *et al.* (2000) [2] reported that membrane fouling increased insignificantly when the MLSS concentration was increased from 2 to 6 g/l while other studies have reported a linear relationship between MLSS and membrane resistance [11].

Colloidal particles: Colloidal matter can be defined as small non-settleable particles with sizes from 1 nm to 1 μm. Colloids include organic macromolecules such as polysaccharides, peptidoglycans, proteins, humic aggregates, and cellular debris [6]. Colloidal matter in MLSS may include residual non-biodegraded polymers such as residual defoamers from influent wastewater, or those that are generated from bacterial metabolism to produce Extracellular polymeric substances (EPS) and Soluble microbial products (SMP) and bacterial lysis [14]. Colloids contribute to membrane fouling by various mechanisms including pore blocking, pore constriction or cake formation and depend on their size relative to the membrane pore size [6]. Colloid deposition on membrane surfaces can improve the membrane removal efficiency by narrowing the pores and by the repulsive forces of colloids, as a result, lower molecular weight substances such as viruses may be removed [6]. The results of a study by Bouhabila *et al.* (2001) [14] showed that residual colloidal matter increased membrane fouling more than colloidal matter formed in the bioreactor and improved biodegradation of influent colloidal matter decreased membrane fouling. Colloids generated in the MBR did not have a significant effect on membrane fouling in their study as they observed that with increasing SRT their concentration increased, however, membrane fouling decreased due to increased biodegradation of influent colloids (from the feed water and from defoamer agents that were employed).

EPS and SMP have been found to represent two of the major biopolymer membrane foulants [17]. However, conflicting reports on the effect of increasing the concentrations of EPS and SMP on fouling exists in the literature which appears to be due mainly to different fouling mechanisms. A higher concentration of EPS may increase the membrane fouling due to its higher attachment to the membrane surface. However, the EPS composition may be more important than its concentration with regards to fouling as the protein to carbohydrate ratio affects the degree of sludge hydrophobicity and flocculation. SMP has two major components (carbohydrate and proteins) with the former having a higher contribution to membrane fouling by pore blocking [13,17].

Leiknes *et al.* (2006) [8] observed that with municipal wastewater when the colloidal concentration decreased in the membrane reactor (due to operation of an MBBR at higher HRTs), membrane fouling decreased correspondingly. Their results indicate a correlation between the concentration of the colloidal fraction and membrane fouling suggesting that decreasing the colloidal fraction may decrease membrane fouling.

1.4.2.3 Operational conditions

Operational conditions such as HRT/ SRT, hydraulics (flux and cross flow velocity), aeration and dissolved oxygen can affect membrane fouling by changing the composition and concentrations in the MBR sludge (for example, particle size distribution or EPS and SMP concentrations and composition with respect to proteins, carbohydrate and polysaccharides), by changing the fouling mechanism or by changing the hydrodynamics at the surface (mainly permeation drag and back transport forces) [4]. Some of the important operational parameters will be discussed briefly in this section. It should be noted that due to the complexity of membrane fouling, the extent that to which each of these operational parameters affect fouling may vary between MBR applications and circumstances.

SRT: MBRs have the benefit of producing a long SRT due to retention of solids in the bioreactor by the membrane and therefore, they have lower sludge production [11]. However, high SRT of MBRs has been reported to produce sludges with lower dewaterability and settling characteristics that likely result from higher EPS concentrations and smaller particle sizes. In a MBR system, operation with an appropriate SRT can minimize SMP concentration [13]. The concentration of EPS and its carbohydrate fraction can also be decreased by operating at an appropriate SRT. For example, in a study with a pre-anoxic MBR, operation at SRTs of 3 and 5 days caused higher fouling than operation with SRTs of 10 and 20 days due to the higher concentrations EPS and SMP [17]. Additionally, operation under low SRTs may limit the biodegradation of foulants from the influent and hence the permeability of the membrane can decrease at low SRTs. As mentioned previously, Bouhabila *et al.* (2001) [14]

found that residual solutes and colloidal matter from the influent can have a higher fouling effect than colloidal matter formed in the MBR due to microbial metabolism and bacterial lyses. In their study, lower fouling was observed at higher SRTs.

Higher SRTs can be achieved by increasing the reactor size thereby increasing the total solids. It should be noted that higher solids concentrations may cause higher fouling. Hence, some studies have suggested the use of a coagulant if higher SRTs are to be achieved from increasing the TS [13]. The negative impact of high TS in membrane bioreactors on fouling is one of the reasons for proposing the replacement of the suspended growth activated sludge process with a moving bed biofilm reactor in MBR processes. By employing a moving bed biofilm reactor a higher SRT can be achieved while sludge production and hence MLSS concentrations are lower than in conventional MBRs [18].

Flux: In general, increasing membrane flux results in an increase in membrane fouling. For each membrane process an optimal flux exists which is low enough to minimize backwashing and chemical cleaning and correspondingly the operational costs and a flux that is still high enough to decrease the required membrane surface and therefore, the capital costs [11]. Each membrane process has a critical flux above which the TMP increases and below which a sustainable flux is obtained and can be operated at a constant TMP. It has been found that it is more economical to operate hollow fiber membranes at higher fluxes than the critical flux since they are back-flushable while it is important to operate the sheet-based membranes at sub-critical fluxes since they are not back-flushable [11]. It is worth noting that operation under sub-critical flux only decreases the deposition of suspended solids on the membrane and has no observable effect on colloidal and soluble matter fouling [4,11]. The critical flux may be increased by increasing the aeration rate and back washing frequency [11].

Cross flow velocity: Cross flow velocity (CFV) has a substantial effect on membrane permeability. Increasing the cross flow velocity increases the shear forces near the membrane surface, and hence increases the particle back transport. In side-stream configurations the cross flow velocity is increased by increasing the pumping rate which increases the flux almost linearly with a slight decrease in permeability due to breakage of larger flocs by higher shear forces. In submerged membranes, however, cross flow velocity can only be increased by increasing aeration and its optimization of operational aspects of the system [11].

Aeration: Aeration is considered as one of the main operational costs in MBRs due to the high energy demand. Therefore, one of the goals in MBR studies is to reduce energy costs associated with the aeration system while maintaining a high permeability. Increasing the aeration intensity can have both beneficial and detrimental effects on membrane permeability. It can decrease the membrane fouling by producing shear forces from the air bubbles at the surface of the membrane and therefore, reduce reversible fouling (i.e. air scouring). On the other hand, higher aeration intensity and increased shear forces can break flocs into smaller flocs and colloidal constituents which may cause more severe and in some cases irreversible fouling [19]. As a result, an optimal point exists, where higher aeration rate does not have or has a small additional benefit and therefore, is not economical.

1.5 MEMBRANE CLEANING/REGENERATION AND COSTS

Membrane fouling can be divided into two types on the basis of the type of cleaning method that is required to return the flux to near initial levels. Reversible fouling results from the formation of a cake layer that consists mainly of loose particle deposits on the surface of the membrane which can be removed by physical cleaning such as aeration and periodic back washing/flushing of the membrane. However, irreversible fouling, which is due to attachment of solutes and colloidal matter on and into the membrane, is more severe and cannot be removed by these methods and may only be removed by chemical cleaning [8]. Reversible fouling can be minimized by optimizing the operational conditions, especially the hydrodynamics, whereas irreversible fouling is less controllable and therefore, can constrain membrane applications [12]. Bouhabila *et al.* (2001) [14] found that they could decrease the membrane resistance by a factor of 3.5 for a flux of 131 LMH by increasing the airflow and by optimizing the frequency and duration of back washing The aeration optimization had a greater effect than backwashing and contributed to 85% of the total fouling reduction.

Implementation of any method that can decrease fouling and hence increase the flux will decrease the capital and operational costs since less membrane surface would be required. The savings for a given membrane process can be calculated from Equation 1-1 [20]. If the membrane surface area, and hence in some cases (such as flat sheet membranes) the number of membrane modules required, is reduced, the system then uses fewer coarse bubble aeration systems for scouring. In order to provide sufficient dissolved oxygen to MLSS, fine bubble aeration is required to compensate for the decrease in coarse bubble aeration applied. Therefore, when calculating the savings associated with the reduction in aeration needed, a factor should be applied to Equation 1-1 to offset the expenses for the addition of fine bubble aeration. Since the efficiency of fine bubble aeration is three times higher than course bubble aeration the fraction of 2/3 was applied in this study [20].

$$\text{Savings}(\%) = \frac{\text{Flux Increase}(\%)}{\text{Flux Increase} + 100} \times 100 \qquad \text{1-1}$$

1.6 INTEGRATION OF BIO-FILM PROCESSES WITH MEMBRANE TECHNOLOGY AS AN ALTERNATIVE TO CONVENTIONAL ACTIVATED SLUDGE MBR

As discussed in the previous section, higher fouling increases MBR costs due to the requirement for higher cleaning frequencies and decrease in membrane life. Optimization of operational conditions and reduction of membrane fouling decreases the MBR costs and can improve their acceptance as an enhanced wastewater treatment process. Hence, the replacement of the suspended growth activated sludge process by a biofilm process has been studied. Application of biofilm processes can decrease membrane fouling and consequently increase operational flux, thereby making the treatment system even more compact, allowing increased organic loading rates and decreased HRTs [21].

In the current study the biofilm process of interest is the moving bed biofilm reactor (MBBR). In order to better understand the advantages of the MBBR process over activated sludge and other biofilm processes and the possible advantages of its combination with membrane separation processes an introduction to these systems is presented here.

1.6.1 Moving bed biofilm reactors

In general, biofilm processes are increasingly being favoured over activated sludge systems for organic carbon and nutrient removal. The advantages of biofilm systems over activated sludge systems are that they are more compact thus the treatment capital costs are reduced. The generation of biomass that needs to be separated is significantly lower and therefore, alternative solids separation systems which have lower footprints and higher efficiency such as floatation and filtration can be considered. The attached biomass in biofilm-based processes results in the ability to operate at high concentrations of active biomass which increases the biological removal rate and makes them more resistant to overloading and toxic compounds [5]. In biofilm-based processes, the biomass can be specialized for specific treatment purposes [22]. For example, nitrification and de-nitrification can successfully be achieved in biofilm-based processes since nitrifiers, which are slower growing micro-organisms, are retained by the biofilm [23,24].

While biofilm systems have been developed to take advantage of these characteristics, they do have their challenges as well. For example, trickling filters require high volumes, rotating biological contactors are subject to mechanical failures, fixed media submerged biofilters have difficulty maintaining even flow distribution on the media surface and granular biofilters require back washing and hence cannot be operated continuously. Moving bed biofilm reactors (MBBR) have been developed to overcome these drawbacks and still benefit from their advantages [22]. Advantages of MBBRs over the other biofilm reactors include the lack of a requirement for back washing, they are not prone to clogging, they can be operated continuously, they provide high surface area for microbial growth, and they have a low head loss [25]. Since their introduction in wastewater treatment in the late 1980's, MBBRs have been successfully used in municipal and industrial wastewater treatment such as treatment of dairy, cheese processing [24], pulp and paper and potato chips manufacturing wastewaters [26].

The advantages of MBBR are achieved by using small suspended carriers which move freely with the liquid phase of the reactor. The carriers are kept in the reactor by a sieve arrangement at the outlet. The carriers are usually small polyethylene cylinders designed to have a high specific surface area for biofilm growth. As a result, the reactor does not require sludge recirculation to reach the required high biomass concentrations and only the surplus biomass needs to be separated from the effluent. Additionally, a high SRT (i.e. sludge age) can be achieved and hence sludge generation is lower than that of conventional activated sludge systems. This is an important advantage due to the rising costs of sludge disposal. The movement of the carriers is caused by coarse bubble aeration in aerobic applications and by mixers in anaerobic MBBR processes.

The most important parameter in designing a MBBR is the biofilm area and hence the effective carrier surface area. The specific surface area in MBBRs is established based on the purpose of the treatment and is achieved by setting the fill ratio. MBBRs can be operated at higher organic and hydraulic loads if sufficient surface area is provided. It is recommended to maintain the filling fraction below 70% in order to allow carriers to move freely with in the reactor [22]. The efficiency of the MBBR can also be increased by increasing the HRT, or through the use of multiple MBBR compartments [1].

Trapani *et al.* (2008) [27] investigated different fill-fractions for MBBR. They concluded that there was an optimal fill-fraction above which the reactor removal efficiency decreased. This was attributed to competition between suspended and attached biomass and the importance of suspended solids in the MBBR. With an increasing fill-fraction the suspended growth concentration decreases, however low suspended biomass can decrease the MBBR removal efficiency since they have a major role in enzymatic hydrolysis and bio-flocculation in the reactor. It was observed that a fill fraction of 35% had higher COD removal efficiency than a 66% fill-fraction. On the other hand, a 66% fill fraction had slightly better nitrification efficiency due to higher concentrations of slow growing nitrifiers which could be retained in the reactor. These results indicate that the fill fraction is an important parameter in MBBR design and must be chosen based on the treatment objectives.

Wang *et al.* (2005) [23] recommended that the dissolved oxygen in the reactor be kept higher than 2 mg/l for efficient COD removal. In their findings decreasing the DO from 2 to 1 mg/L decreased the COD removal efficiency by 13% indicating that DO became a limiting factor. On the other hand, increasing the DO from 2 to 6 mg/l increased the COD removal efficiency only by 5.8%. Their results also showed that simultaneous nitrification and de-nitrification (SND) could be achieved in a single MBBR reactor with an HRT of 6 hours due limitation of oxygen diffusion into the biofilm. The highest N-removal efficiency (89.1% on average) was obtained when the DO was kept at 2 mg/l. At lower DO concentrations, anoxic conditions occurred and ammonia conversion to nitrite or nitrate was limited and at higher DO concentrations anoxic condition and hence de-nitrification in the deeper layers of the biofilm did not occur.

It has been shown in various studies that the concentration of the biomass, in both attached and suspended forms, in the MBBR volume is approximately the same as activated sludge processes (2-5 kg/m^3 volume of the tank), however, the removal efficiency of the MBBR is several times higher which suggests that the biomass in MBBR processes are more viable. Rusten *et al.* (1998) found that at higher organic loading rates MBBRs have higher SS concentrations in the effluent [25]. However, it should be noted that the final suspended solids concentration may be affected differently if the loading rates are chosen in different ranges.

Sludge production in MBBR has been reported in the literature. Both Aygun *et al.* (2008) [24] and Orantes and Martinez (2002) [29] concluded that the sludge (TSS) production was linear to the COD loading rate and was lower than conventional activated sludge processes. The results of Aygun *et al.* (2008) [24] showed that the observed yield increased from 0.12 to 0.56 kg TSS/ kg total COD with increasing influent COD concentrations from 500 to 8000 mg/l [24]. Orantes and Martinez (2002) obtained the same result with yield coefficients increasing from 0.12 to 0.40 kg TSS/kg total COD when the organic loading rate was increased from 5.7 to17.8 g total COD/ m^2.d [29]. However, increasing the loading rate further to 35.7 g total COD/ m^2.d decreased the yielded coefficient to 0.34 kg TSS/kg total COD. The sludge production was 979 g TSS/d at the highest organic loading rate in this study (35.7 g total COD/ m^2.d). Helness *et al.* (2005) have suggested a yield coefficient of 0.5 g TSS/g filtered (soluble) $COD_{degraded}$ [28].

Orantes and Martínez (2004) [29] observed that the attached biomass on the carriers increased with the loading rate up to the threshold loading (30 g $COD/m^2 \cdot d$) above which the amount of biomass on the carriers could not be increased further. As a result, a maximum removal efficiency was achieved at the threshold loading rate since the removal efficiency of the MBBR is affected by the biomass concentration in the reactor.

Xiao and Ganczarczyk (2006) [30] investigated the effect of influent flow rates to the MBBR and found a shift towards larger particles with increasing flow rate. They attributed this observation to the higher collision of particles so that the repulsive forces were overcome and higher collision frequencies, resulting in more aggregation and larger flocs. Another conclusion from these results is that since the size of the flocs under different operation conditions may vary, this will affect the performance of the post solid separation process. For example, if a membrane is to be used the fouling mechanism may differ and, correspondingly, fouling rate would vary with the MLSS floc sizes.

If MBBRs are operated with high organic loading rates, the hydraulic residence time would be quite low for complete organic carbon removal. In these systems, soluble COD is consumed quickly while the majority of particulate COD passes through the reactor unchanged [22]. A portion of the particulate COD may be hydrolyzed (which makes the analysis of the MBBR soluble COD removal efficiency complicated). As a result, the TSS in the effluent of the MBBR operated at high organic loading rates can be estimated as the sum of influent TSS and the biological sludge production [28]. This explains the higher TSS of effluent than influent in various MBBR studies such as Orantes and Martinez (2004) [29] and Helness *et al.* (2005) [28].

A challenge associated with MBBRs operated at high organic loading rates is that the settleability of the sludge decreases [22]. The lower settleability in highly loaded MBBRs may be due to the higher fraction of non-flocculated biomass leaving the reactor [25]. If an enhanced solids separation process, such as membrane were implemented, MBBRs could likely be operated at significantly higher loading rates or low HRTs. The HRT should be high enough for soluble organic matter (low molecular weight matter) biodegradation and low enough to hinder the hydrolysis and biodegradation of particulate matter in the feed (including colloidal solids and high molecular weight matter) [23,28]. As a result, a compact wastewater treatment process which can handle a high loading rate and has high removal efficiency might be achieved. Several studies have evaluated the efficiency of MBBR and coagulation/sedimentation [23], and high rate MBBR coagulation/ flotation [28], and membrane filtration separation [1,5,16,31] for treatment of municipal wastewater and gave promising results.

1.6.2 Combination of moving bed biofilm reactors and membranes

Combining moving bed biofilm reactors and MBRs can compensate for the drawbacks of both of these systems and further increase their acceptance and application in the wastewater treatment area. As mentioned previously, one of the drawbacks of MBR systems is the potential for high fouling due high operating MLSS concentrations. The replacement of the suspended growth of the activated sludge process with an MBBR would decrease solids production and lower the solids concentration into the membrane hence reducing fouling. Readily biodegradable COD constituents will be removed in MBBRs and hence the biological activity in membrane reactors and on membrane surfaces would likely be minimized and reduce biofouling. For typical municipal wastewater, the effluent solids concentrations in the MBBR is in the range of 100-200 mg/l which is significantly lower than the solids concentration in activated sludge processes [31]. The concentration of solids in MBBR-MRs in the literature was found to be in the range of 450-1100 mg/l [16,31] depending on the wastewater loading rate, whereas recent enhanced MBR processes have been reported to operate at MLSS concentrations of 10-15 g/l [9]. As a result, it is expected that replacement of activated sludge processes with MBBRs would decrease fouling due to high concentrations of suspended solids and as a result, higher sustainable fluxes may be achieved. Leiknes and Ødegaard (2007) [1] have shown that MBBR-MR processes can be operated with municipal wastewater at COD loading rates as high as 2-8 kg/m^{3}d and HRTs less than 4 hours had a relatively high sustainable flux of 50 LMH and consistently achieved a high COD removal efficiency. MBRs by comparison are typically operated at lower COD loading rates of 1-3 kg/m^{3}d, require higher HRTs of 4-10 h and yield lower fluxes of 15-25 LMH [1].

The combination of membrane bioreactors and MBBR is beneficial for MBBR applications as well. The sludges produced in MBBRs have poorer settling characteristics (especially when operated at high loading rates) as compared to activated sludge process [5]. Therefore, their efficiency is limited by the sedimentation tank performance and they require a larger settling surface. Application of an enhanced particle separation system like a membrane would eliminate this constraint of MBBRs and increase their applicability.

Since the readily biodegradable or soluble biodegradable matter is removed in the MBBR and the particulate matter both from the influent and the biomass produced in the MBBR are separated by the membrane, these systems can be operated at a relatively short HRT and high organic loading rates. Therefore, the loading rate should be kept high enough or HRT should be kept low enough to minimize hydrolysis and biodegradation of particulate matter and high enough to allow for maximum removal of soluble organic matter [28]. MBBR-MR have the potential to be compact and produce a consistent high effluent quality for reuse purposes which makes them an interesting option for industrial wastewater treatment.

1.6.3 Potential strategies for enhancement of MBBR-MRs and reaction of membrane fouling

The characteristics and concentrations of sludge produced in a MBBR-MR are different from a conventional MBR system. As a result, the MBBR-MR optimal operating conditions and design criteria may be different and need to be investigated to minimize membrane fouling and improve the process [16]. Several operational and design factors such as HRTs and loading rates, configurations, aeration, the application of a flocculation zone have been investigated in the literature and are presented in this section. The focus of these studies was on fouling control and minimization of membrane surface area requirements.

Configurations: MBBR-MRs can be installed in two different configurations. The membrane can be immersed into the MBBR tank or can be installed in a separate tank. Both of these configurations have been reported in the literature, and all of these studies have evaluated hollow fiber membranes.

Lee *et al.* (2006) [5] immersed a hollow fiber membrane in the tank of an MBBR and employed a sieve around the membrane to prevent the collision of carriers with the membrane surface. They observed that the collision of suspended carriers with the membrane surface increased the frictional forces providing abrasion which detached the biofilm from the membrane and decreased membrane fouling. They also observed that increasing the air flow rate and carrier fill-fraction increased the collision energy and further reduced fouling despite the fact that these two factors decreased floc sizes. The decrease in floc sizes may have been due to the higher collision frequency and energy. Additionally, the EPS concentrations were decreased slightly by increasing these two factors which may be another reason for the reduction in fouling. The clean water membrane resistances were characterized over one year of operation and it was found that the collision forces did not damage the polyethylene membrane.

Flocculation: The application of pre-flocculation can reduce membrane fouling by decreasing the concentration of colloidal matter through its incorporation into larger flocs. Ivanovic *et al.* (2008) [21] applied a flocculation zone (F-Zone) beneath the aeration device of the hollow fiber membrane. Their results showed lower fouling rates for the first 8 days of the filtration when F-Zone was applied resulting in 4 days longer filtration time before the TMP reached a point where chemical cleaning was required (0.45 bar in their study). COD fractionation data showed a decrease in the number of colloidal particles ("submicron particles") around the membrane and a shift towards larger particles (from 0.70 to 0.84 μm) which likely was responsible for the decrease in membrane fouling. The sludge dewaterability and filterability also improved as compared to the configuration without the F-zone which was favourable for excess sludge handling [21]. The settleability of sludge in the MBBR-MRs without the F-zone was lower than that of typical MBRs, however implementation of a flocculation zone improved the sludge settleability to the extent that it was comparable to MBR sludge with good settleability. As a result, a better solids separation was obtained and the MLSS concentration around the membrane was decreased (40% lower) which was another reason for lower fouling with F-zone application [32].

Aeration: In conventional MBR systems, aeration rates are based on previous operational experience and are normally recommended by the membrane manufacturers. Membranes used in MBBR-MRs are operated with different sludge concentrations and characteristics and if installed in separate units the membranes are devoted to separation of particulate matter. As a result, their optimal operational conditions need further investigation [33]. The effect of aeration in MBR processes was discussed in section 1-4-2-3. Ivanovic and Leiknes (2008) [33] have proposed an approach for finding an optimal aeration with the least energy demand while maintaining high permeability. In their approach, they monitored membrane fouling and particle size distribution as a function of aeration rate. They obtained an optimal aeration range where the positive and negative effects of aeration were balanced. The range of aeration rates, above which the decrease in fouling became insignificant and below which particles became too small was defined as optimal. Ivanovic and Leiknes (2008) [33] did not observe any noticeable effect on MBBR-MR removal efficiency and sludge characteristics including dewaterability, filterability and settleability by changing the aeration. The optimal aeration rate in each MBBR-MR system would be different depending on the membrane design and configuration, and operational conditions such as HRT, loading rate and wastewater characteristics.

In this work, aeration was not used in the membrane separation process, however since the results of this project may be a stepping stone for a pilot scale project, one should keep in mind the effects that aeration may have when the findings are extended.

HRT and loading rates: Only a few studies have investigated the combination of MBBR and membrane filtration and most have addressed the effect of HRT on performance of the whole system and on membrane fouling. The work discussed in this section is that of Melin *et al.* (2005) [16], Leiknes and Ødegaard (2007) [1], Leiknes *et al.* (2006) [8] and Ahl *et al.* (2006) [31]. These researchers have considered high loading rates where only COD removal could be achieved and low loading rates where both COD removal and nitrification were achieved. The change in HRTs was achieved by the addition of MBBR compartments with the same volume to the test set-up. For example, Leiknes and Ødegaard (2007) [1], Leiknes *et al.* (2006) [8] and Ahl *et al.* (2006) [31] used one reactor for high-rate treatment and four reactors with the same individual volumes for low rate treatment. All the reactors had a volume of 65 L and fill fractions of 67%-70% with external submerged hollow fiber membranes with pore sizes of 0.04 micron. Melin *et al.* (2005) [16] were the exception and used a pore size of 30 kDa.

Melin *et al.* (2005) [16] investigated membrane fouling for high and low loading rate conditions for the MBBR under a range of membrane fluxes. They observed a shift towards larger particles at the lower loading-rates (i.e. higher HRT); however, this did not have a significant effect on membrane fouling except at the highest flux tested (5.6 LMH). In most of the fluxes tested (3.9, 4.51, 4.01, 5.61 LMH), a lower TMP was observed after the back washing of the membrane for lower-rate treatment; however, the final TMP became almost equal to that of the high-rate conditions at the end of each production cycle. It was concluded that the high SS and higher number of small particles in the high-rate system may have formed a compact cake layer in a shorter time compared to low-rate systems after the backwash. Since operation under different loading rates in this study did not change the membrane performance significantly despite the higher SS in the membrane reactor for high-rate operation, it was concluded that SS did not affect the membrane fouling. The insignificant contribution of SS may have been due to its relatively low concentration (467 and 1,075 mg/l for high and low-rate, respectively) in membrane reactor for MBBR-MRs as compared to conventional MBRs. In the literature, various thresholds have been suggested for the TSS which determined if the membrane performance would be affected by the changes in SS concentration [16]. However, the defined thresholds may vary from study to study based on the differences in feed water, configuration, or operating conditions. In this experiment the threshold may have been above the operational SS concentration range in the membrane reactor.

The results of Melin *et al.* (2005) [16] have shown that the MBBR-MR had only a slightly better COD removal efficiency (4%) when operated at low-rate conditions as compared to high rate conditions. Despite the fact that the soluble COD removal of the MBBR was lower (about 20%) in the high-rate system, only a small fraction (19-21%) of the MLSS COD was in the size range that could pass through the membrane. The low proportion of residual soluble COD explains the insignificant difference in COD removal of the whole system under low and high loading rates, since residual particulate COD was removed by the membrane. Leiknes and Ødegaard (2007) [1] and Leiknes *et al.* (2006) [8] also found a consistent high COD removal efficiency (85% - 90% and 88% - 90%, respectively) regardless of the operating mode (high-rate vs. low-rate). It is worth noting that the removal efficiency of MBBR-MR processes may be affected differently by the loading rate in different circumstances. For example, if the influent wastewater has a higher percentage of soluble COD (which may be a case in industrial wastewaters) then the importance of membrane COD removal will decrease while the importance of the MBBR removal efficiency and consequently the importance of its operating conditions such as HRT increases.

Particle size distribution data reported by Melin *et al.* (2005) [16], Leiknes and Ødegaard (2007) [1] and Ahl *et al.* (2006) [31] have shown that the majority of particulate matter was in the range of 1µm and larger. They also found that there was a shift towards larger particles at lower loading-rates (i.e. higher HRT). Leiknes and Ødegaard (2007) [1] suggested that this could be due to further hydrolysis of colloidal matter or better flocculation mechanisms in low-rate systems. These reasons can also explain the larger and stronger flocs (aggregates) formed in low-rate systems since they have less breakage due to the shear forces by membrane aeration.

In all of the studies the settleability of the flocs in the high-rate systems was lower than the low-rate systems which may be one of the reasons for the higher TSS concentration in the membrane reactor for high-rate systems. The low settleability at higher loading rates may have been due to the breakage of the flocs in the high-rate systems since higher aeration rates were required or it may have been due to higher colloidal matter concentrations that would be present at higher loadings [16]. The flocs formed in low-rate system, in contrast, were more stable and the settled flocs did not resuspend in the aeration in membrane tank [1,31]. Leiknes *et al.* (2006) [8] found that the sludge from low-rate systems consistently had better dewatering and filtering characteristics and better floc structure.

In contrast to the results of Melin *et al.* (2005) [16], other studies including Leiknes and Ødegaard (2007) [1], Leiknes *et al.* (2006) [8], and Ahl *et al.* (2006) [31] found that operating under low-rate conditions reduced membrane fouling. Ahl *et al.* (2006) [31] found that low-rate operation resulted in better aggregation (i.e. better flocculation) of submicron particles (colloids) into larger and more stable flocs. Therefore, the number of submicron particles was reduced significantly in the membrane for the low-rate system while for the high-rate MBBR the changes in the fraction of submicron particles were insignificant. Since the fouling rate decreased with the decrease in submicron particles in the lower loading rate systems, it was concluded that submicron particles were an important fouling contributor.

Leiknes *et al.* (2006) [8] investigated the impact of particle size distribution (PSD) and filtered COD fraction distribution on fouling in the MBBR effluent, membrane reactor and the concentrate for high rate and low rate operations. They reported that higher values of the FCOD fraction below 1.2 µm in the MBBR effluent and higher amounts of submicron colloidal particles below 0.45 µm were measured in the membrane tank during high rate operation. Both the PSD and the fractional distribution of FCOD indicated that the higher concentrations of submicron colloids below 0.45 µm in the high-rate mode of operation are significant contributors to membrane fouling. Additionally, analysis of particle size distribution (PSD) on MBBR effluent showed that in low-rate systems the majority of particles were in the range of 100 µm while for high-rate systems the majority of particles were in the range of 20-30 µm. The larger particle size distribution for the low-rate systems may result in higher cake porosity and consequently, decreased the cake layer resistance and reversible fouling [34].

1.6.4 Pre-treatment of membrane influent by coagulation

The use of feed pretreatment for membranes has been studied widely and is often employed at full-scale in water treatment. The two main objectives of employing a pretreatment method are to reduce membrane fouling by improving the feed water/wastewater characteristics and to increase the removal of certain contaminants such as phosphorous. As a result, membrane costs may decrease and their application increase. In some cases where the addition of a pretreatment step increases the costs it may still be necessary to use them to meet the regulatory requirements for the permeate. Pretreatment methods can increase the membrane performance efficiency by increasing the particle sizes which would decrease pore blockage, by removing foulants, by decreasing their affinity to the membrane surface and therefore, decrease irreversible fouling. It may also be improved by preventing growth of undesirable micro-organisms on the membrane surface [6].

The most common pretreatment methods include coagulation, adsorption, oxidation and pre-filtration and among them coagulation has been the most successful option for fouling reduction since it had given the most predictable and promising results [6]. Other treatment processes have drawbacks that impede their application. For example, adsorption by powdered activated carbon (PAC) requires removal of residual PAC powder from the treatment facility and the capacity of activated carbon is quickly exhausted by dissolved organic matter and low molecular weight substances which may have very low fouling effects [12]. Oxidation can form disinfection byproducts (DBPs) and if the oxidants are not compatible with the membrane material, they can damage the membrane [6].

1.6.4.1 Coagulation fundamentals

Coagulation is a process which is used to destabilize the colloidal particles by several mechanisms so that they can be removed in subsequent separation processes such as filtration or sedimentation. These mechanisms include: compression of the double layer of the particles, adsorption and neutralization of the surface charge, adsorption and inter particle bridging and, enmeshment of the particles in a precipitate or sweep flocculation [35]. During coagulation several destabilization mechanisms are typically exploited simultaneously, however, depending on water chemistry one mechanism might dominate [35].

The adsorption and charge neutralization mechanism is when the particles can be destabilized by adsorption of counter ions. Usually, colloidal particles such as bacteria and viruses have a negative charge at a neutral pH in water or wastewater. Therefore, cationic coagulants can neutralize the charge on the particles [6].

The principal coagulants used in water and wastewater treatment include inorganic metal compounds and synthetic organic polymers. The most common inorganic coagulants for pre-treatment include aluminium and iron salts such as aluminium sulphate and ferric chloride. These two metal salts form a series of hydroxide species in water and depending on the pH and temperature of the water one species will dominate and correspondingly a coagulation mechanism will dominate. Depending on the pH of the samples ferric chloride forms monomeric and polymeric hydroxides including $Fe(OH)^{2+}$, $Fe(OH)_2^{-}$, $Fe_2(OH)_4^{2+}$, $Fe_3(OH)_4^{5+}$, neutral $Fe(OH)_3$ and negatively charged $Fe(OH)_4^{-}$ [36]. For example, at neutral pH the dominant species would be uncharged precipitate and low charged compounds and therefore, the dominating mechanism is sweep flocculation and to a lower extent charge neutralization [35]. Additionally, depending on the DO of the wastewater, ferric chloride may appear as Fe(II) or Fe(III). It is expected that if the reactor is not sufficiently aerated the Fe(III) can be readily converted to Fe(II) which reduces the efficiency of iron in removing colloidal matter [23].

Alum forms $Al(H_2O)_6^{3+}$ when added to water which is then further hydrolyzed to produce dissolved species with positive or negative charges (such as $Al(OH)^{2+}$, $Al(OH)_2^{1+}$,and $Al(OH)_4^{1-}$) or a precipitate $Al(OH)_3(s)$ depending on the temperature and the pH of the sample. Therefore, for a higher efficiency of alum, it may be required to adjust the pH [35,45].

Coagulation with pre-hydrolyzed coagulants or cationic polymers such as poly-aluminium chloride (PACl) forms hydroxide species with high positive charge and hence has high efficiency in charge neutralization. Additionally, since they are polymers they can cause bridging between particles [6].

Some of the advantages of PACl over aluminium salts are that they have a higher destabilization effect and therefore, colloids form aggregates more readily, form stronger flocs which are more easily separated, have significantly lower sludge volume, have lower aluminium residuals, have high efficiency at low temperature and over a larger range of pH, and have higher efficiency at lower dosages, however, its cost is substantially higher [12].

Organic polymers are normally used as a flocculation aid in order to increase floc size and strength and hence their settleability is mainly driven by inter-particle bridging. Polymers can also be used for sludge conditioning and as a filtration aid as primary coagulants [23]. There are few studies that discuss the use of organic coagulants with membrane filtration in wastewater treatment.

1.6.4.2 Effect of pre-coagulation on membrane fouling

The pre-coagulation of the membrane feed has been widely studied in water treatment with respect to removal of natural organic matter (NOM) and to a much less extent in wastewater treatment for removal of colloids formed in bioreactors. As discussed previously, several studies on MBBR-MRs have indicated that decreasing the concentration of colloidal matter by incorporating flocculation [21] or operating at lower organic loading rates and higher HRTs [8] decreased UF membrane fouling. The previous studies have not investigated the use of coagulation as a membrane pretreatment strategy that could decrease colloidal matter in MBBR-MRs. Coagulation can effectively remove undesirable inorganic and organic colloids (viruses, protein, polysaccharides with acidic groups in EPS and SMP) by incorporating them into larger flocs which would be rejected by a membrane or by sweep flocculation and precipitation. As a result, membrane performance with respect to fouling reduction and contaminant removal efficiency may increase. Pre-coagulation, if practical, could eliminate the constraint of operation of the MBR under low TS concentrations for decreasing the fouling and therefore, the MBRs could be operated at longer SRTs [13]. A few examples of studies that have evaluated pre-coagulation of membrane feed streams are presented here.

Yoon *et al.* (2005) [13] investigated coagulant addition to a pilot scale MBR with submerged flat sheet membranes. This MBR was seeded with sludge from a sewage wastewater treatment plant and acclimated with a high strength synthetic feed (COD of 10,500 mg/l) for a month in order to promote high fouling conditions. They obtained a 50% reduction in polysaccharide concentrations (from 41 to 21 mg/l) by the addition of a proprietary cationic polymer (referred to as membrane performance enhancer (MPE). Fouling was reported to be reduced significantly, the TMP surge interval was increased from 5 to 30 days and they were able to operate the membrane with longer intervals between cleaning. Yoon and Collins (2006) [20] also investigated pre-coagulation in full-scale and pilot scale municipal MBRs and observed an increase of the critical flux. Additionally, the membrane was operated at a 39% higher flux (47.25 LMH) than the critical flux (34 LMH) and they observed a constant, low rate of fouling with addition of the coagulant. Operation without the coagulant at a flux (35 LMH) that was 35% higher than the critical flux (26 LMH) increased fouling significantly [20]. For long term filtration, the MBR could be operated with a 50% higher flux and the surge interval was at least 8 days longer than operation without the coagulant. In studies by Yoon *et al.* 2005 [13] and Yoon and Collins (2006) 10–20% higher oxygen transfer rates were observed when the coagulant was added and there was a decrease in the permeate COD.

Pre-coagulation prior to the membrane can be employed in two configurations including coagulation and sedimentation or inline-coagulation. For the former, colloids that are destabilized and enmeshed in the precipitates are removed in a sedimentation tank prior to filtration. In this configuration, it is preferable to provide conditions where sweep flocculation is maximized to obtain the highest removal of colloids. Haberkamp *et al.* (2007) [12] investigated pre-coagulation with alum and ferric chloride for tertiary wastewater filtration and observed that the highest efficiency for the membrane occurred when the feed pH was maintained at neutral. They concluded that alum and ferric chloride had the highest efficiency of DOC removal since the formation of metal hydroxide precipitates and hence co-precipitation of DOC was higher at neutral pH.

Inline-coagulation is more compact than coagulation/sedimentation. In this approach, coagulant hydroxides and aggregated colloids enter the membrane where they can accumulate on its surface and can severely increase fouling if they have a high affinity for the membrane surface or are close to the membrane pore size (due to pore blockage) [6,37]. This disadvantage of inline-coagulation can be compensated for by choosing a membrane material that these compounds have less affinity to and by choosing a proper pore size. For example, Gray *et al.* (*2006*) [38] observed that pre-coagulation prior to an MF membrane with an aluminum-based coagulant increased polypropylene membrane fouling while it decreased polyvinylidene fluoride membrane fouling. In addition, decreasing the membrane pore size can convert the pore blockage mechanism of these compounds to cake formation which is easier to remove. This appears to be membrane specific as Howe and Clark [37] observed that fouling was lower in UF membranes as compared to MF membranes in a pre-coagulation-membrane system.

Another disadvantage of inline coagulation may be that the shear forces at the membrane may break the floc bond and re-release colloids and therefore, the efficiency of coagulants may be reduced [6]. As a result pre-coagulation of membrane feed may be more effective if a sedimentation tank is employed to separate metal hydroxides and aggregated colloids prior to the membrane.

For optimal efficiency of pre-coagulation a proper dosage of coagulant should be added to membrane feed. Figure 1-4 indicates the potential fouling mechanisms for MF and UF membranes when inline pre-coagulation is employed (Huang *et al.* (2009) [6]). It can be observed from Figure 1-4 that under dosage of coagulant forms fine aggregates with poor settleability which can cause pore blockage. This is more of a problem for MF membranes as compared to UF membranes due to the relative sizes of formed flocs and coagulant residuals to membrane pore size. The optimal dosage of coagulant increases the floc sizes and their settleability and therefore, less fouling is expected (the decrease in fouling for MF membranes may be more significant than UF membranes) and also pore blockage may be converted to cake formation. Over dosage of feed may further increase the floc sizes, and hence decreases pore-blockage, in addition, it may further remove undesirable colloidal matter and therefore reduces membrane fouling. However, overdosing of the cationic coagulant can cause charge reversal and hence restabilize the particles that have precipitated.

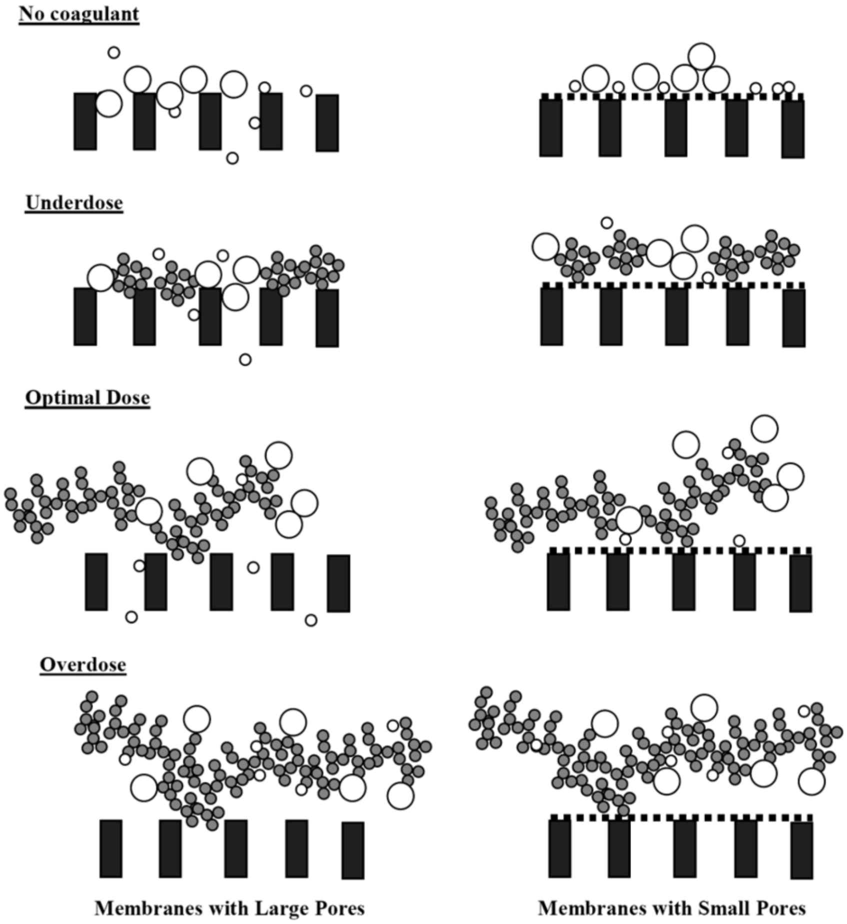


Figure 1-4 Fouling mechanism of UF and MF membranes under various coagulant dosages, for inline pre-coagulation membrane systems (From Huang *et al.* (2009) [6], Permission conveyed through Copyright Clearance Center)

Howe and Clark (2006) [37] observed that over-dosage of river water decreased membrane fouling for MF membranes, while the performance of a UF membrane remained unchanged. Therefore, it may be preferable to utilize a UF membrane when pre-coagulation is applied. A disadvantage of pre-coagulation is its higher excess sludge production which increases the costs of sludge disposal and handling [13].

A potential disadvantage of pre-coagulation may be the difficulty of maintaining a proper dosage of coagulant for wastewaters with varying characteristics such as in industrial wastewater treatment. Finding the optimal pre-coagulation conditions for membranes is a complex matter and to some extent unpredictable since it depends on several factors such as type of coagulant, membrane material and pore size, and feed characteristics.

The optimal dosage of coagulant may be obtained by jar tests that identify the dosage that yields the lowest COD or turbidity of the supernatant, by a visual test to observe which dosage yields the largest floc sizes, or by filterability tests as suggested by Yoon and Collins (2006) [20]. For the latter method the coagulated samples are filtered through a 0.45 μm filter and the dosage which yields the highest volume of permeate in 5 minutes of filtration time is identified. It was proposed that the optimal dosage would then be a dosage which is 50% higher than the dosage obtained.

While coagulation has been found in many cases to reduce fouling, it should be noted that an improper coagulant type or dosage may increase membrane fouling. Howe *et al.* (2006) [39] investigated the performance of MF and UF membranes filtering river water when pre-coagulation with ferric chloride and alum were employed and observed that MF permeability deteriorated with the addition of coagulants while UF permeability improved. It was found that alum had a lower efficiency than ferric chloride due to the different floc characteristics and sizes and hence different fouling mechanisms that resulted from this coagulant. Choo *et al.* (2007) [40] investigated the effect of several types of coagulant on the performance of a cross-flow UF membrane for treatment and reclamation of textile wastewater. It was observed that coagulation with a polyamine (an organic polymer) increased membrane fouling since its residuals acted as a foulant even at immeasurable concentrations. On the other hand, inorganic coagulants all decreased the membrane fouling with PACl having the highest and alum having the lowest efficiency. These results were observed despite the fact that all the coagulants had approximately the same efficiencies in turbidity and TOC removal. This suggests that preliminary jar tests alone cannot provide sufficient predictability for the effect of coagulant types and dosage on membrane performance.

1.7 RESEARCH NEEDS AND OBJECTIVES

Despite the potential benefits of a MBBR-MR technology there have only been a limited number of studies of this configuration. A review of the literature revealed few publications on MBBR-MR and most of these studies were conducted for municipal wastewater treatment. Additionally, there were no studies that had been performed with pretreatment of the MBBR effluent by coagulation in order to reduce membrane fouling. The overall goal of the present work was to investigate the feasibility and potential of the MBBR-MR process. The specific goals of this study were to:

- Assess membrane fouling and COD removal efficiency in a MBBR-MR system treating a food industry wastewater with relatively high concentration of organics
- Assess the impact of hydraulic residence time on these responses
- Investigate the effect of pre-coagulation of MBBR effluent with alum, a blend of polyamine and polyaluminum chloride, and ferric chloride on membrane fouling and COD removal efficiency of the whole system (MBBR-MR)
- Optimize the pre-coagulation by determining the suitable coagulant type and dosage based on membrane fouling and COD removal of the system.

Chapter 2

EXPERIMENTAL PLAN AND MATERIALS AND METHODS

2.1 EXPERIMENTAL PLAN

The purpose of this research was to evaluate the performance of a combined moving bed biofilm process and a UF membrane separation system (MBBR-MR) for treatment of an industrial wastewater for potential reuse. Specific re-use opportunities within the plant had not been identified at the time of this study as the effluent quality that could be obtained with the technology was to be determined a part of the study. The wastewater in this project was obtained from the Frito-lay potato chip factory in Cambridge, Ontario, Canada. The characteristics of the influent to the MBBR and the effluent from the MBBR were regularly monitored for more than five months and the results are presented in this section. The performance of the MBBR-MR system under high and low HRTs was investigated.

Additionally, the effect of pre-coagulation on the performance of the membrane including its COD removal efficiency and fouling was investigated. A series of jar test experiments were performed to investigate several coagulant types and obtain their optimal dosages for the subsequent ultra-filtration trials. Wastewater characteristics of the samples from the MBBR's effluent were measured in order to investigate the possible effect of each of the wastewater characteristics on the results of coagulation jar tests and ultra-filtration trials.

A fractionation of filtered (soluble) COD into colloidal COD and FFCOD was performed. The purpose of this was to understand the contribution of these various COD fractions to membrane fouling. Additionally, by comparing SCOD fractions of the coagulated and non-coagulated samples the effect of coagulation on each of these fractions was observed to assist with understanding the potential influence of coagulation on membrane performance.

2.2 INDUSTRIAL WASTEWATER DETAILS AND MBBR EFFLUENT QUALITY

This project involved a study of treatment of a starch recovery line in the Frito-lay potato chip processing factory in Cambridge, ON. The starch recovery line provided the feed to the MBBR tank. The feed water to the MBBR showed significant fluctuations mainly due to operational variability in the factory. The quality of the effluent from the MBBR varied daily or more frequently corresponding to the fluctuations of the influent quality. A brief description of the water process cycle before the starch recovery tank is presented to better understand the reason for these fluctuations.

In the process, potatoes are initially washed with a mixture of 60% city water and 40% recycled water. The water temperature ranged from 7 to 15°C, depending on the season. The potatoes are then sent to two separate potato lines namely, PC32 and PC50. These two lines are independent and run at 100 GPM and 80 GPM (6.3 and 5.04 L/s), respectively. The potatoes are then peeled and sliced and sent into the wash box, where the sliced potatoes are washed. The PC50 line has a heated wash-box while PC32 does not. The wash-box would normally run at temperatures of about 32°C. After the wash box, potatoes are sent to production for further processing, while the starchy water is run through screens which are each 1.22 m in diameter and have a 92 mesh size and separate larger matter than starch such as potato peels from the starchy water. The water lines from the PC50 and PC32 lines are joined together prior to the screens, then split apart and directed to the two separate screens. The water with separated solids from the screens is sent to the Fines tank and the starchy water is sent to starch tanks which have a residence time of 10-15 minutes. The flow then enters the next section of the starch recovery process which is the hydroclones. The starch tanks are both equipped with level sensors in order to ensure that there is enough positive head on the pump suction to maintain the desired pressure on the hydroclones (620-689 kPa). A common problem that occurs in these tanks is that when water level is not high enough, the pressure drops and hence the working efficiency of the hydroclones decreases. The hydroclones create centrifugal forces by converting the incoming liquid velocity into rotary motion. Therefore, the starch is separated from water based on their differences in specific densities. From the top of the hydroclones diluted water exits and is sent to the starch recovery (recycle water) tank. The starch exits with the underflow from the bottom of the hydroclones and is sent to the drum/vacuum. There are two sets of 6 hydroclones in that operate in parallel; however, normally only 10 of the hydroclones are operated since the pressure is decreased to lower than 620-689 kPa (which is the optimal pressure for the maximum efficiency of the hydroclones) if all hydroclones are operated. If the efficiency of the hydroclones decreases, the water that exits from its top and enters the starch recovery tank has a higher concentration of starch. Therefore, The MBBR influent had higher concentration of starch at these times.

The hydroclones concentrate the starchy water and then the concentrated starchy water enters the vacuum filter drum. The starch that is separated from the drum in the vacuum filter is sent to a starch dryer to reduce the moisture content, after which it is collected in a starch bag. The over flow from the vacuum filter drum is sent to starch tank #1 and the clean filtered water from the drum is sent to the starch recovery tank. The water in the Fines tank is recycled back to the screens. The water from the starch recovery tank is run through a Tsunami system to process the water and is then recycled back to be mixed with city water and to go through the water process again. Tsunami® (Ecolab Inc., Mississauga, Ontario) is a chemical approved by USDA and EPA for water that is applied in fruit and vegetable processes. Tsunami® hinders bacterial growth and biofilm formation on processing equipment. The fruits and vegetables should be rinsed with potable water after contact with the Tsunami®. The excess water to the recycled water tank is discharged to the city sewer after going through a centrifuge for further treatment.

Any changes or problems that occurred in the water circulation and starch recovery process resulted in changes in the quality and characteristics of the influent water to the MBBR. One common problem was that the hydroclones and the starch tank drum/vacuum did not separate the starchy water efficiently. The vacuum/drum efficiency decreased if its feed water was dilute and the starch concentration was not high enough. The feed may have been dilute because the hydroclones did not operate properly or if only city water (instead of a mixture of recycled water and city water) was run through the system due to problems such as spills in the plant. Although recycled water should always have been running, it was often shut off in certain areas. The efficiency of the drum/vacuum also depended on the condition of the fabric belt and the level of starchy water to be picked up by the drum in the box (or starch slurry tank in which the drum is located). The level of water also depended on the number of hydroclones running. The starch concentration in the starch recovery tank and hence, in the MBBR influent increased if the efficiency of the drum/vacuum for starch separation decreased.

Another problem in the water cycle was that one or both of the PC lines was not always working due to operational issues. On average each of them may have been off for 2-4 h each day. If one of the lines was not running, the flow decreased, and hence the required pressure for the hydroclones was not provided.

Another possible source of variation of the MBBR feed quality was the frequent variation of the types of potatoes used. There were a minimum of three types used each day. Additionally at certain times of the year fresh or stored potatoes may be used which are supplied from different places.

The feed to the MBBR was provided by a T connection to the starch recovery line from the recycled water (starch recovery) tank which was pumped to tsunami process. Prior to the MBBR a flow-meter (RMC-143-SS, Dwyer Instruments Inc., Michigan City, IN) was installed to adjust the influent flow to the MBBR. A picture of the MBBR and the starch recovery tank at Frito-lay is presented in Figure 2-1.

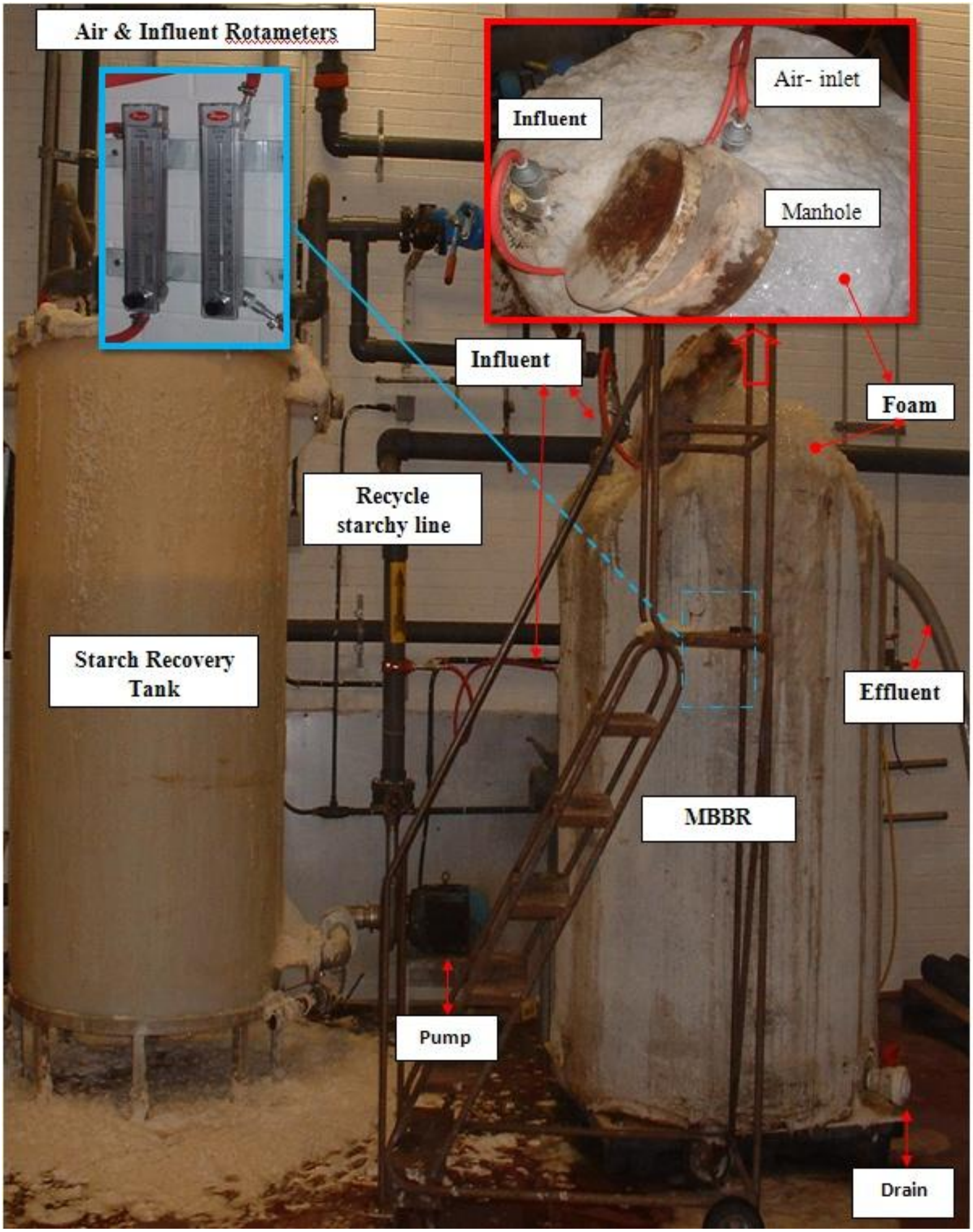


Figure 2-1 Picture of the MBBR and its connections at Frito-lay

2.3 MOVING BED BIOFILM REACTOR

The study was carried out using a pilot-scale moving bed biofilm reactor. The pilot MBBR had a working volume of 1.8 m^3 and carrier fill fraction of 30% of reactor volume. The MBBR for this study was supplied by Headworks Bio Canada Inc. of Victoria, BC. The active cell biofilm carriers had a specific gravity slightly lower than water and they are mixed throughout the reactor by aeration provided at the bottom of the tank. The carriers in this study were composed of polyethylene and shaped like small cylinders with diameter of 22 mm and a length of 15 mm. The carriers had a surface area of 402 m^2 per m^3 bulk volume of carriers which yielded a total biofilm surface area of 214.6 m^2 in the reactor. Figure 2-2 presents a picture of the active cell biofilm carriers from the MBBR in this study in a beaker with clean water. The picture was taken prior to steady state conditions and the carriers had lower attached biomass concentration than at steady state. It can be seen from Figure 2-2 there was insignificant biofilm growth on the outside surface of the carriers which may be due to the carriers' collision in the reactor. The carriers provided a high protected surface area where a dense population of bacteria could grow.

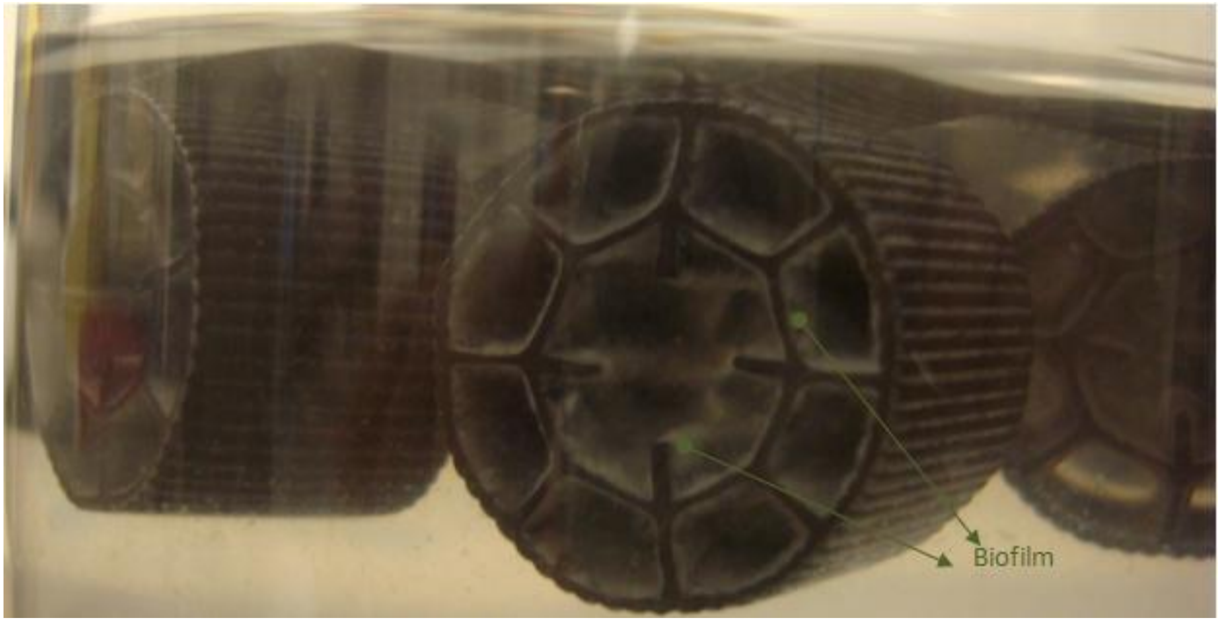


Figure 2-2 Active-cell biofilm carriers

In order to evaluate the effect of different HRTs and hence organic loading rates on the performance of the MBBR and consequently the MBBR-MR system, the MBBR was operated at two HRTs (4.6 h and 2.6 h). The organic loading rates depended on the HRT and the influent COD concentration which fluctuated frequently, however, average loading rates of approximately 158 ± 43 $g/m^2/d$ and 223 $g/m^2/d$ were obtained for HRTs of 4.6 (9.3 m^3/d) and 2.6 h (16.4 m^3/d), respectively. The HRTs were varied by changing the feed flow-rates with the influent rotameter (flow-meter).

The influent and effluent wastewater characteristics were regularly monitored for over 5 months based on a comprehensive sampling protocol presented in Table 2-1. The influent samples were obtained from a sampling valve on the MBBR influent line and the effluent samples were obtained from the open end of the effluent line. The influent and effluent samples were transported to the laboratory at the University of Waterloo and in order to perform all the analysis in Table 2-1.

Table 2-1 Sampling and analysis protocol

Location	Water Flow	Temp	D.O.	Air Flow	pH	Alkalinity	TSS	VSS	NH_3-N	TCOD	SCOD	TP	SP	TKN	Attached biomass
Unit	GPM	°C	mg/l	SCFM		$mgCaCO_3/l$	mg/l	mg/l	mgN/l	mg /l	mg/l	$mgPO_4^{3-}/l$	$mgPO_4^{3-}/l$	mgN/l	g/carrier
MBBR Influent	2/day				2/week		2/week	2/week	2/week	2/week	2/week	2/week	2/week	2/week	
MBBR In-Basin		2/week	2/day	2/day	2/week		2/week	2/week	2/week	2/week	2/week	2/week	2/week	2/week	1/month
MBBR Effluent					2/week	2/week	2/week	2/week	2/week	2/week	2/week	2/week	2/week	2/week	

A common problem that occurred during the sampling of the effluent was that the settled starch and biomass in the effluent line would detach and enter the sampling containers and hence, for example, a higher TCOD or TSS would be obtained for the effluent as compared to the samples obtained from the basin. Hence, the predominant sampling method for the MBBR effluent was obtaining to obtain samples from in the basin through the manhole on the top of the MBBR using sampling containers that had the top covered to prevent the carriers from entering them.

The samples were analyzed in triplicate for alkalinity, TSS, VSS, TCOD, SCOD, ammonia, TKN and phosphorous based on relevant sections in Standard Methods (APHA 1996) [41]. The samples were completely mixed and homogenized prior to each analysis. COD was measured based on a method modified from section 5220D (closed reflux, colorimetric method) of Standard Methods. In this modified method, potassium dichromate and concentrated sulphuric acid have been used as oxidants and the reflux time has been extended from 2 to 3.5 hours to ensure a complete reaction. For soluble COD, ammonia and soluble phosphorous analysis, the samples were filtered through a Whatman® glass microfibre filters with nominal pore size of 1.2 µm (934-AH™, Whatman Inc., Clifton, NJ). The pH was measured in duplicate by a calibrated Orion pH-meter (model 710A with an Ag/AgCl reference electrode, New Hyde Park, NY). For TKN measurements samples were digested with a digestion solution of sulphuric acid in high temperatures (first at 220°C for 1.5 h and then at 380 °C for 2.5 h) in order to convert organic nitrogen to ammonia (this method was developed in Water Technology Center (Burlington, Canada)). In order to prepare the digestion solution, 40 gram potassium sulfate and 2 ml Selenium oxychloride (97%) were dissolved in 250 ml concentrated sulfuric acid and after this solution cooled down, it was diluted with dionized water to a volume of 500 ml. Ammonia was measured by an alkaline phenate method (4500-NH_3 F).The solids analysis for TSS and VSS measurements was done in accordance with section 2540 D and E, respectively, of Standard Methods (APHA 1996) [41]. Alkalinity and phosphorous measurements were based on sections 2320 and 4500-P C.

The objective of the wastewater analysis indicated in Table 2-1 was to optimize the influent flow rate and operational conditions to meet the effluent quality of interest mainly with respect to effluent soluble COD. For example, the influent flow and loading rates would be decreased if the effluent soluble COD is higher than the soluble COD of interest. The data obtained was used for assessment, troubleshooting, and optimization of the MBBR.

Ammonia and phosphorus concentrations in the influent and effluent were measured to ensure that sufficient amounts of nutrients were available for biomass growth. A ratio of influent concentrations of BOD: N: P of 100:5:1 is required and effluent concentrations of residual ortho-phosphate above 0.5 mg/l and residual ammonia-N above 2 mg/l should be available (Headworks Bio Inc., Victoria, BC).

The amount of attached biomass on carriers can affect the MBBR performance. The amount of attached biomass on the carriers was measured by the attached growth total solids (AGTS) test. The method was provided by the Headworks Bio. and is presented in the appendix A. Continuous aeration was supplied by four coarse bubble diffusers (with hole sizes in the range of ¼ to 3/8 inches (or 6.35 to 9.525 mm) underneath the MBBR. It is recommended by Headworks Bio Inc. to keep the DO of the MBBR in the range of 2-4 mg/l. The average DO of the MBBR was 3.5 mg/l, however there were changes in influent characteristics which had an effect on the DO which ranged from 8 to less than 0.5 mg/l. DO was manually measured on site using a SympHony DO meter (Model SP70D, Mississauga, ON) two times a day. If the DO was lower than 2 mg/l or higher than 4 mg/l the DO was adjusted manually using an air rotameter. Occasionally, especially in the summer, an airflow of 20 SCFM the highest airflow level for the rotameter was insufficient to meet the required dissolved oxygen in the MBBR. This may have been due to the higher biological activity of the biomass caused by a higher COD loading rate and biomass concentrations. At DO concentrations lower than 1 mg/l, there was undesirable smell and bugs and flies were attracted to the MBBR. It was also noted that the DO in different locations of the MBBR tank were different. During a portion of the testing a layer of settled solids developed at the bottom of the MBBR (about 30 cm depth) and it was suspected that anoxic conditions developed at the bottom of the tank. The impact of these conditions and effect of the changing influent conditions were beyond the scope of this study.

Foaming of the MBBR proved to be challenging. Foaming normally occurs during the start-up of a MBBR system when there is a high BOD load and aeration. However, due to fluctuations of the influent quality in this study, excessive foaming occurred frequently. A non-toxic defoamer (KFO™ 6450FL, Emerald Performance Materials LLC, Cuyahoga Falls, OH) was employed for the recycled starch recovery line at the plant was dosed into the MBBR. A bucket of defoamer was placed on the top of the MBBR and the defoamer was dripped into the MBBR. Occasionally the valve clogged and the defoamer had to be added manually. Approximately 2.5-4 litre of the defoamer was required daily. The defoamer was not added to MBBR for 3-5 hours determined based on the HRT prior to sampling as it was suspected that residual defoamer might affect coagulant performance. This assumption was based on a few experiments where the initial turbidly was relatively high and coagulants showed low turbidity removal efficiencies when a high concentration of defoamer was added prior sampling.

The characteristics of the MBBR influent and effluent are presented in Table 2-2. It can be observed from Table 2-2 that the COD of the MBBR influent varied widely throughout the period of data collection and had an average value of 3708 mg/l. The highest and lowest values measured were 5857 and 1579, respectively. pH values did not show significant variation and ranged from 6.9 to 8.6 which indicated pH adjustment and buffer addition were not required. The alkalinity of the effluent had an average of 663 mg/L with a minimum of 433 and maximum of 930 as ($CaCO_3$) which indicates that sufficient alkalinity was present to prevent a pH drop in the reactor. The temperature in the MBBR fluctuated over a small range 19-25 °C.

Table 2-2 Characteristics of the MBBR influent and effluent (n=26)

Location	Parameter	pH	TCOD	SCOD	TSS	VSS	TKN	NH_3-N	TP	SP
			mg/l	mg/l	mg/l	mg/l	mg N/l	mg N/l	mgPO_4^{3-}/l	mgPO_4^{3-}/l
Influent	Mean	7.4	3708	1709	1384	1344	236	21.0	31.0	16.2
	Standard Deviation	0.3	1030	572	524	508	107	10.3	11.8	5.1
	Minimum	6.7	1579	440	763	730	76	7.6	18.4	10.7
	Maximum	7.8	5879	2631	2712	2453	438	48.0	51.9	24.4
Effluent	Mean	7.9	2664	277	2216	1653	196	50.7	3.1	3.2
	Standard Deviation	0.4	1144	94	1410	400	56	22.4	1.5	1.6
	Minimum	6.9	898	164	1340	1127	111	21.0	1.6	1.6
	Maximum	8.6	5161	634	3120	2512	273	90.0	15.9	5.0

Table 2-2 also indicates that there was sufficient residual nitrogen and phosphorous in the effluent and hence nutrient addition was not required with respect to the amount of biodegradable COD removal of the MBBR. The AGST results showed an average attached biomass of 50 ± 4.6 mg/carrier.

The performance of the MBBR was evaluated by its COD removal efficiency (obtained from $TCOD_{Influent}$ - $FCOD_{Effluent}$ removal percentage which is common efficiency measurement for MBBRs). The MBBR had a COD removal efficiency of 93% ± 2% which is considered a relatively high efficiency for a single reactor. Higher TSS and VSS were observed at the MBBR effluent compared to influent. The reason was that the MBBR does provide high particulate matter removal, however, there is biomass growth in the MBBR, therefore, higher particulate matter was observed at the effluent.

2.4 ULTRA-FILTRATION SETUP AND EXPERIMENTS

All filtration trials were carried out as batch dead-end filtrations using three bench scale Amicon stirred cells with a working volume of 400 ml (Model 8400, Millipore Inc., Bedford, MA). The membrane area was 41.8 cm^2. Figure 2-3 presents a schematic of the ultra-filtration cell set-up. Filtration experiments were conducted using a 0.05 micron membrane that was composed of polyethersulfone (PES) and generated permeates with a turbidity of <0.1 NTU (Model SpiraSep-900, TriSep Inc., Goleta, CA).

The stirred cells were placed on magnetic stir plates. The cells were pressurized using nitrogen gas. The pressure was regulated using a regulator connected to the nitrogen tank. The permeate was collected from the permeate port using a 100 ml graduated cylinder.

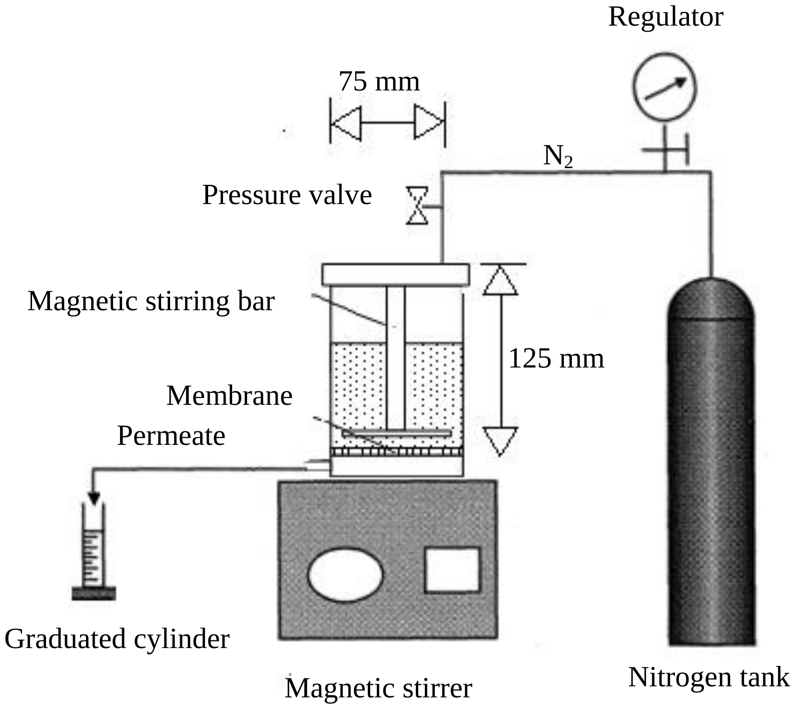


Figure 2-3 Schematic of ultra-filtration system

2.5 FILTRATION EXPERIMENTS

All filtration experiments were carried out with an initial feed volume of 350 ml and normally 150 ml of sample was filtered. For each filtration trial a new membrane was cut and placed in a beaker filled with de-ionized water for 24 hours prior to the filtration trial. The membranes were then washed with de-ionized water to remove any residual chemicals and organics and placed in the cell. The contents of the stirred cell were kept well mixed during the ultra-filtration using a magnetic stir bar at 150 ±10 rpm. This speed was chosen since it was high enough to prevent the flocs from settling but was not too high to cause breakage of the flocs. It was also near the highest stirring speed prior to formation of a vortex that could change the distribution of the flocs over the membrane which may affect fouling behaviour.

The transmembrane pressure (TMP) was set to 30 psi (207 kPa) during the filtration of the samples and the times required to collect incremental volumes of permeate (5 or 10 ml fractions) were recorded. The filtration of 150 ml of non-coagulated samples could take up 1.5-3 hours depending on the effluent characteristics. The membrane apparatuses were installed in a parallel configuration and the filtration trials were performed simultaneously in order to minimize the effect of changes in wastewater characteristics on the analysis and to ensure that the ultra-filtration trials were performed under the same conditions (such as operational pressure and samples characteristics). A picture of the ultra-filtration set-up is presented in Figure 2-4.

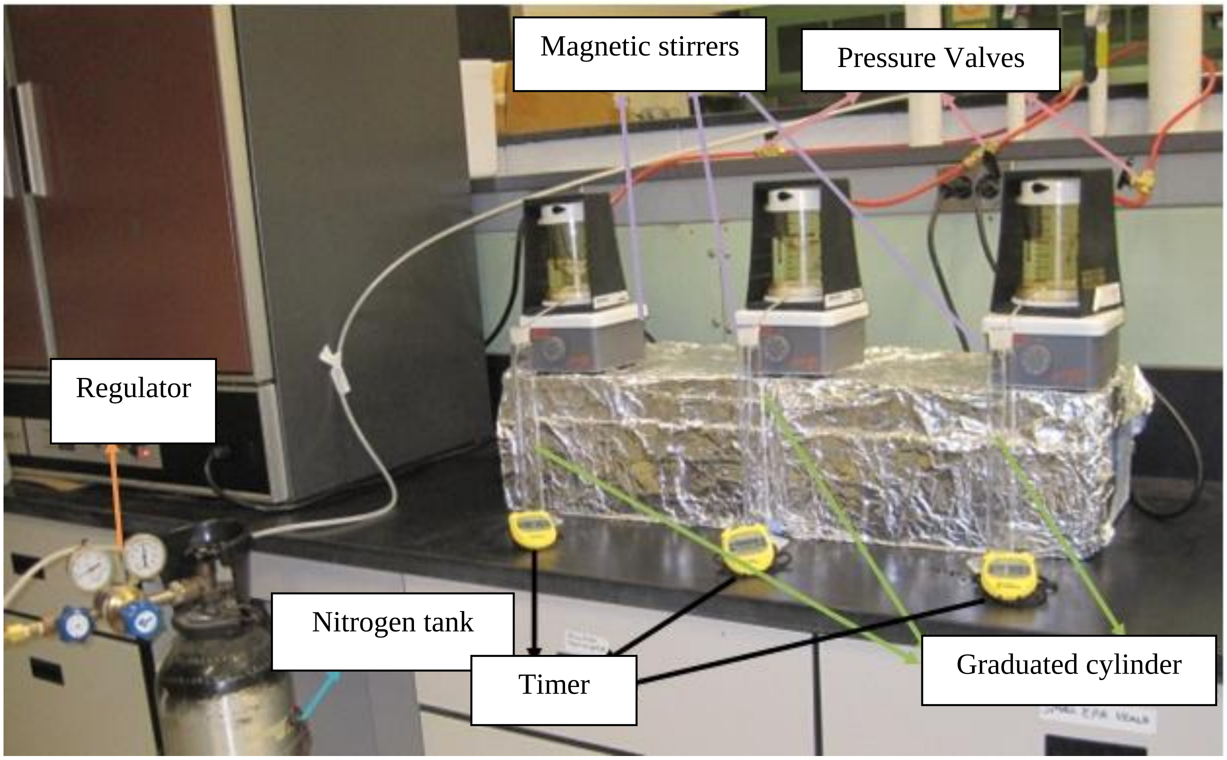


Figure 2-4 Picture of the ultra-filtration set-up

2.5.1 Evaluation of Membrane Resistance and Flux

The performance of the membrane separation unit was evaluated by its flux decline, reversible and irreversible membrane fouling and permeate COD. The flux for each time interval for collection of 10 ml of permeates was calculated by Equation 2-1.

$$J = \frac{Q}{A} = \frac{\Delta V}{(\Delta t \times A)}\,[L/m^2 H] \tag{2-1}$$

Where J is the filtration flux, Q is the permeate flow, A is the membrane surface area, and V is the permeate volume collected in the time interval of Δt. The flux of the permeate is proportional to the transmembrane pressure (TMP) and inversely proportional to the permeate dynamic viscosity (μ) and total resistance (R) according to Darcy's law. Therefore, the membrane resistance was obtained from Equation 2-2.

$$R = \frac{TMP}{(J \times \mu)}\,[m^{-1}] \tag{2-2}$$

Prior to filtration of each sample, in order to measure the membrane resistance, de-ionized water was filtered at pressures of 1.38×10^2, 2.07×10^2 and 2.76×10^2 kPa (20, 30, 40 psi). Filtration of de-ionized water prior to filtration tests pre-compacts the membranes to obtain sustainable permeability [12]. Measuring the clean membrane flux at three different pressures minimizes the possible experimental error in measuring the clean membrane resistance. The membrane resistance from the fluxes obtained at the three pressures was calculated from Equation 2-3 [42]:

$$R_m = \frac{1}{(a \times \mu)} \tag{2-3}$$

Where R_m is the clean membrane resistance and, a is the slope of the line (permeate flux vs. TMP). The dynamic viscosity of permeate was assumed to be close to that of water at 25˚C.

After the clean water tests, 350 ml of sample was placed in the stirred cell and normally 150 ml was filtered. Again the fluxes and the resistances for each time interval for collection of 10 ml of sample were calculated from Equations 2-1 and 2-2, respectively. The resistance measured at this point was the sum of clean membrane resistance (R_m) and fouling resistance (R_f) which included reversible (R_r) and irreversible (R_{irr}) fouling resistances (Equation 2-4 [42]).

$$R_t = R_m + R_f = R_m + R_{irr} + R_r \tag{2-4}$$

In order to measure irreversible fouling, the fouled membrane obtained from each filtration trial was rinsed with warm tap water for 20 minutes to remove the cake layer (which causes reversible fouling) and then rinsed with de-ionized water and placed back into washed stirred cell. De-ionized water was filtered at the three pressures previously mentioned and the membrane resistance was measured in a manner similar to that employed to calculate the clean membrane resistance from Equation 2-3. The irreversible fouling was calculated as the difference between the resistance obtained at this point (sum of clean membrane and cake layer resistance) and the clean membrane resistance. Correspondingly, the irreversible fouling resistance calculated in this study, includes fouling by pore blockage.

2.5.2 Coagulation

In order to determine the effect of coagulation on MBBR effluent properties, jar test trials were performed. Jar test trials indicate the performance of each coagulant with respect to residual turbidity, final pH, and floc formation observations and hence an optimal dosage of each coagulant could be estimated. The results of jar test trials were used to determine the coagulant doses that were employed in subsequent pre-coagulation-ultrafiltration trials.

For each coagulant, multiple jar tests were performed with samples that were collected on different days to cover a range of MBBR effluent characteristics. Jar test trials were conducted with four types of coagulant including alum, ferric chloride, Zetag®8125 (more information on Zetag is provided in Appendix B), and a blend of poly aluminum chloride (PACl) and polyamine. These coagulants were recommended by the vendors for this wastewater. The blend of coagulants consisted of 90% PACl with 9.07% AL_2O_3 and 10% poly amine. The coagulants where provided by Northland Chemical Inc. Mississauga, ON.

Two jar testing units were employed in these tests and this allowed for 9 simultaneous jar test trials (three of the paddles did not work). For each jar test, 6 to 9 beakers were filled with 1 liter of effluent sample. Each beaker was dosed with a different quantity of a coagulant. Samples were then stirred at approximately 100 rpm (velocity gradient of 70 s^{-1}) for 2 minutes (rapid mixing phase). The stirring speed was then reduced to 20 rpm (velocity gradient of 10 s^{-1}) and the mixing was continued for 20 minutes (slow mixing phase). The mixers were then turned off to allow settling of the solids for 45 minutes. The mixing speeds and time intervals were obtained from standard jar test practice that are employed for both water and wastewater treatment [43].

Samples were taken from supernatant near the top (1 cm from the top) of the beakers. To be able to quantify the efficiency of each coagulant and its dosage during the jar test trials the turbidity of the supernatant and the pH were measured. The turbidity of the supernatants was measured in duplicate with a portable hand held Hach turbidimeter model 2100P (Hach Co., Loveland, CO). The detection limit of the turbidimeter was set to 1000 NTU.

The optimal dosage was defined as the coagulant dose which yielded the lowest turbidity concentration or the lowest dosage above which the decrease of residual turbidity was insignificant (less than 2%). The optimal dosages obtained from these trials were employed for the subsequent pre-coagulation ultra-filtration experiments. Figure 2-5 illustrates a jar test unit.

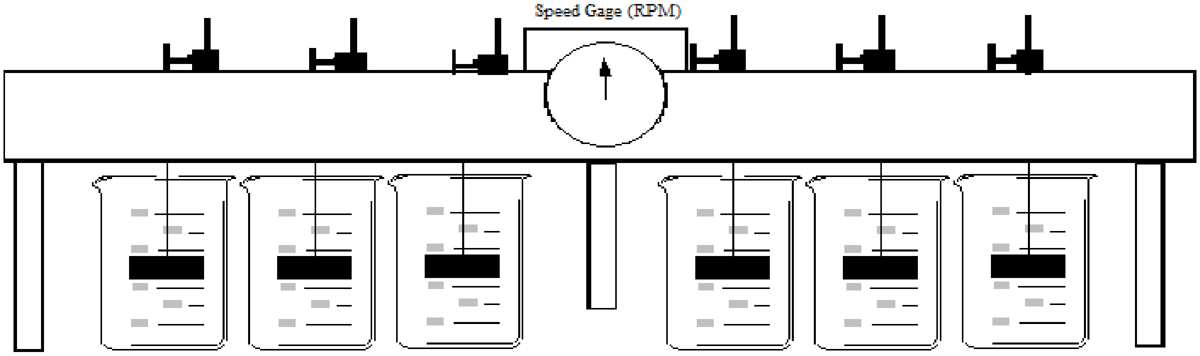


Figure 2-5 Jar testing unit

2.5.3 Pre-coagulation and Ultra-filtration Experiments

One purpose of the project was to evaluate the effect of pretreatment of the effluent by inline coagulation on ultra-filtration performance. To be able to imitate inline pre-coagulation, all trials were conducted in the following sequence:

1- A specific dosage of coagulant was added into a 1L beaker containing 1 litre of sample
2- The samples were mixed for 2 minutes at the speed of 100 rpm (similar to rapid mixing phase of jar testing) to ensure a complete and uniform distribution of coagulant
3- Immediately after the mixing 350 ml of the sample was measured into a 500 ml graduated cylinder and added to the stirred cell membrane. This step had to be performed quickly to prevent precipitation of solids
4- The ultra-filtration experiments described in section 2-5 were conducted
5- The permeate COD was collected to be measured later to assess the treatment efficiency of the whole MBBR-MR system
6- The supernatants from the remainder of the settled coagulated samples in the beakers were collected for further COD fractions

The last step was performed to assess the effect of coagulation on COD fractions of the effluent. This data was used to assist in explaining the effect of coagulation on membrane performance. The supernatant was filtered through a glass fiber filter with nominal pore size of 1.2 µm to obtain Filtered COD (FCOD). In order to have an estimate of the colloidal COD, the FCOD was coagulated with alum and centrifuged for five minutes and then was filtered through a 0.45 µm filter to obtain flocculated-filtered COD (FFCOD) which is more representative of the truly soluble COD. The colloidal COD was then calculated as the difference of the FCOD and FFCOD.

2.5.4 Ultra-filtration Experimental Plan Design

The membrane trials were separated into six phases:

1- None-coagulated MBBR influent and effluent samples (replicated)
2- Non-coagulated and coagulated MBBR effluent samples with ferric chloride (replicated)
3- Non-coagulated and coagulated MBBR effluent samples with alum (replicated)
4- Non-coagulated and coagulated MBBR effluent samples with the coagulant blend at high (4.6 h) and low (2.6 h) MBBR HRTs
5- None-coagulated and coagulated MBBR effluent samples with optimal dosages of alum and ferric chloride
6- Coagulated MBBR effluent samples with optimal dosages of alum, the coagulant blend and ferric chloride

The replication of the experiments in phases 1-3 was conducted to assess the reproducibility of the results considering the fluctuations of the effluent characteristics. Samples were obtained on different days to evaluate reproducibility and account for different effluent qualities.

The tests conducted in phase 1 were employed to assess the impact of the MBBR on the performance of the membrane. Phases 2-4 were performed to assess the efficiency of each type of coagulant and its different dosages on the membrane performance. Phase 4 was the same as phases 2 and 3 except that the samples were obtained on two different days when the MBBR was operated at different HRTs. Hence the effect of HRT on the performance of the pre-coagulation and ultrafiltration membrane and the COD removal efficiency of the whole MBBR-MR system could be evaluated.

Phases 5 and 6 were performed on one sample which was separately coagulated and filtered with different types of coagulant. The purpose was to eliminate the possible effect of effluent characteristics on the efficiencies of the coagulants and hence to allow a more direct comparison of the different coagulants.

The optimal dosages employed in these trials, were the optimal dosages obtained in a jar test that was conducted prior to each ultra-filtration trial. For phases 2- 3, three samples were prepared and ultra-filtered: One was not dosed, one was dosed at approximately half of the optimal dosage, and one was dosed with the optimal dosage. Table 2-3 provides a summary of the ultra-filtration experiments that were performed.

Table 2-3 Ultra-filtration experimental design summary

(High HRT= 4.6 h and low HRT=2.6 h)

Trial	Sample	HRT	Coagulant	Coagulant dose
Trial-1	Influent	-	None	-
	Effluent	High	None	-
Trial-2	Effluent	High	None	-
			Ferric chloride	Half optimal dosage
				Optimal dosage
Trial-3	Effluent	High	None	-
			Alum	Half optimal dosage
				Optimal dosage
Trial-4	Effluent	High	None	-
			Blend	Half optimal dosage
				Optimal dosage
	Effluent	Low	None	-
			Ferric chloride	Half optimal dosage
			Alum	Optimal dosage
Trial-5	Effluent	High	None	-
			Ferric chloride	Optimal dosage
			Alum	
Trial-6	Effluent	High	Ferric chloride	Optimal dosage
			Alum	
			Blend	

Chapter 3

PRELIMINARY COAGULATION TESTS

3.1 INTRODUCTION AND OBJECTIVES

In this section the results obtained from coagulation of the MBBR effluent during the jar testing trials are presented. The purpose of these trials was to provide a quick evaluation of four coagulants and to determine their effective dosages. The results obtained in this section were employed in the next phase of experimentation which involved coagulation and ultra-filtration of MBBR effluent. A number of coagulation tests were carried out but the results of each test were not always the same due to changes in the quality of the effluent. The MBBR effluent samples showed variations in the following characteristics: TSS, COD, soluble COD, alkalinity, and initial pH and turbidity. Therefore, each jar test trial may yield a different optimal dosage. As a result, a range of optimal dosages were obtained for each coagulant in this section. Therefore, before each ultra-filtration trial a jar test was performed on the fresh sample to find the optimal dosage of coagulant for that particular sample. It should be noted that the optimal dosage in this project was identified as the dosage that corresponded to a high turbidity removal (more than 97%) and that addition of more coagulant would result in very little or no change in turbidity. In this section the impacts of initial turbidity, and soluble and colloidal COD on coagulant performance were assessed.

The coagulants employed in this study were alum and ferric chloride, Zetag, and a blend of poly aluminum chloride and polyamine. These coagulants represent inorganic (alum and ferric chloride), organic classes (Zetag) and a mixture of both (the blend of poly aluminum chloride and polyamine). The efficiency of these three coagulants was evaluated with respect to turbidity removal and their effect on pH. Also the effect of initial TSS, total COD, turbidity and pH on the efficiency of each coagulant for turbidity removal was evaluated.

Finally, a comprehensive comparison of the performance of the coagulants with regard to their efficiency in reduction of turbidity, their effect on pH, and floc formation observations, and the consistency of the results was conducted. Based on preliminary jar test trials ferric chloride, alum, and the coagulant blend were chosen for the next part of trials and Zetag was eliminated was not considered further.

3.2 JAR TEST TRIALS WITH FERRIC CHLORIDE

During the jar test trials for ferric chloride, a range of dosages of ferric chloride were added to 1 litre samples of the MBBR effluent and the turbidity and pH at each dosage was measured. Four trials were chosen and are presented in this section. The wastewater characteristics and the optimal dosages of iron for turbidity removal are presented in Table 3-1. The DO of the MBBR could not be kept stable during the experimental period and for ferric chloride samples it varied from 1.2 to 5 mg/l. In trial 4 (Fe-4), the turbidity could only be decreased to 58 NTU which was significantly higher than the final turbidity other trials. In a few other trials also the turbidity remained relatively high. This may be due to the high TSS of Fe-4 samples. It should be noted that coagulation of the same sample with alum and the coagulant blend was even less efficient than ferric chloride decreasing the turbidity to 72 NTU at 400 mg/l of alum and 575 NTU at 400 PPM of the blend (these dosages were the optimal dosages of alum and the blend found in previous trials). Therefore, the low turbidity removal for this sample was low irrespective of coagulant type and was due to characteristics of the wastewater. However, in the rest of the trials smaller variations of TSS did not have observable effect on coagulant efficiency and the optimal dosage. Initial pH did not affect coagulant efficiency and the optimal dosage. The decrease in pH with addition of ferric chloride was linear and it dropped between 1.28-1.89 units at the optimal dosage. The pH at the optimal dosage was in the range of 5.7- 6.6. Except for trial Fe-4, the optimal dosages of ferric chloride varied from 500-550 mg/l $FeCl_3$ (4.6×10^{-3} - 5.1×10^{-3} mol Fe/l) and turbidity decreased from 380 - 1000 NTU to 3.74 - 8 NTU yielding a 99% turbidity removal in these trials.

Table 3-1 Wastewater characteristics for ferric chloride coagulation and its effect on pH

Trial	Influent flow (m^3/d)	D.O. (mg/l)	TSS (mg/l)	TCOD (mg/l)	SCOD (mg/l)	Initial pH	Drop of pH per 50 mg/l Fecl	Optimal dosage (mg/l)	Total pH drop @ optimal dosage	pH @ optimal dosage	Turbidity @ optimal dosage (NTU)
Fe-1	9.3	2	3910 ± 14	4957 ± 17	451 ± 23	8.02	0.15 ± 0.09	550	1.32	6.6	7.9
Fe-2	9.3	5	2230 ± 14	3150 ± 144	452 ± 9	7.72	0.19 ± 0.05	550	1.47	5.7	7.0
Fe-3	2.7-10.9	1.2	2990 ± 14	3831 ± 80	239 ± 26	7.74	0.14 ± 0.03	500	1.89	5.9	3.7
Fe-4	2.7-9.3	1.2	5160 ± 0	7571 ± 251	658 ± 70	7.11	0.14 ± 0.04	>600	1.28	-	58.0

The detailed results obtained from the coagulation trials with ferric chloride are presented in Figure 3-1. All the curves in Figure 3-1 followed a similar trend. Turbidity decreased quickly at low doses in all the trials until it essentially levelled off at some dosage value. At this dosage the majority of the colloidal particles were likely neutralized. This dosage was considered as the optimal dosage for ferric chloride at each trial.

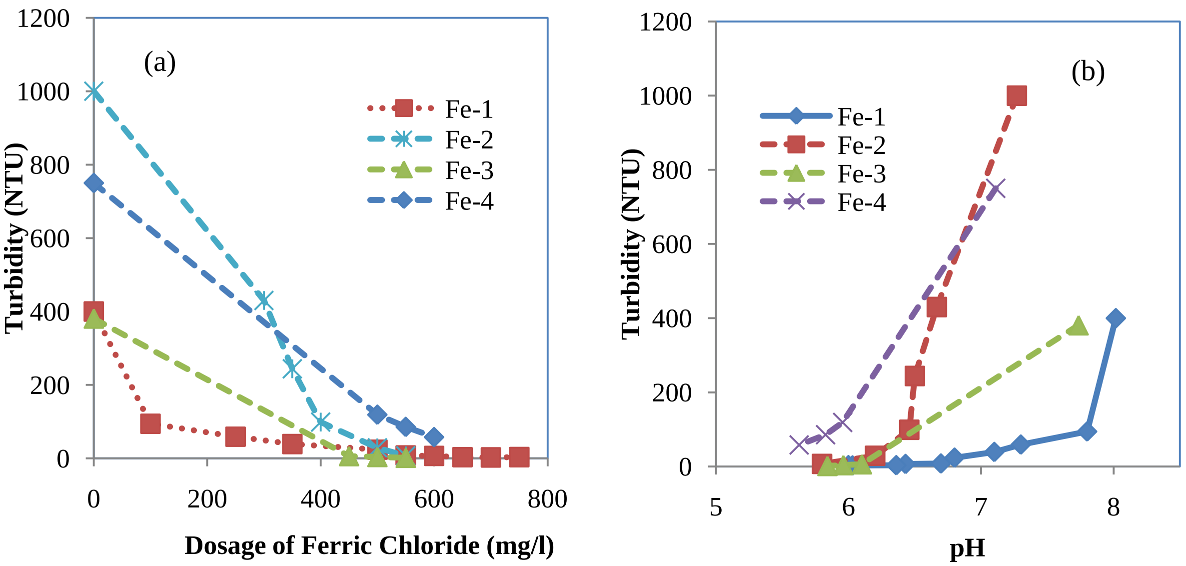


Figure 3-1 Coagulation with ferric chloride: residual turbidity (a) vs. dosage and (b) vs. pH

No significant correlation was observed between the optimal dosage of the ferric chloride and turbidity removal with each of the effluent characteristics alone including TSS, DO, initial pH, turbidity and alkalinity.

3.3 JAR TEST TRIALS WITH ALUM

Four jar test trials with alum were performed on four MBBR effluent samples obtained on different days. The characteristics of the samples of each trial and the optimal alum doses are presented in the Table 3-2. The purpose of these trials was to assess the efficiency of alum for turbidity elimination and hence consider it as an option for pre-treatment for ultra-filtration. As with ferric chloride, in a few trials the turbidity could not be decreased effectively and TSS and DO did not appear to have an observable effect on coagulant efficiency and optimal dosage. The pH decreased linearly with addition of alum and in the optimal dosage it decreased between 0.7 - 1.5 units at the optimal dosage.

Table 3-2 MBBR effluent characteristics for alum coagulation and its effect on pH

Trial	Influent flow (m^3/d)	D.O. (mg/l)	TSS (mg/l)	TCOD (mg/l)	SCOD (mg/l)	Initial pH	Drop of pH per 50 mg/l alum	Optimal dosage (mg/l)	Total pH drop @ optimal dosage	pH @ optimal dosage	Turbidity @ optimal dosage (NTU)
AL-1	9.3	0.3	3225 ± 35	3993 ± 0	402 ± 9	7.44	0.21 ± 0.07	350	1.44	6.0	11.2
AL-2	9.3	3	2150 ± 42	2675 ± 176	946 ± 88	8.12	0.16 ± 0.08	350	1.50	6.6	18.0
AL-3	9.3	5	2230 ± 14	3150 ± 144	452 ± 9	7.27	0.09 ± 0.03	400	0.70	6.6	23.1
AL-4	2.7-10.9	1.2	2990 ± 14	3831 ± 80	239 ± 26	7.73	0.11 ± 0.06	400	1.46	6.3	11.5

The turbidity and pH of the samples at various dosages are presented in Figure 3-2. The turbidity decreases quickly at low dosages (from 230-1000 NTU) in all the trials until it effectively levelled off at a low turbidity value (11-23 NTU) yielding more than 95% turbidity removal. This dosage was considered as the optimal dosage for alum at each trial. From Figure 3-2 it can be observed that the optimal dosage for alum was in the range of 300 to 400 mg/l alum which corresponded to 1.8x10-3 to 2.4x 10-3 mol/l of aluminium. The pH at the optimal dosage was in the range of 6 to 6.5 for all the trials.

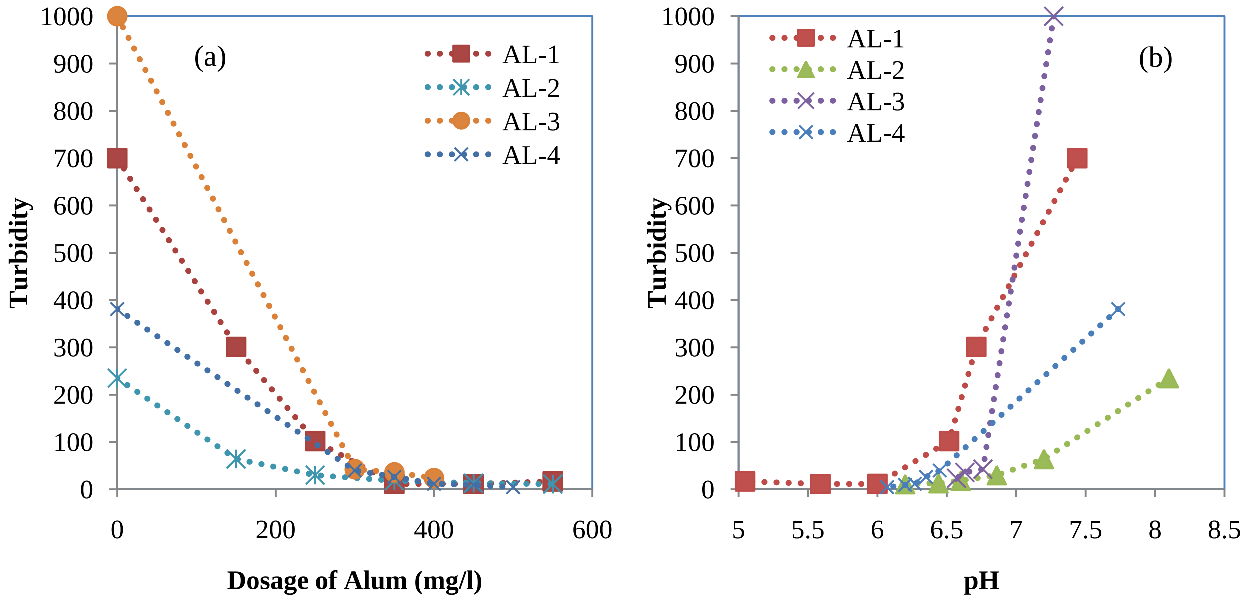


Figure 3-2 Coagulation with Alum: residual turbidity (a) vs. dosage and (b) vs. pH

From the pH of the solution it can be concluded that the dominant species of alum were precipitates and low-charge alum hydroxides. Therefore, the turbidity removal was more likely dominated by a sweep floc mechanism. This implies that when alum is added to the samples it forms alum hydroxides that contact with colloidal matter and enmesh them when precipitating [45].

3.4 JAR TEST TRIALS WITH THE COAGULANT BLEND

This part of experiment involved conducting four jar test trials with the PACl-polyamine blend on four different samples obtained on four different days. As mentioned before, the blend consisted of 90% PACl with 9.07% AL_2O_3 and 10% poly amine. The purpose of these trials was to assess the efficiency of turbidity removal, and hence its evaluation for subsequent pre-treatment of ultra-filtration.

The characteristics of each sample and the optimal dosage conditions are presented in Table 3-3. The changes in turbidity and pH of the samples at various dosages are presented in Figure 3-3. It should be noted that concentration of the blend refers to ml of blend (as provided by Northland Chemical Inc.) in ml of sample (i.e. 1 ml of the blend in 1 litre of samples yields 1000 ppm).

Table 3-3 Wastewater characteristics for coagulation with coagulant blend and its effect on pH

Trial	Influent flow (m^3/d)	D.O. (mg/l)	TSS (mg/l)	TCOD (mg/l)	SCOD (mg/l)	Initial pH	Drop of pH per 50 PPM blend	Optimal dosage (ppm)	Total pH drop @ optimal dosage	pH @ optimal dosage	Turbidity @ optimal dosage (NTU)
Blend-1	16.4	3	1640 ± 56	2930 ± 238	827 ± 26	7.37	0.05 ± 0.0224	200	0.27	7.2	2.9
Blend-2	9.3	5	2230 ± 14	3150 ± 144	452 ± 9	7.27	0.028 ± 0.010	400	0.11	7.2	7.7
Blend-3	2.7-10.9	1.2	2990 ± 14	3831 ± 80	239 ± 26	7.74	0.051 ± 0.045	400	0.15	7.6	3.9
Blend-4	9.3	4	2440 ± 0	2500 ± 63	233 ± 17	7.77	0.0738 ± 0.057	400	0.30	7.4	5.6

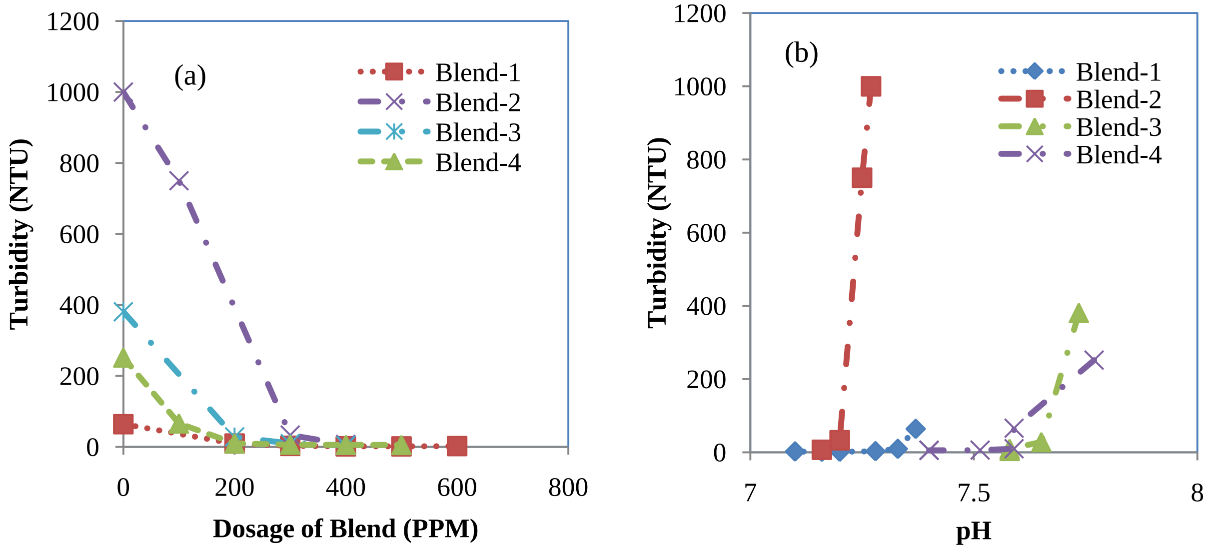


Figure 3-3 Coagulation with the coagulant blend: residual turbidity (a) vs. dosage and (b) vs. pH

It can be seen from Figure 3-3, regardless of the effluent characteristics, including initial turbidity, pH, TSS, COD, DO the final turbidity was as low as 2.9 to 7 NTU. It can be seen from Table 3-3 and Figure 3-3 that the effect of the blend on the pH was negligible. The total pH drop at the optimal dosage was less than 0.3 for all the trials.

More than 98% turbidity removal was obtained with a dosage in the range of 200-400 ppm and this was considered as the optimal dosage range. The high efficiency of the blend at the low optimal dosage can be explained by the coagulation mechanisms of PACl and polyamine. According to the pH of the samples, the dominant species of PACl were Al_{13}^{7+} polymers which have a much higher coagulation capacity as compared to Al^{3+}. The coagulation mechanism at this pH range is charge neutralization and bridging. On the other hand polyamine has a high charge density that favours the absorption of colloids onto the floc; also it has a high molecular weight that can enhance settleability of flocs. Therefore, it increases the size of the floc by bridging between the smaller flocs. Due to the high efficiency of the coagulant blend in turbidity removal, it was considered as a coagulant option from pre-treatment of MBBR effluent for ultra-filtration [35,45].

3.5 JAR TEST TRIALS WITH ZETAG®8125

Two jar tests were performed on the samples from two different days. Zetag is a synthesized poly acrylimide which has high molecular weight and low cationic charge. It is usually used in dissolved air flotation (DAF) for solid separation. More information on Zetag is provided in Appendix B. Trial 1 was performed on the same sample that was employed for the jar test AL-1 and trial 2 was performed on the same sample that was tested with Blend-4. The solution of Zetag was first prepared at 0.1% (0.1 g Zetag in 100 ml of water). However, during the rapid mixing of the solution Zetag would form a large floc around the mixing paddle. Therefore, to avoid this problem, the 0.1% solution was diluted 10 times yielding a concentration of 0.01%. It should be noted that 1 ppm in this section refers to 1 milligram/liter of Zetag (i.e. 10 ml of 0.01% solution into 1 litre yields 1 ppm). The results are presented in Figure 3-4.

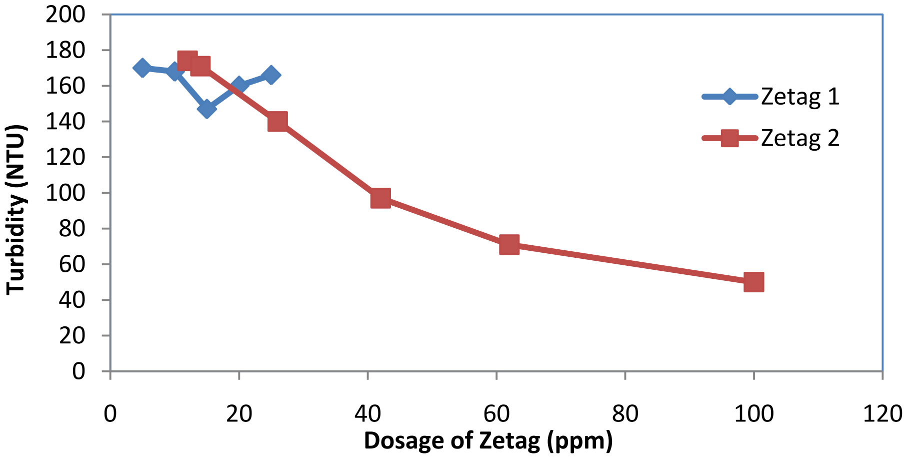


Figure 3-4 Coagulation with Zetag: residual turbidity vs. dosage

It can be seen from Figure 3-4 that Zetag did not have a high efficiency in decreasing the turbidity compared to the other three coagulants. In trial Zetag-1, the lowest turbidity was obtained at the dosage of 15 ppm and was 147 NTU, while coagulation of the same sample with 350 mg/l of alum yielded a turbidity of 11 NTU. In trial Zetag-2, a higher range of Zetag dosages was examined. The lowest turbidity obtained was 50 NTU at the dosage of 100 ppm. The initial pH did not change with addition of Zetag; coagulation of the same sample (zetag-2) with 400 ppm of the coagulant blend yielded a turbidity of 5.6 NTU. Zetag has a low cationic charge while the effluent was believed to have high anionic charge due to the fact that the MBBR influent consisted primarily of starch and protein. This likely explains the low efficiency of Zetag as compared to other coagulants which have higher cationic charges. It should be noted that addition of higher dosages of Zetag was not feasible due to its high viscosity. The other three coagulants could decrease the turbidity to less than 23 NTU. Addition of higher dosages of Zetag was not possible due to its high viscosity. Therefore, Due to the low efficiency of Zetag compared to the other three coagulants, it was not considered as an option for filtration trials.

3.6 SUMMARY AND CONCLUSIONS

In this section the ability of the three coagulants with respect to turbidity removal was assessed and this information is to be used in the selection of appropriate coagulants for the membrane experiments. Table 3-4 presents a summary of the results of ferric chloride, the blend and alum which were obtained

Table 3-4 Summary of results of jar test coagulation trials

Coagulant		Ferric chloride	Alum	Coagulant Blend
Optimal dosage range		500-550 mg/l (4.6x10^{-3}-5.1x 10^{-3} mol Fe/l)	300 - 400 mg/l (1.8x10^{-3} to 2.4x 10^{-3} mol Al /l)	200-400 ppm
Turbidity at optimal dosages (Turbidity removal at optimal dosage)		3-8 NTU (98%-99%)	11-23 NTU (92%-98%)	3-7 NTU (98%-99%)
pH	Effect on pH	Large	Large	Minor
	Average pH drop	0.15 per 50mg/l	0.14 per 50 mg/l	0.05 per 100 ppm
	pH at optimal dosage	5.7-6.6	6.0-6.6	7.2-7.6
Floc formation		Fast Floc formation during the rapid mixing Settled fast (10 min)	Moderate Floc formation during the slow mixing	Fast floc formation during the rapid mixing

All the coagulants except Zetag showed a high efficiency in turbidity removal, lowering the turbidity to less than 23 NTU at their optimal dosages. However, turbidity removal efficiency with alum was lower than that of ferric chloride and the blend. The blend and ferric chloride had similar removal efficiencies and produced turbidity measures as low as 3 NTU. Their results were more consistent than alum taking into account the variation in effluent characteristics. The better performance of ferric chloride and the blend were likely due to their coagulation mechanism and the resulting floc structures. It should be noted that the coagulation trials in this study were performed in the lab and at room temperature (about 25°C); however, if coagulation is to be applied on site in the factory the temperature variations may become critical to coagulation and the tests performed under lower temperature may favor the coagulant blend.The blend had the least effect and ferric chloride had the highest effect on pH. Alum had slightly lower effect on pH than ferric chloride. The pH at the optimal dosage of the blend dropped 0.2 units on average while for ferric chloride and alum it was 1.5 and 1.2, respectively (i.e. at optimal dosage for alum and ferric chloride the pH for alum mixture was higher than ferric chloride). If ferric chloride was chosen as the coagulant pH readjustment may be required to reuse the water in the plant. The variation found in replicated trials was attributed to the effluent's daily and hourly quality variability.

Overall, an improved understanding of each coagulant and its effect on the MBBR effluent was achieved. Ferric chloride, alum and blend were chosen due to their high efficiency in turbidity removal and optimal dosages were determined which was used for subsequent experiments. Section 4 presents the results of pre-coagulation and ultra-filtration trials conducted with these three coagulants.

Chapter 4

ULTRA-FILTRATION TRIALS AND COD FRACTIONATION

4.1 INTRODUCTION AND OBJECTIVES

In this section, the results obtained from ultra-filtration tests of the MBBR's influent and effluent is presented. In each experiment, 300 ml of non-coagulated or coagulated effluent samples was added to a membrane cell. A volume of sample (150 ml in most trials) was filtered through a 0.05-micron polyethersulfone (PES) membrane. The filtration of 150 ml of non-coagulated sample required between 10 minutes to 3 hours depending on the effluent characteristics. The trans membrane pressure (TMP) was set to 30 psi (207 kPa) during the filtration of the samples and the times required to collect incremental volumes of permeate (5 or 10 ml) were recorded. The samples were mixed during ultra-filtration at a speed that was high enough to prevent the flocs from settling but not too high to cause breakage of the flocs. All the ultra-filtration tests in a set of trials were performed simultaneously in parallel membrane apparatuses to avoid the effect of changes in wastewater characteristics on the analysis of data.

Using the methods explained in chapter 2, membrane resistances, reversible and irreversible fouling resistances and fluxes were calculated for each test. It should be noted that in this study the fouling caused by pore blockage is accounted for as being at least partially irreversible and not reversible resistance due to the cleaning method employed. The irreversible fouling was calculated as the differences between the rinsed membrane resistance after filtration and the clean membrane resistance.

From the data obtained in this part of experiments, the effects of three coagulants, namely ferric chloride, alum and the blend, at different dosages, on the membrane performance and its fouling mechanisms were assessed. In addition, a comparative assessment of the three coagulants was conducted and the best option for this MBBR-MR system is suggested. To assess the effect of under-dosage of samples on filtration efficiency, three filtration tests were carried out for each coagulant with each sample. One sample was not dosed, one was dosed at a dosage that was approximately half of the optimal dosage, and one was dosed with the optimal dosage found in the jar test trial.

The role of the MBBR in increasing the treatment efficiency of the whole process and reducing the fouling potential of the raw wastewater was assessed by comparing the results obtained from filtration of the MBBR's influent and effluent. From the results of this section the necessity of MBBR for this specific treatment was determined.

In order to determine the effect of pressure on membrane fouling, tests were performed at 30 (207 kPa) and 40 psi (276 kPa). The results of this experiment were employed to define the tests conditions that were used in all of the other tests. The pressure differential was restricted by the apparatus used.

The total COD of the non-coagulated effluent, and the SCOD and FFCOD of the coagulated and non-coagulated effluent were measured. The objective was to assess the effect of coagulant on removal of soluble and colloidal matter. These results were used to help interpret the effect of coagulant on the membrane fouling mechanism.

The permeate COD of each filtration test was measured to assess the treatment efficiency of each part of the system including the MBBR, coagulation and ultra filtration as well as the whole system. All the trials were replicated at least twice in order to ensure the reproducibility of the experiment.

It should be noted that the contribution of each sludge fraction in this study may be different from an actual membrane application. In this study tests were performed with dead-end Amicon stirred cells, with no aeration, low cross flow velocity (which was produced by stirring paddles), the effluent samples had high TSS concentrations, and the system was operated at 206.8 kPa (30 psi); Based on the discussions in section 1.4.2.3 each of these conditions can increase membrane reversible fouling. Additionally, it is expected that the dominant mechanism will be cake formation and its higher formation and resistance should decrease the irreversible fouling. Hence, the relative changes of reversible and irreversible fouling under different conditions are more important in this study and can yield helpful results and conclusions.

4.2 ULTRA-FILTRATION TRIALS AND REVERSIBLE AND IRREVERSIBLE FOULING CALCULATIONS

An example of the filtration of a non-coagulated MBBR effluent is presented to demonstrate the method for calculating the membrane's reversible and irreversible fouling. Figure 4-1 is typical of that which was obtained for all the filtration trials in order to obtain the membrane resistances.

Deionized water was initially filtered through a clean pre-soaked membrane (which had been stored in deionized water for 24 hours prior to the test). Fluxes were obtained at pressures of 138, 207, and 276 kPa (20, 30, and 40 psi, respectively). Obtaining the membrane resistance by measuring the fluxes at different pressures minimizes the possible experimental error. The time required to collect typically 50 ml permeate was recorded and the flux was determined using Equation 4-1:

$$Flux = \frac{V}{(T \times A)} \tag{4-1}$$

Where V is the permeate volume, T is the time required to collect a specific volume of permeate, and A is the membrane surface area (4.18E-3 m^2).

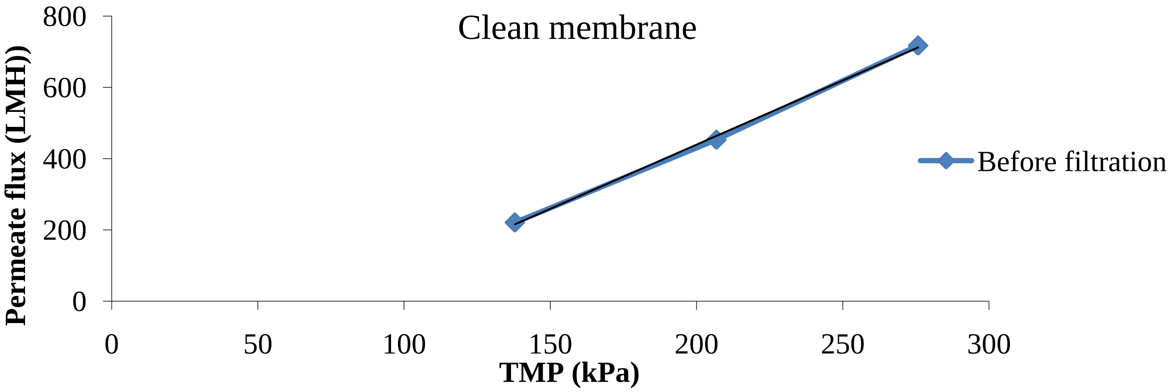


Figure 4-1 Calculation of clean membrane resistance

The clean membrane resistance was obtained from Equation 4-2 [42]:

$$R_m = \frac{1}{(a \times \mu)} \tag{4-2}$$

Where R_m is the clean membrane resistance, a is the slope of the line, and μ is the dynamic viscosity of the permeate at 25˚C. Therefore, for this example the clean membrane resistance was calculated as:

$$R_m = \frac{1}{(10^{-9}\ (m/s/pa) \times 8.91 \times 10^{-4}(pa \cdot s))}$$

$$R_m = 1.17\times 10^{12}\ (m^{-1})$$

After the clean membrane resistance was obtained a 300 ml sample of MBBR effluent was added to the cell and filtered at 30 psi (207 kPa). The flux was obtained from the time required to collect 5 - 10 ml permeate and using Equation 4-1 again. The membrane resistance at each point was then calculated by Equation 4-3.

$$R = \frac{TMP}{(Flux \times \mu)} \tag{4-3}$$

Where TMP is equal to 30 psi (207 kPa). Total resistance of the membrane (R_t) includes clean membrane resistance (R_m) and fouling resistance (R_f). Therefore, the fouling resistance was obtained from Equation 4-4:

$$R_f = R_t - R_m \tag{4-4}$$

Table 4-1 presents an example of the results of calculations for each ultra-filtration trial. From Table 4-1, Figure 4-2, which indicates the decline of flux and development of fouling resistance, was obtained. (The trend of the flux decline rate, which decreases with time, is comprehensively explained in section 1-4-2-2).

Table 4-1 Results of an ultra-filtration trial of a non-coagulated MBBR effluent sample of average wastewater quality

Cumulative permeate volume (ml)	Time (min)	Flux (LMH)	$R_t(m^{-1})$	$R_f(m^{-1})$
10	1.03	69.44	1.60E+13	1.60E+13
20	2.35	30.54	3.65E+13	3.65E+13
30	3.23	40.00	5.02E+13	5.02E+13
40	3.97	18.09	6.16E+13	6.16E+13
50	4.75	15.11	7.38E+13	7.38E+13
60	5.37	13.37	8.33E+13	8.33E+13
70	5.80	12.37	9.01E+13	9.01E+13
80	5.98	11.99	9.29E+13	9.29E+13
90	6.45	11.13	1.00E+14	1.00E+14
100	6.68	10.74	1.04E+14	1.04E+14
110	6.97	10.30	1.08E+14	1.08E+14
120	7.17	10.01	1.11E+14	1.11E+14
130	7.33	9.79	1.14E+14	1.14E+14
140	7.55	9.50	1.17E+14	1.17E+14
150	7.62	9.42	1.18E+14	1.18E+14

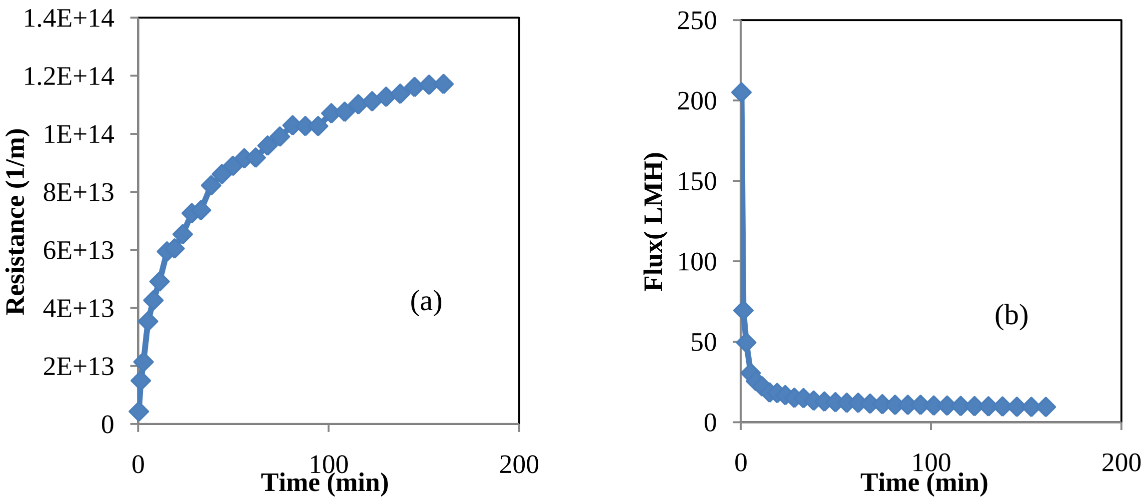


Figure 4-2 (a) Fouling resistance and (b) flux of a non-coagulated MBBR effluent sample of average waste water quality (obtained from calculations in Table 4-1)

After filtration of the effluent sample, the membrane was washed for 20 minutes to remove the cake layer, which was assumed to cause reversible fouling. It is worth noting that the irreversible fouling obtained by this method includes fouling due to adsorption of organic matter into the pores and pore blockage since the latter could not be effectively removed by the washing method. The resistance of the membrane at this point is the sum of the irreversible (R_{irr}) and the clean membrane resistance and was determined in the same way as the clean membrane resistance. Deionized water was filtered and fluxes were measured at the three pressures previously mentioned. The resulting plot of flux vs. TMP is presented in Figure 4-3. It can be seen that the flux of the washed membrane after filtration was lower than clean membrane and therefore, the slope after filtration was lower than before filtration (6.5×10^{-7} and 10^{-6}, respectively) which means there was higher resistance due to the irreversible fouling.

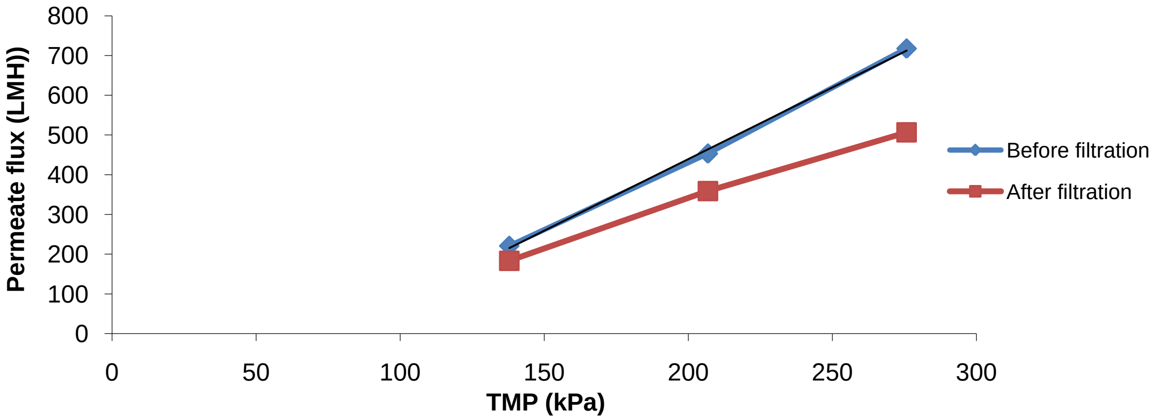


Figure 4-3: Membrane resistances before and after filtration with MBBR effluent

The reversible resistance (R_{rev}) was then calculated by Equation 4-5:

$$R_{rev} = R_f - R_{irr} \tag{4-5}$$

In order to characterize the experimental error in the ultra-filtration analysis method, three replicates with the same effluent were performed under the same conditions. Three 300 ml samples were taken from a batch of effluent. In parallel configurations, 150 ml volumes were filtered simultaneously. The flux, total fouling resistance, reversible and irreversible resistances were obtained for each sample. The standard error, standard deviation, and error percentages that were obtained from these replicates are presented in Table 4-2. These errors should be taken into consideration when the results of this part of experiments are assessed. As it can be seen from Table 4-2, the changes of resistances and flux were lower than 10% and were considered as insignificant with respect to the conclusions that were arrived at in this study.

Table 4-2 Experimental Error calculations and percentages for replicates (associated with n=3)

Parameter	R_f (m^{-1})	R_{irr} (m^{-1})	R_{rev} (m^{-1})	Flux (LMH)
Standard Error	1.08×10^{12}	4.34×10^{10}	1.07×10^{12}	3.11
Standard Deviation	1.88×10^{12}	7.52×10^{10}	1.86×10^{12}	5.39
% Error	6%	10%	6%	7%

One potential source of experimental variability was the variation in membrane resistances used in this project. The clean membranes had different resistances although all the membranes used in this project were cut from the same roll of membrane. In this trial, to account for the error that could be introduced by variations in membrane resistances, each replicate was performed using membranes with different initial resistances.

4.3 ULTRA-FILTRATION OF THE MBBR EFFLUENT AT TWO DIFFERENT PRESSURES (30 AND 40 PSI)

Two trials were performed on a sample of MBBR effluent at pressures of 30 and 40 psi (207 and 276 kPa) to determine the effect of pressure on membrane fouling behaviour. In both trials, 90 ml of the effluent was filtered and the fouling resistances and fluxes were calculated. Figure 4-4 presents the fouling resistance with time and reversible and irreversible fouling at the end of the filtration. Figure 4-4 (a) indicates that operation under higher pressure had higher fouling rates than low pressure operation which was approaching a constant value at the end of the test. From Figure 4-4 (b), it can be observed that filtration with the higher pressure (40 psi or 276 kPa) resulted in higher reversible and irreversible fouling; however, it had more effect on the latter. The irreversible fouling of the high-pressure trial was 15 times higher than low-pressure trial, while the reversible fouling was increased only by a factor of 1.4 times. It appears that when the pressure was higher, small particles continued to penetrate through the cake layer and membrane pores which increased reversible and irreversible fouling, respectively.

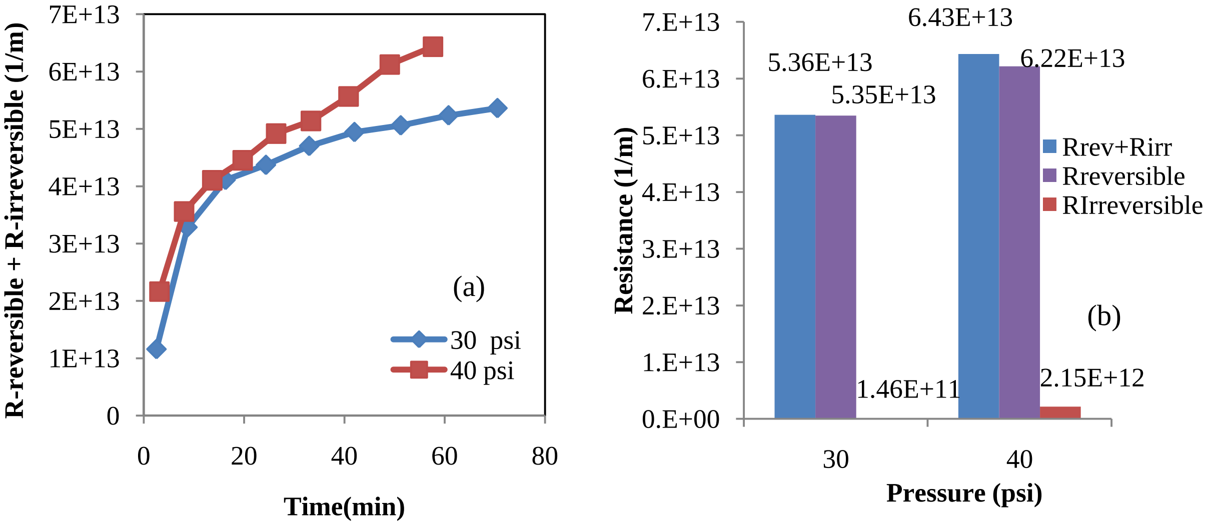


Figure 4-4 Fouling resistances at 30 and 40 psi (a) development of total fouling vs. time (b) total, reversible and irreversible fouling resistances at the end of filtration

A comparison of the fluxes indicates that the high-pressure trial had only a 12% higher flux at the end of the filtration of 90 ml of sample. This difference would be further reduced with filtration of higher volumes of effluent. Therefore, operation at higher pressure did not decrease the ultra-filtration time significantly, and the experiments would have a more un-realistic condition at higher pressures and cause more change in the fouling mechanisms. Hence, through the rest of the filtration trials the trans membrane pressure was set to 30 psi (207 kPa).

4.4 ULTRA-FILTRATION OF THE MBBR INFLUENT AND EFFLUENT

In order to assess the role and importance of the moving bed bio-film reactor with respect to fouling reduction and treatment efficiency, two sets of trials were carried out. In each set both influent and effluent samples were collected at the same time and were filtered simultaneously, in parallel configurations. From the results of the testing the effect of the MBBR on the fouling behaviour of membrane and COD removal could be assessed.

Two sets of trials were performed on the samples obtained on two different days. In each trial, both influent and effluent samples were obtained at the same time and filtered simultaneously. The characteristics of the influent and effluent for each trial are presented in the Table 4-3. It can be seen that ultra-filtration of the influent yielded an average total COD removal of 69% (74% and 63% in trial 1 and 2, respectively) while when the MBBRs effluent was filtered the total COD removal was 97% in both trials. This is due to removal of soluble COD by MBBR which can pass through UF membrane. The values for TSS, TCOD, SCOD, permeate COD are averages of three replicates.

Table 4-3 Influent and effluent characteristics and UF permeate CODs

Trial	Influent flow (m^3/d)	D.O. (mg/l)	Influent				Effluent			
			TSS (mg/l)	TCOD (mg/l)	SCOD (mg/l)	Permeate COD (mg/l)	TSS (mg/l)	TCOD (mg/l)	SCOD (mg/l)	Permeate COD (mg/l)
1	9.3	2	1279 ± 37	3606 ± 88	1728 ± 9	940 ± 8	2293 ± 83	3017± 70	232 ± 35	111 ± 8
2	2.7-10.9	1.2	903 ± 14	3117 ± 23	2060 ± 17	1143 ± 163	5100 ± 28	6658 ± 17	226 ± 8	109 ± 35

Volumes of 90 ml and 160 ml of influent and effluent were filtered in trials 1 and 2, respectively. The fluxes and resistances of the ultra-filtration trials are presented in Figure 4-5. From Figure 4-5 it can be seen that higher fouling occurred during ultra-filtration of the influent. At the end of the filtration period, the total fouling caused by reversible and irreversible fouling of the influent were higher by factors of 1.6 and 1.8 for trials 1 and 2, respectively.

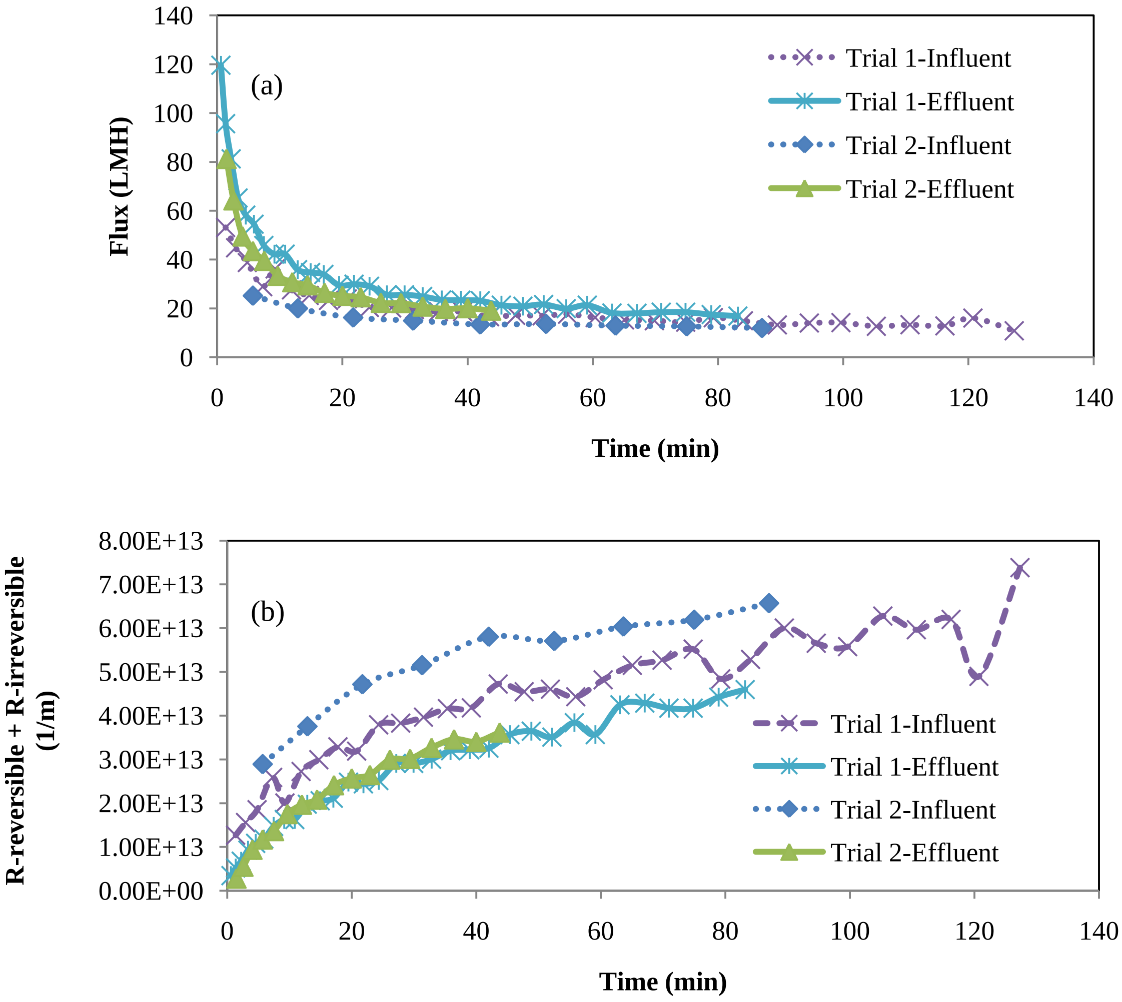


Figure 4-5 Ultra filtration of influent and effluent of volumes of 160 and 90 ml in trial 1, respectively: (a) Flux vs. time (b) fouling resistance vs. time

In the previous analysis of MBBR influent, a high TKN concentration was observed which shows the existence of proteins in the influent. Starch, which is a polysaccharide carbohydrate, is also a major component in the influent. Polysaccharide carbohydrates and proteins are known as two major polymer foulants [44]. The results suggest that the micro-organisms in the MBBR degrade and remove these organic compounds which contribute to membrane fouling including colloids and solutes, therefore, less fouling was observed for the filtration of effluent. Besides the fact that the colloidal and solutes concentrations are higher in MBBR feed, Bouhabila et al. (2001) [14] results showed that the residual colloidal and dissolved matter in MBRs influent can have higher fouling potential than those generated from bacterial metabolism and bacterial lyses such as EPS and SMP.

Hence, using the MBBR resulted in a 29% higher treatment efficiency with respect to COD removal in comparison to not using the MBBR and direct filtration of the water from the starch line. In addition, the MBBR decreased the degree of membrane fouling.

4.5 MEMBRANE TREATMENT TRIALS USING FERRIC CHLORIDE AS COAGULANT

The objective of this portion of the study was to evaluate ferric chloride for pre-coagulation of the MBBR's effluent prior to ultra-filtration. In order to assess the reproducibility of the results, the tests were replicated on two water samples obtained on different days. The characteristics of each sample were different as seen in the Table 4-4.

Table 4-4 Characteristics of effluent samples obtained for pre-coagulation by ferric chloride and ultra-filtration

Trial	Influent flow(m^3/d)	D.O. (mg/l)	TSS (mg/l)	TCOD (mg/l)	SCOD (mg/l)
Fe-1	9.3	2.0	3910 ± 14	4957 ± 17	451 ± 23
Fe-2	2.7-10.9	1.2	2990 ± 14	3831 ± 80	276 ± 26

Samples likely had different characteristics due to variations of the MBBR feed. In trial Fe-2, the influent flow had dropped to 0.5 GPM (2.7 m^3/d) due to clogging of the flow and was adjusted to 2 or 1.7 GPM (10.9 or 9.3 m^3/d) after the sample was collected. In trials Fe-1 and 2 the HRT was about 4.61 hours. The total COD loading rates to MBBR-MR were higher than 45.9 and 35.5 kg/l volume of MBBR (or 214 and 165 g/m^2/d), respectively.

In both trials, the experiments were performed on a non-dosed sample and dosed samples with the optimal dosage of $FeCl_3$ as determined by the previously described jar test. The optimal dosages, obtained from jar tests on fresh samples, were 550 and 500 mg/l in trials 1 and 2, respectively. In trial 1, experiments were also performed on a dosage which was approximately half of the optimal dosage (250 mg/l) to evaluate the impact of under-dosage on COD fractions and membrane fouling.

4.5.1 Coagulation with ferric chloride and COD fractionation

The effect of coagulation with ferric chloride on different COD fractions was assessed by measuring soluble COD fractions including colloidal COD and flocculated filtered COD (FFCOD). The colloidal COD was estimated as the difference between SCOD and FFCOD measurements. Figure 4-6 shows the COD fractions for the two samples separately. As can be seen in Figures 4-6 (a) and (b), there was a sharp decrease in both SCOD and colloidal COD with addition of ferric chloride; however, addition of coagulant did not have a significant effect on FFCOD (the small changes in FFCOD were within measurement error).

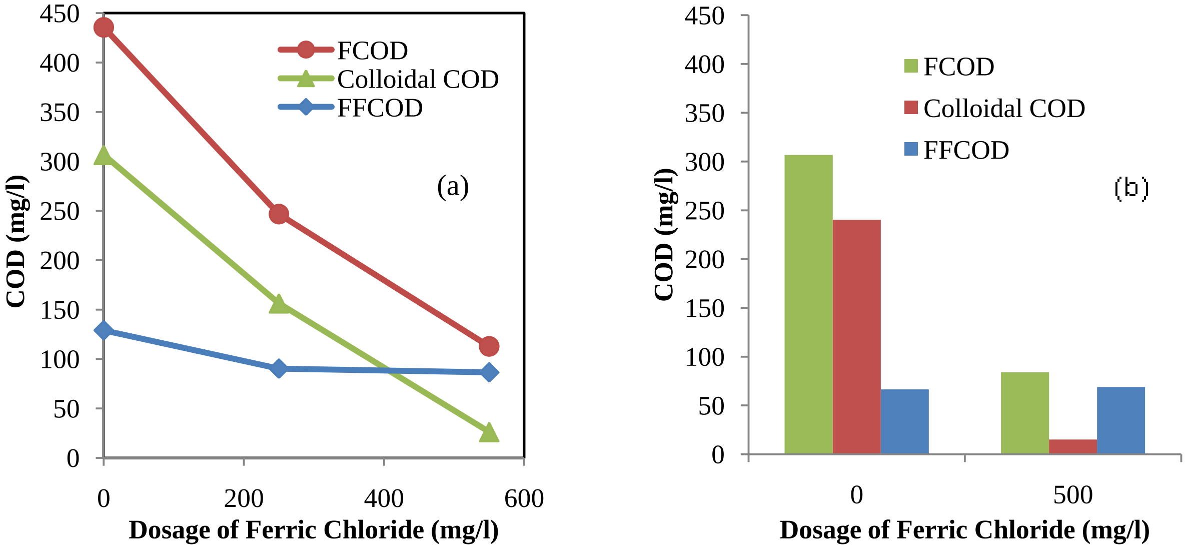


Figure 4-6 COD fractions for samples of (a) Fe-1 and (b) Fe-2

The effects of coagulation on the COD fractions were calculated as removal percentages compared to non-dosed samples and are presented in Table 4-5 in order to evaluate the extent of ferric chloride’s effect. From Table 4-5 it can be observed that when the dosage of ferric chloride was increased from 250 mg/l to 550 mg/l, the removal efficiency of SCOD and colloidal COD increased 32% and 43%, respectively.

Table 4-5 Average removal efficiencies at different ferric chloride dosages from trials Fe-1 and Fe-2

Dosage of Ferric Chloride	Soluble COD	FFCOD	Colloidal COD
250 mg/l	42%	19%	50%
550 mg/l	73%	20%	92%

From the results obtained in this study, it was anticipated that there would be a decrease in irreversible fouling for the samples coagulated with ferric chloride since it reduced the dissolved organic matter, which is known as an important foulant. In addition, it was expected that there would be less fouling for the samples coagulated with the optimal dosage than the sample with half dosage of ferric chloride.

4.5.2 Pre-Coagulation ferric chloride and ultra-filtration of MBBR effluent

In this portion of the study, the effect of pre-coagulation with ferric chloride on membrane performance was investigated. Two sets of trials on samples Fe-1 and Fe- 2, described previously, were performed. In each trial, ultra-filtration of ferric chloride dosed and non-dosed samples was performed simultaneously in parallel setups. The total fouling (combined reversible and irreversible fouling) resistances versus filtration time are presented in Figure 4-7.

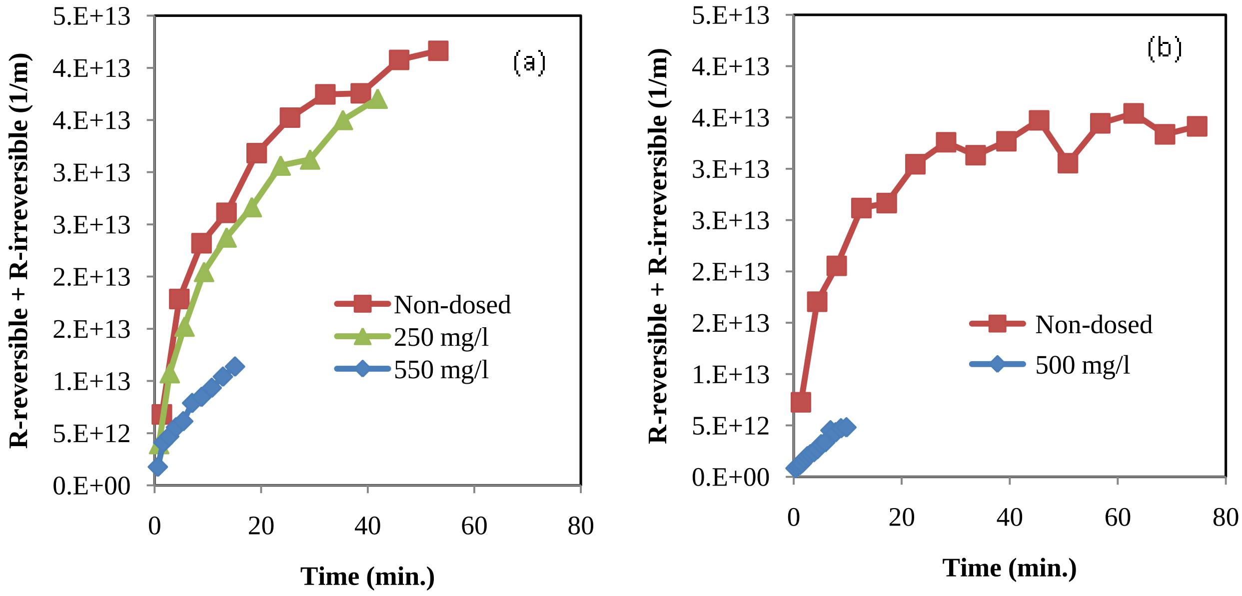


Figure 4-7 Impact of Ferric chloride pre-coagulation on membrane total fouling resistance development for trials (a) Fe- 1 and (b) Fe-2

From Figure 4-7 it can be observed that there was a significant decrease in fouling when ferric chloride was added at its optimal dosage as obtained in the preliminary jar test. When ferric chloride was under-dosed (250 mg/l), the fouling was only slightly less than that of the non-dosed effluent. Lower permeability (higher total resistance) was observed for trial 2 which may be due to its lower TSS, TCOD, and SCOD.

Figure 4-8 shows the effect of ferric chloride on the reversible and irreversible fouling and the contribution of each resistance to the total resistance at the end of the test. From Figure 4-8 it can be seen that addition of coagulant decreased both reversible and irreversible fouling in both trials. The decrease in reversible fouling may have been due to a change in the porosity of the cake layer. The non-coagulated samples would be expected to form a less porous structure on the membrane than the coagulated samples due to the smaller sizes of the particles [34]. The lower irreversible fouling was likely due to reduced pore blockage of the membrane as a result of the removal of colloidal matter with addition of ferric chloride as observed in the section 4-5-1. Further study on the particle size distribution of the coagulated and non-coagulated samples would be useful to better understand these results better.

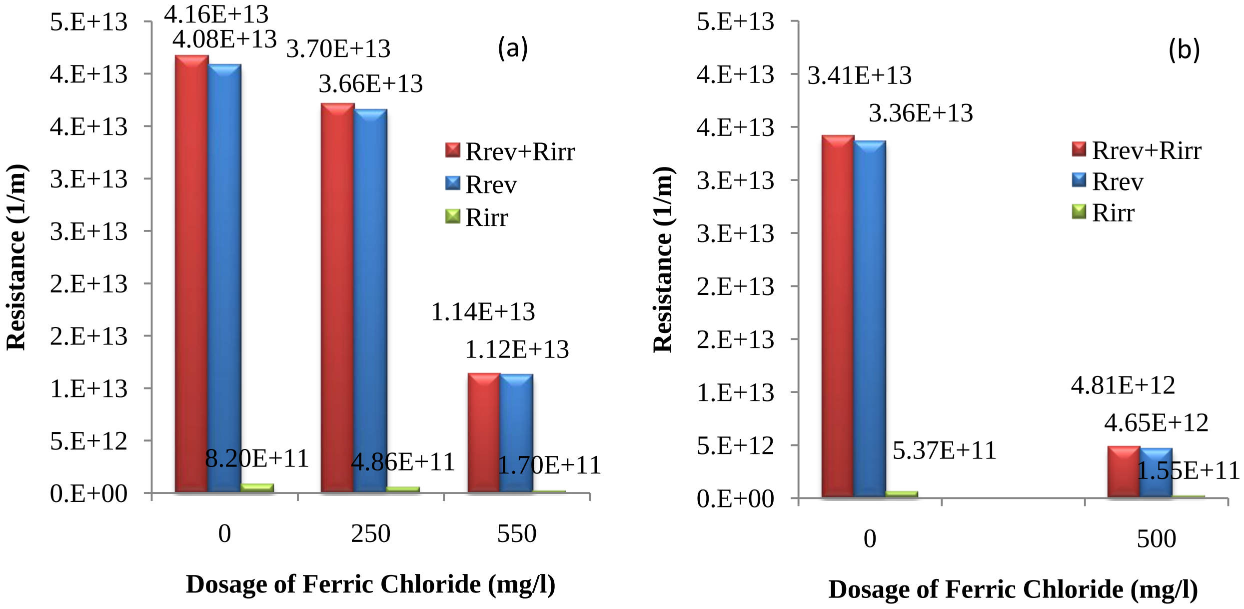


Figure 4-8 Impact of ferric chloride on total, reversible and irreversible fouling at the end of the test for trials (a) Fe-1 and (b) Fe-2

Table 4-6 shows the improvement of membrane performance by pre-coagulation with ferric chloride. From Table 4-6 it can be observed that reversible and irreversible resistances decreased significantly (60% and 39%, respectively) when the dosage increased from 250 mg/l to 550 mg/l (optimal dosage of ferric chloride); these results correspond to the considerable increase in permeability of the membrane at ferric chloride's optimal dosage compared to non-dosed and under-dosed sample.

Table 4-6 Impact of ferric chloride on membrane performance

Trial	Average	Trial 1 (Fe-1)		Trial 2 (Fe-2)
Dosage of Ferric chloride (mg/l)	0	250	550	550
% Reduction of total fouling resistance (R_f)	-	11%	73%	86%
% Reduction of Irreversible resistance	-	41%	80%	71%
% Reduction of Reversible resistance	-	10%	73%	86%
% Increase in flux	-	73%	224%	485%
% $R_{irreversible}$ / R_f	1.9%	1.3%	1.5%	3.2%
% $R_{reversible}$ / R_f	98.0%	98.6%	98.5%	96.7%

It was concluded that the optimal dosage found during the jar test trials of the sample was a good indicator of the optimal dosage for ultra-filtration. However, to confirm this conclusion it is suggested that more tests with a greater range of ferric chloride dosages be performed to better characterize this relationship.

Table 4-7 presents the permeate COD concentrations measured. From Table 4-7 it can be observed that there was not a significant difference in COD removal efficiencies of non-coagulated and coagulated samples with ferric chloride. This was expected since coagulation doesn’t remove FFCOD (section 4-5-1) and the smaller compounds would be expected to pass through membrane with pore size of 0.05 micron. Therefore, there was no change in permeate COD as well. Hence, it is concluded that fouling which is caused by adsorption of the solutes on the pore walls was not significantly affected by addition of ferric chloride since this fraction of COD was not removed by coagulation.

Table 4-7 Permeate COD concentrations of non-coagulated and coagulated samples by ferric chloride for samples of Fe-1 and Fe-2

Permeate COD (mg/l)			
Dosage (mg/l)	0	250	500-550
Fe-1	142 ± 7	142 ± 4	143 ± 8
Fe-2	79 ± 2	-	93 ± 1

4.6 MEMBRANE TREATMENT TRIALS USING ALUM AS COAGULANT

The objective of this part of the study was to evaluate coagulation of the MBBR's effluent with alum as a pre-treatment method for ultra-filtration. In order to assess the reproducibility of the results, the tests were replicated on two samples (AL-1 and Al-2) obtained on different days. The characteristics of each sample were different and are presented in the Table 4-8. Samples had different characteristics due to variations of MBBR feed as the MBBR was operated at an HRT of 4.61 hours.

Table 4-8 Characteristics of effluent samples obtained for pre-coagulation by alum and ultra-filtration

Trial	Influent flow(m^3/d)	D.O. (mg/l)	TSS (mg/l)	TCOD (mg/l)	SCOD (mg/l)
AL-1	9.3	0.3	3225 ± 35	3993 ± 0	402 ± 9
AL-2	9.3	3	2150 ± 42	2675 ± 176	101 ± 8

In each trial, the experiments were performed with a non-dosed sample and dosed samples that included the optimal dosage and an under-dosed condition as determined by preliminary jar tests. The optimal dosages, obtained from jar tests were 350 mg/l for both trials. A dosage of 150 mg/l was chosen as an intermediate point of dosage to evaluate under-dosage of effluent in both parts of the experiment including COD fractionation and ultra-filtration.

4.6.1 Coagulation with alum and COD fractionation

The effect of coagulation with alum on soluble COD, FFCOD and colloidal matter of the effluent was assessed. Figure 4-9 presents the COD fractions for the two samples separately.

It can be seen in Figure 4-9 that in both trials a decrease in SCOD and colloidal COD with increasing alum dosage was observed suggesting that coagulation with alum could remove these fractions.

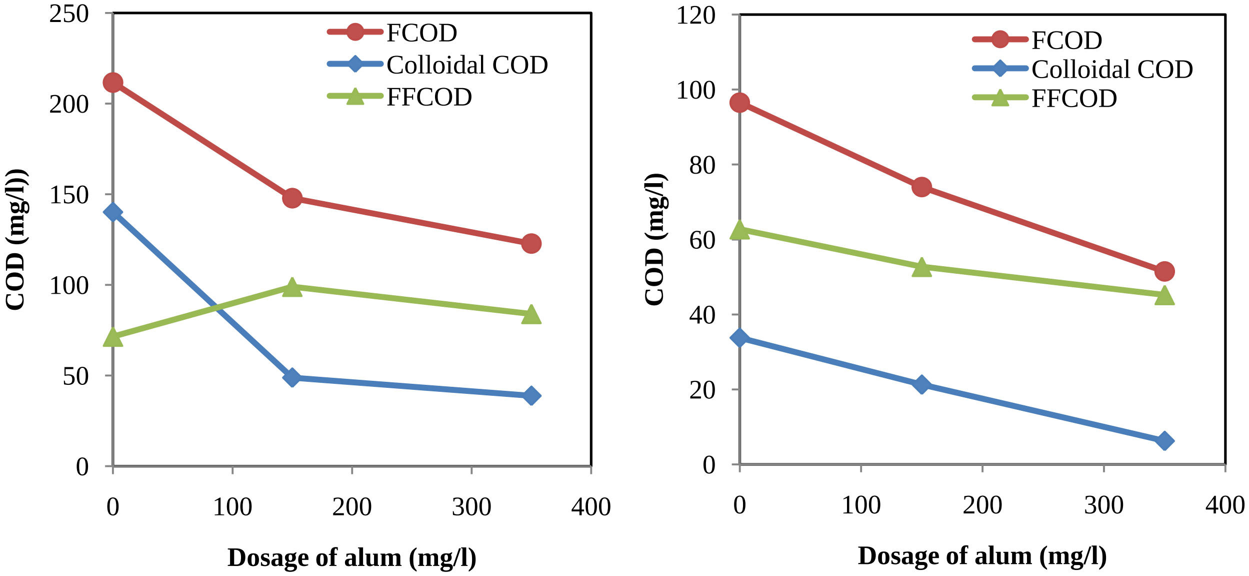


Figure 4-9 COD fractions for samples of (a) Al-1 and (b) Al-2

The average COD removal efficiencies of alum are presented in Table 4-9. Alum at its optimal dosage increased SCOD and colloidal COD removal efficiencies by 18% and 26%, respectively, as compared to the under-dosed sample. The effect of alum on FFCOD was negligible and was within experimental error.

Table 4-9 Average removal efficiencies of alum at different dosages from trials Al-1 and Al-2

Dosage of alum	Soluble COD	FFCOD	Colloidal COD
150 mg/l	27%	-11%	51%
350 mg/l	44%	5%	77%

4.6.2 Pre-Coagulation with alum and ultra-filtration of MBBR effluent

The effect of coagulation with alum on fouling was assessed in UF-filtration tests. The fouling with coagulated samples that had dosages of 150 mg/l and 350 mg/l (optimal dosage) was compared. Figure 4-10 shows the development of total resistance for sample with alum coagulation.

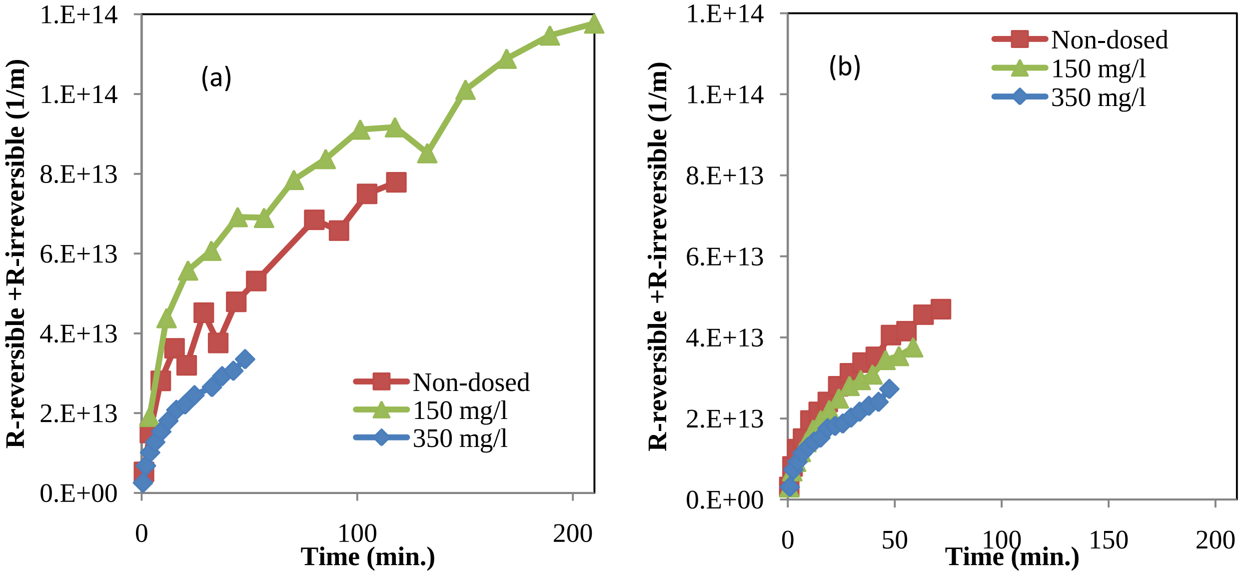


Figure 4-10 Impact of alum pre-coagulation on membrane total fouling resistance development for trials (a) Al- 1 and (b) Al-2

From Figure 4-10 it can be observed that there was lower fouling for trial 2 as compared with trial 1. The concentrations of the COD fractions and TSS in trial 2 were lower than in trial 1 which likely explained the lower resistances that were observed in trial 2. In trial 1, unexpectedly, the sample dosed with 150 mg/l of alum had significantly higher fouling than the non-dosed sample, while in trial two it was lower. Figure 4-11 presents a comparison of reversible and irreversible fouling and their contribution to total fouling as a function of alum dose. In trial 1, the under-dosed sample showed higher reversible and irreversible fouling than the non-dosed sample, however, in trial 2 the results were the opposite. The higher fouling of the under-dosed sample in trial 1 could not be explained and may have been due to experimental error.

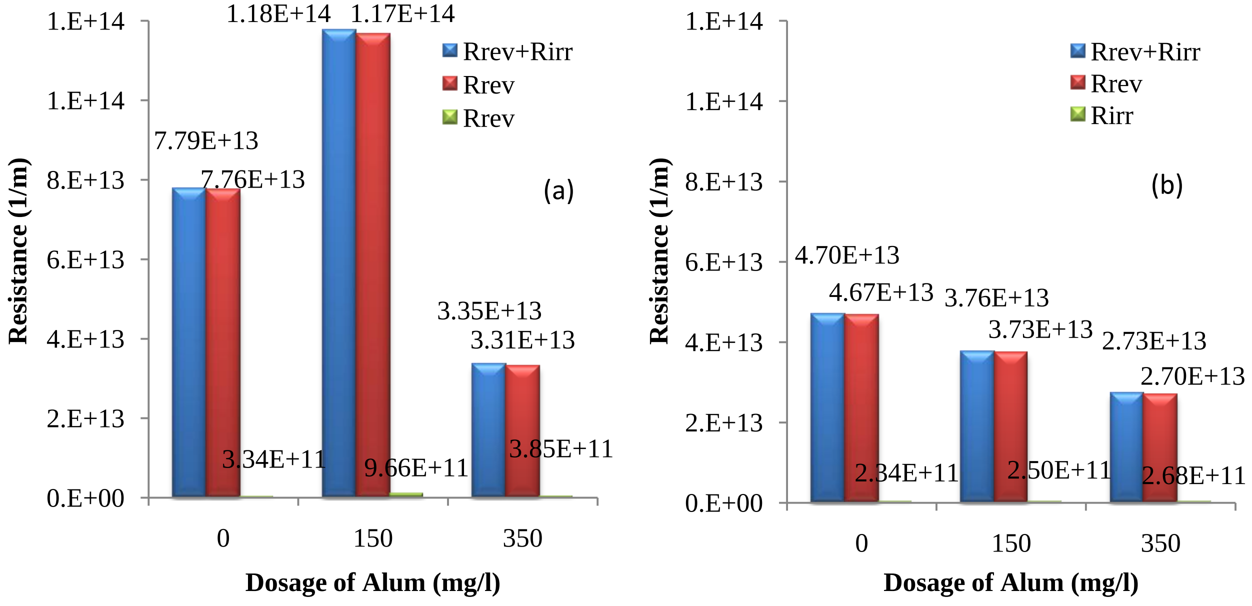


Figure 4-11 Impact of Alum on total, reversible and irreversible fouling at the end of the test for trials (a) Al-1 and (b) Al-2

Table 4-10 shows the effect of coagulation with alum on membrane resistance expressed as a percentage change with respect to the non-dosed effluent for trials 1 and 2. Table 4-10 also includes the results of a third trial of coagulation with alum where the effluent characteristics were in the same range as those present in trials 1 and 2. This trial will be discussed further later but is presented here as a more comprehensive analysis of the effect of alum on fouling. As can be seen in Table 4-10, the addition of alum decreased the reversible fouling significantly while it had a negligible effect on irreversible fouling. In trial 2, the reversible fouling was 22% less for the optimally dosed sample as compared to the under-dosed sample. The decrease in reversible fouling was likely due to changes in the porosity of the cake layer.

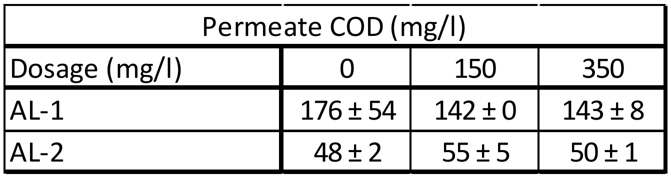
The non-coagulated samples were expected to form a less porous structure on the membrane than the coagulated samples which had larger flocs [34]. Coagulation with alum did not decrease the irreversible fouling of the membrane which presumably resulted from pore blockage in spite of the fact that the COD fractionation in the previous section showed removal of colloidal matter by alum. This may have been due to the relatively negligible contribution of irreversible fouling to total fouling in trials 1 and 2. The effect of alum on irreversible fouling might be better observed if higher volumes of sample were filtered or another membrane apparatus was used. Pictures from surface of the fouled membrane (by SEM) would also be helpful to understand the effect of coagulants on the fouling mechanism due to changes in floc structure and sizes.

Table 4-10 Impact of alum on membrane performance

Trial	Trial 1 (Al-1)	Trial 2 (Al-2)		Trial 3 (Al-3)
Dosage of alum (mg/l)	350	150	350	350
% Reduction of total fouling resistance (R_f)	57%	20%	42%	49%
% Reduction of Irreversible resistance	-15%	-7%	-14%	9%
% Reduction of Reversible resistance	57%	20%	42%	50%
% Increase in flux	128%	23%	62%	91%
% $R_{irreversible}$ / R_f	1.1%	0.6%	0.9%	2.8%
% $R_{reversible}$ / R_f	98.8%	99.3%	99.0%	97.1%

The permeate COD values of the coagulated and non-coagulated samples are presented in Table 4-11. It can be seen that coagulation with alum did not affect the COD removal efficiency of the whole system. This was expected since, same, as with ferric chloride, alum did not have any significant effect on FFCOD removal (discussed in section 4-6-1).

Table 4-11 Permeate COD concentrations of non-coagulated and coagulated samples by alum



Permeate COD (mg/l)			
Dosage (mg/l)	0	150	350
AL-1	176 ± 54	142 ± 0	143 ± 8
AL-2	48 ± 2	55 ± 5	50 ± 1

4.7 MEMBRANE TREATMENT TRIALS USING COAGULANT BLEND

The objective of this section was to evaluate the blend that consisted of organic and inorganic coagulants for pre-treatment of the MBBR's effluent for ultra-filtration. The test was performed on two samples obtained on different days in an attempt to capture some of the variability of effluent water characteristics. The characteristics of each sample were different and are presented in Table 4-12. From Table 4-12 it can be observed that the samples employed in trial 1 were obtained when the MBBR was operated at a higher influent flow, and therefore, lower hydraulic residence time (HRT). The HRT values for trials 1 and 2 were 2.6 and 4.6 hours, respectively. As expected, trial 1 showed better results in removing organic matter. The MBBR effluent soluble COD was 827 mg/l for trial 1 and 233 mg/l for trial 2. The results suggest that in trial 2 the readily biodegradable COD was mostly removed and only a small residual was left. Higher TSS were observed for trial 2 with the higher HRT, which was expected since more soluble COD was consumed and converted to biomass. Other parameters (such as influent quality, in particular influent COD concentration) may also have been responsible for the different effluent characteristics for trial 1 and 2.

Table 4-12 Characteristics of effluent samples obtained for pre-coagulation by the blend and ultra-filtration

Trial	Influent flow(m^3/d)	D.O. (mg/l)	TSS (mg/l)	TCOD (mg/l)	SCOD (mg/l)
Blend-1	16.4	3.0	1640 ± 56	2930 ± 238	827 ± 26
Blend-2	9.3	4.0	2440 ± 0	2500 ± 63	233 ± 17

In both trials, the experiments were performed with non-dosed samples and dosed samples where the optimal dosage, as determined by the jar tests, was employed. The optimal dosages, which were obtained from the primary jar test, were 200 and 400 ppm for trials 1 and 2, respectively. The higher dosage that was required for trial 2 may have been due to the higher TSS concentration. In trial 1, a third sample was overdosed with 400 ppm and in trial 2 a third sample was under-dosed with a dosage of 200 ppm. The purpose was to evaluate the impact of over-dosage and under dosage of the blend on the COD fractions and ultra-filtration.

4.7.1 Coagulation with the coagulant blend and COD fractionation

To investigate the effect of coagulation with the coagulant blend on the different COD fractions, SCOD and FFCOD were measured. The colloidal COD was estimated from the difference of SCOD and FFCOD. Figure 4-12 shows the COD fractions for the two samples separately.

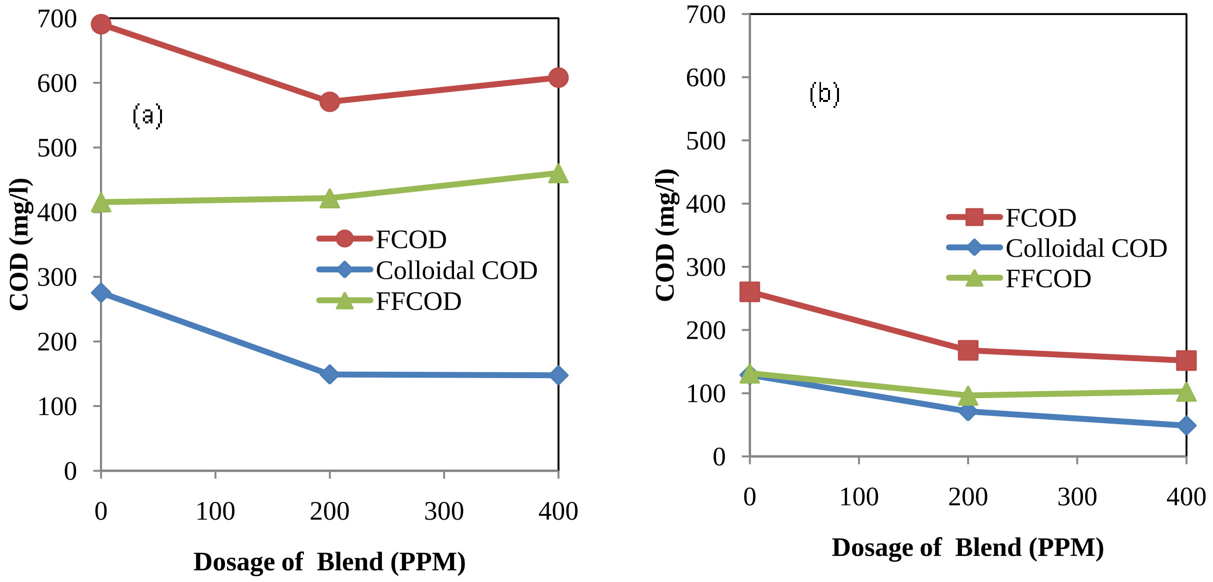


Figure 4-12 COD fractions for samples of (a) Blend-1 and (b) Blend-2

As can be seen in Figure 4-12, both SCOD and colloidal COD decreased with the addition of the coagulant blend. In trial 1, the over-dosage of coagulant did not further reduce the soluble COD fractions as compared to optimal dosed sample.

The effect of coagulation on COD fractions is presented as removal percentages in Table 4-13. In order to better understand the impact of coagulation, samples were over-dosed and under-dosed in trials 1 and 2, respectively. Table 4-13 shows a slight increase in SCOD and no change in colloidal COD when the samples were overdosed in trial 1which indicated that over-dosage of samples may not decrease fouling further. In trial 2 when the samples were under-dosed the removal efficiencies of colloidal matter decreased by 44% and no significant change in SCOD was observed. Therefore, it was expected to see higher fouling for the samples that were non-dosed and under-dosed. The FFCOD increased slightly with addition of the blend in both trials but the increases were small as compared to the variability of the analysis. This increase of FFCOD if not due to experimental error was expected to increase the irreversible fouling particularly when over-dosed since solutes are one of the contributors to membrane fouling.

Table 4-13 Removal efficiencies of the blend of coagulants at different dosages from trials Blend-1 and Blend-2

Trial	Condition	Dosage of Blend (ppm)	Soluble COD	FFCOD	Colloidal COD
Blend-1	Optimal dosage	200	17%	-2%	46%
	Over-dosage	400	12%	-11%	46%
Blend-2	Under dosage	200	36%	27%	37%
	Optimal dosage	400	42%	22%	81%

4.7.2 Pre-Coagulation with coagulant blend and ultra-filtration of MBBR effluent

The effect of coagulation with the coagulant blend on fouling of the membrane was assessed in this part of the study. Membrane fouling for coagulated samples with 200 and 400 ppm were compared to investigate the under-dosage and over-dosage of the coagulant blend. Figure 4-13 shows the development of total resistance for sample with the coagulant blend coagulation.

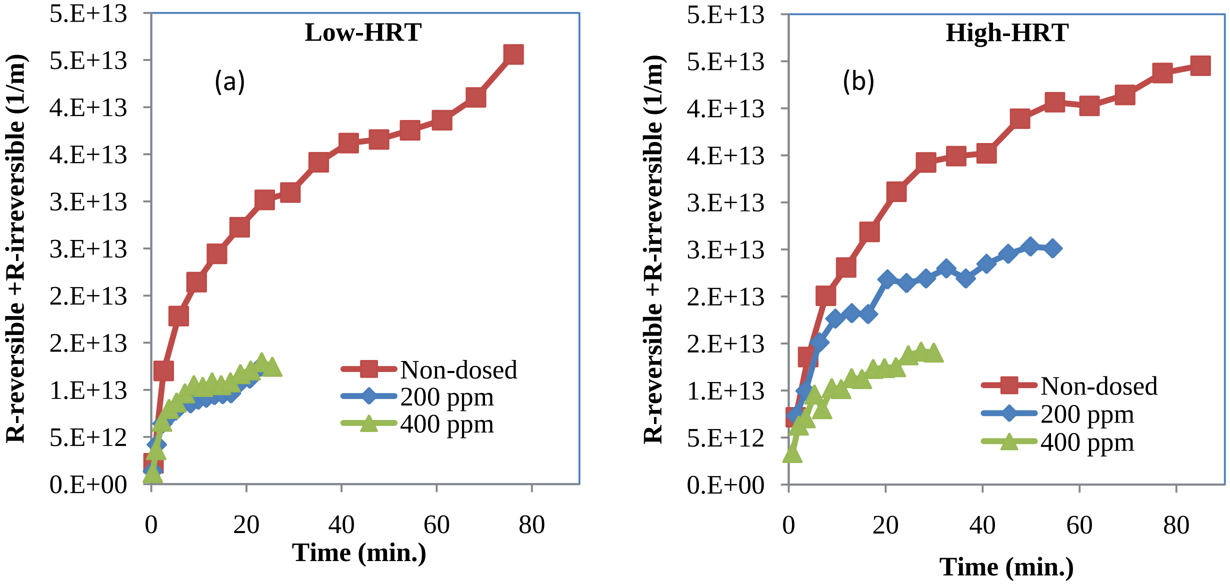


Figure 4-13 Impact of the pre-coagulation on membrane total fouling resistance development for trials (a) Blend- 1 (Low HRT) and (b) Blend-2 (High HRT)

The total fouling of non-dosed samples was similar. As shown in Table 4-12 the wastewater characteristics employed in trial 1 (with low HRT) had higher SCOD (3.5 times higher) than trial 2 but lower TSS (1.5 times less). It was expected that an increased SCOD would increase fouling while a decreased TSS would reduce fouling. The results indicate that the total membrane fouling did not change and hence it would appear that the two effects may have cancelled each other. As was mentioned before, HRT was probably not the only parameter affecting the results of trial 1 and therefore, for a better understanding of the effect of HRT more experiments should be performed under more controlled conditions.

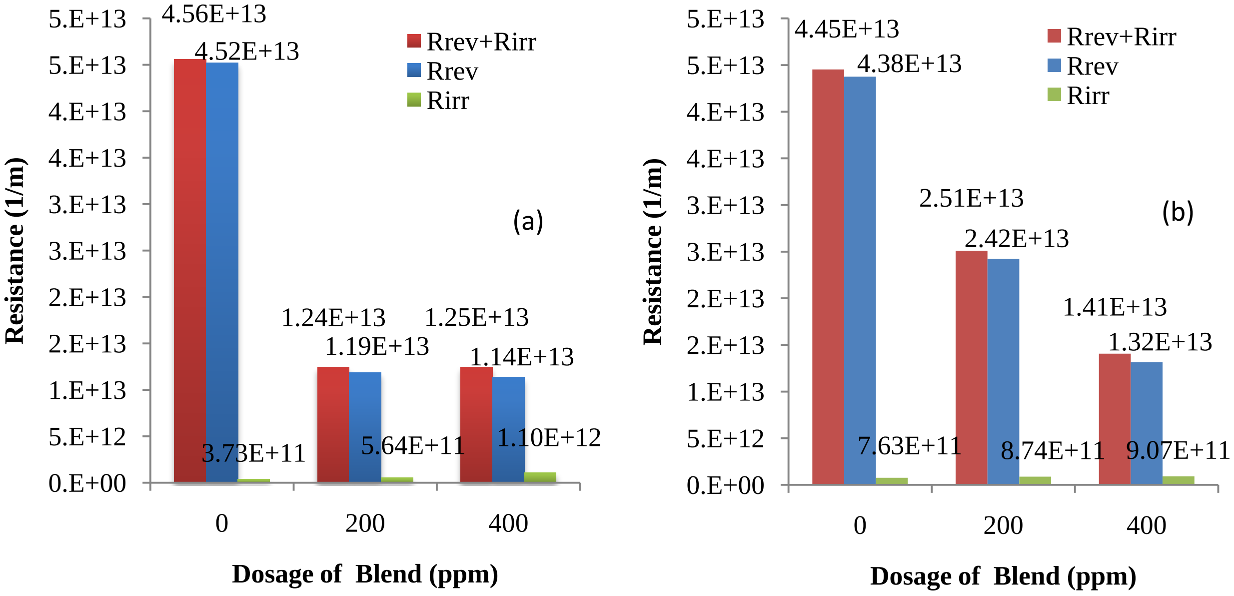


Figure 4-14 Impact of the coagulant on total, reversible and irreversible fouling at the end of the test for trials (a) Blend-1 and (b) Blend-2

From Figure 4-14 it can be seen that for non-dosed samples, the irreversible fouling in trial 1 (low HRT) was lower than trial 2 (high HRT). COD fractionations (section 4-7-1) showed that trial 1 (with lower HRT) had higher residual biodegradable SCOD and FFCOD and slightly higher colloidal COD concentrations than trial 2 and therefore the results contradicted the expectation of higher irreversible fouling with this feed. The lower irreversible fouling in trial 1 may have been due to the effect of it different fouling mechanism. For example, sometimes the deposition of matter on the surface of the membrane decreases the irreversible fouling since it works as a pre-filter to the membrane [9]. This filter separates the dissolved matter that can penetrate into the pores and cause irreversible fouling. These phenomena might explain the lower fouling in trial 1, since it has higher colloidal matter.

Other MBBR operating conditions in trial 1 and 2 such as influent qualities and in particular influent COD concentrations and dissolved oxygen could have affected the effluent composition with respect to SMP and EPS concentrations thereby increase the irreversible fouling. Operation at a higher DO can increase the cell surface hydrophobicity, which causes formation of flocs with higher strength, and therefore particle sizes increase [9]. Analysis of particle size distribution and SEM pictures of washed membranes after filtration runs (fouled membrane after washing the cake layer) may provide insight into the effect of different COD fractions on membrane fouling, which could change with HRT.

Table 4-14 shows the effect of coagulation with the blend on membrane resistance expressed as a percentage change with respect to the non-dosed effluent for trials 1 and 2. It can be observed from Table 4-14 that the addition of the blend at its optimal dosage decreased the reversible fouling by more than 70% in both trials and increased the flux by more than 200%. The over-dosed sample in trial 1 had the same reversible fouling and flux as the sample with optimal dosage. However, the under dosed sample in trial 2 had considerably higher reversible fouling as compared to the optimal dosed sample.

Table 4-14 Impact of the coagulant blend on membrane performance

Trial	Trial 1 - Low HRT			Trial 2 - High HRT		
Dosing condition	Non-dosed	Optimal -dosage	Over-dosed	Non-dosed	Under -dosed	Optimal -dosage
Dosages of Blend (ppm)	0	200	400	0	200	400
% Reduction of fouling resistance (R_f)	-	73%	73%	-	44%	68%
% Reduction of Irreversible resistance	-	-51%	-196%	-	-15%	-19%
% Reduction of Reversible resistance	-	74%	75%	-	45%	70%
% Increase in flux	-	254%	254%	-	72%	201%
% $R_{irreversible}$ / R_f	0.8%	4.5%	8.8%	1.7%	3.5%	6.5%
% $R_{reversible}$ / R_f	99.2%	95.5%	91.2%	98.3%	96.5%	93.5%

In trial 1, the irreversible fouling increased 51% when dosed at the optimal dosage and 196%, when over-dosed. It would appear that residual polyamine has the potential of becoming a foulant especially when overdosed. However, in trial 2, the blend only slightly increased the irreversible fouling and was within the range of experimental error. It would appear that the effect of the blend on irreversible fouling was dependent on the wastewater characteristics and it was possible that it may cause irreversible fouling. More investigation is required to investigate the effect of blend on irreversible fouling. The results do however indicate that the coagulant blend did not reduce irreversible fouling.

The permeate COD concentrations from the coagulated and non-coagulated samples are presented in Table 4-15. It can be seen that coagulation with the blend did not affect the COD removal efficiency of the whole system. As observed in trial 2 (with high HRT) MBBR had higher organic removal efficiency and after ultra-filtration of the MBBR effluent, the permeate COD of trial 1 was higher by a factor of 3 than trial 2. For trial 1, with lower HRT, the permeate COD was 463 mg/l representing a total COD removal of 84% while for the trial 2, with higher HRT, it was 149 mg/l representing a total COD removal of 95%. It is suggested that a higher range of HRTs be tested to assess the effect of HRT on the COD removal efficiency of the whole system and on fouling behaviour of the membrane. An optimal HRT for this system should maximize SCOD removal and minimize particulate COD hydrolyzing.

Table 4-15 Permeate COD concentrations of non-coagulated and coagulated samples using the coagulant blend

Permeate COD (mg/l)			
Dosage (ppm)	0	200	400
Blend-1	468 ± 5	473 ± 1.	448 ± 48
Blend-2	156 ± 2	144 ± 0	147 ± 10

4.8 DIRECT COMPARISON OF PRE-COAGULATION WITH ALUM, FERRIC CHLORIDE AND COAGULANT BLEND AS A PRE-TREATMENT METHOD FOR ULTRA-FILTRATION

In this part of the study, COD fractionation and ultra-filtration of coagulated samples with the three chosen coagulants (blend, alum, and ferric chloride) and non-coagulated samples were simultaneously investigated. Two sets of trials were performed on the samples obtained on different days to account for variability in water quality. In the first trial, a non-dosed sample and samples with optimal dosages of alum and ferric chloride were prepared. In the second trial, the coagulant blend was also compared with the two other coagulants. In these trials the coagulants were added to the solutions at their optimal dosages as obtained from preliminary jar tests. The effluent characteristics for the two trials are presented in the Table 4-16. It can be observed from Table 4-16 that trial 1 had higher TSS, TCOD and SCOD than trial 2. The MBBR HRT in trial 1 had fluctuated somewhat during the sampling day and was approximately 4.6 hours as in trial 2. From the results of this part of study it can be observed which coagulant had a greater effect on membrane fouling reduction despite the variations in wastewater quality.

Table 4-16 Characteristics of effluent samples obtained for pre-coagulation and ultra-filtration

Trial	Influent flow(m^3/d)	D.O. (mg/l)	TSS (mg/l)	TCOD (mg/l)	SCOD (mg/l)
Trial-1	2.7-10.9	1.2	2990 ± 14	3831 ± 80	276 ± 26
Trial-2	9.3	5.0	2230 ± 14	3150 ± 144	452 ± 9

The objective of the parallel trials was to account for the effect of effluent quality variation when comparing the three coagulants. This facilitated a comparative assessment and comprehensive conclusions regarding the impact of coagulants on membrane fouling.

4.8.1 Coagulation with alum, ferric chloride, and coagulant blend and COD fractionation

The data obtained from COD fractionations for the two trials are presented in Figure 4-15. From the results, the effects of each coagulant on FFCOD, FCOD and colloidal COD were compared. As can be seen from Figure 4-15, coagulation with the three coagulants had only a minor effect on FFCOD and a larger effect on colloidal COD. Ferric chloride reduced the colloidal COD and soluble COD to the greatest extent. In the first trial, ferric chloride reduced the SCOD and colloidal COD by 73% and 94%, respectively; while alum reduced the SCOD and colloidal COD by 53% and 71%, respectively. In the second trial, it can be seen that ferric chloride again had the highest efficiency and the blend had slightly better efficiency than alum in colloidal COD removal. On the basis of the removal of SCOD and colloidal COD it was expected that ferric chloride would have the lowest fouling while alum would have highest.

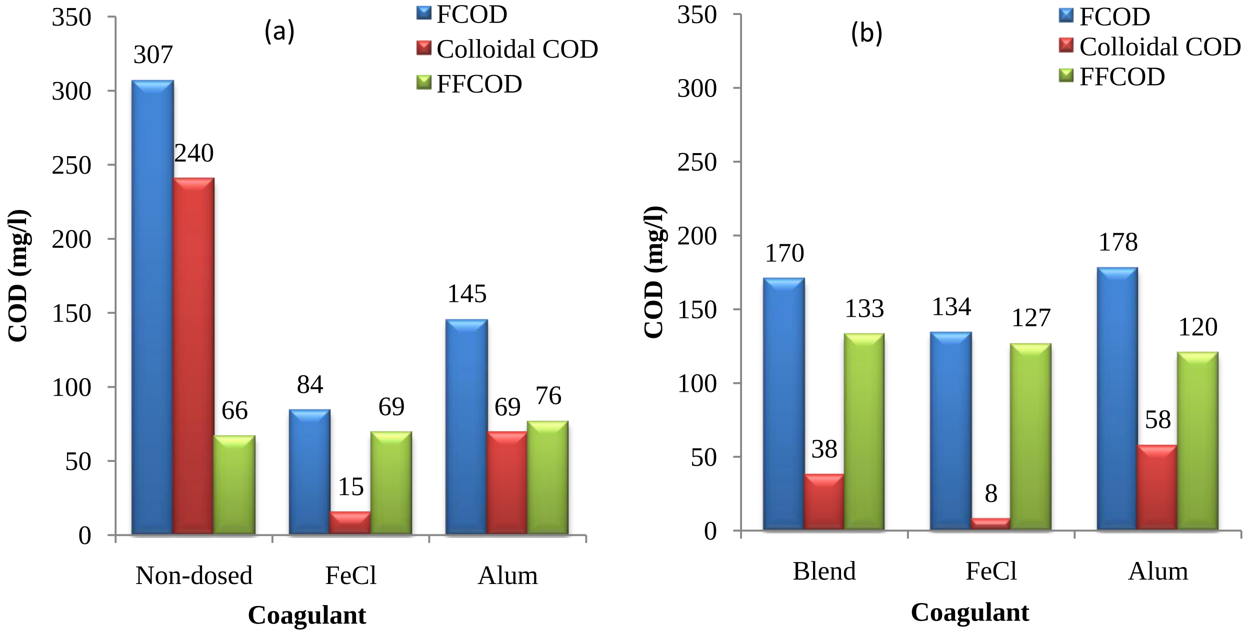


Figure 4-15 COD fractions for samples of (a) Trial-1 and (b) Trial 2

4.8.2 Pre-Coagulation with alum, ferric chloride, and the coagulant blend and Ultra-Filtration of MBBR Effluent

The results of the previous ultra-filtration tests showed that the addition of all the three coagulants reduced fouling of the membranes. The purpose of this section was to directly compare the effects of the three coagulants with respect to fouling by using the same wastewater sample for all coagulants. Samples for each trial were obtained from the same effluent and the non-coagulated and coagulated samples were filtered in parallel simultaneously. Figure 4-16 presents the development of total fouling for non-coagulated and coagulated samples with different coagulants at their optimal dosages. From Figure 4-16 (a) it can be seen that alum and ferric chloride both significantly decreased total fouling and 150 ml of sample was filtered in a significantly shorter time compared to non-dosed sample. It can also be seen that ferric chloride had higher efficiency in reducing the fouling than alum. Figure 4-16 (b) compares the three coagulants and it can be seen from trial 2 that the blend and alum had almost the same fouling development and both had higher fouling than ferric chloride.

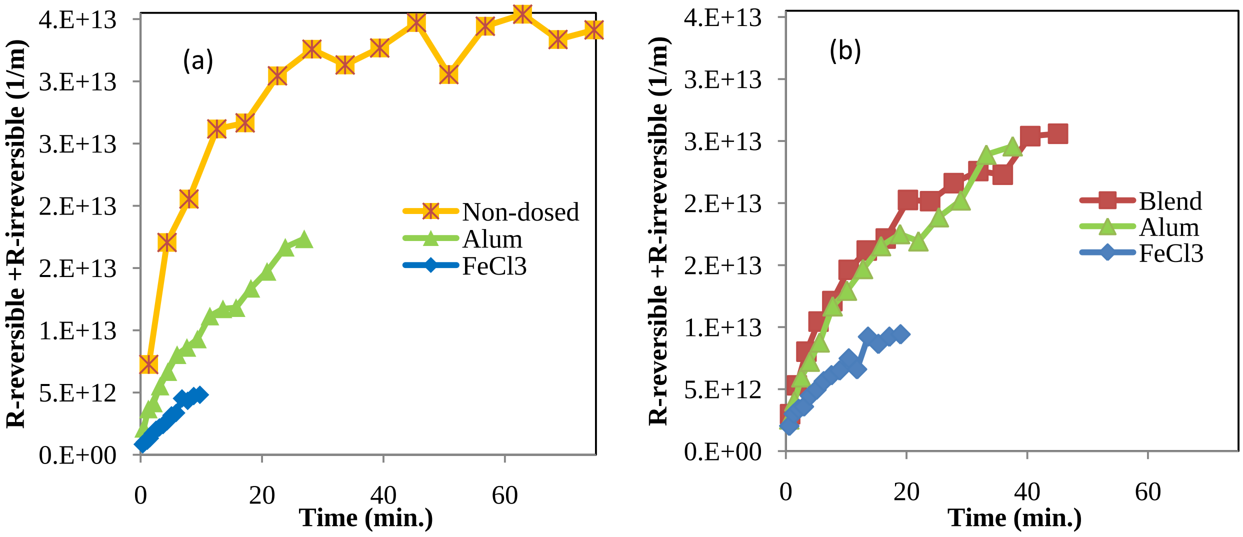


Figure 4-16 Impact of pre-coagulation on membrane total fouling resistance development for trials (a) Trial- 1 and (b) Trial-2

The effects of the coagulants on reversible and irreversible fouling at the end of the tests are presented in Figure 4-17. From Figure 4-17 it can be seen that ferric chloride had the lowest reversible and irreversible fouling as compared to alum and the blend. In trial 1, ferric chloride reduced the total fouling resistance 86% while alum decreased the total fouling 46% as compared to the non-coagulated sample. As shown by the results of the COD fractionations (section 4-8-1), ferric chloride had the highest colloidal COD removal and this likely explains the lower irreversible fouling. The lower reversible fouling of the samples with ferric chloride may be due to the size, structure, and strength of flocs. Floc characteristics should be further assessed and compared to obtain a better understanding of the higher efficiency of ferric chloride.

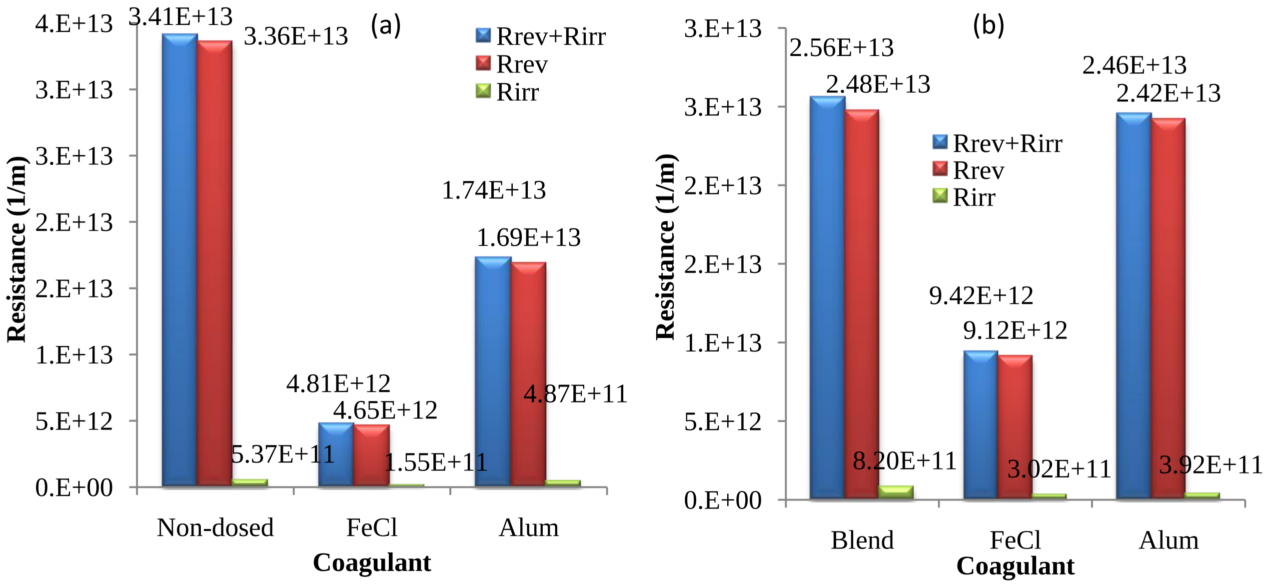


Figure 4-17 Impact of pre-coagulation on total, reversible and irreversible fouling at the end of the test for trials (a) Trial-1 and (b) Trial-2

4.9 GENERAL COMPARISON OF THE THREE COAGULANTS

In order to make comprehensive conclusions about the three coagulants a summary of the results was prepared. The results obtained from the ultra-filtration trials of coagulated effluents and non-coagulated effluents for samples that were collected at different times and which were presented previously are summarized in Figure 4-18 and Table 4-17. The 95% confidence levels of the means are also presented. It is worth noting that the standard deviations presented in Figure 4-18 are high due to the variation of wastewater characteristics during the trial period.

Table 4-17 Summary of the results of the effect of the three coagulants on membrane performance

Efficiency compared to non-coagulated sample				
Coagulant dosage		Ferric chloride	Alum	Blend
% Reduction of total fouling resistance	Average	79%	49%	71%
	Max	86%	57%	73%
	Min	73%	42%	68%
% Reduction of Irreversible Resistance	Average	75%	-7%	-107%
	Max	79%	9%	-19%
	Min	71%	-15%	-196%
% Reduction of Reversible Resistance	Average	79%	50%	72%
	Max	86%	57%	75%
	Min	73%	50%	70%
% Flux improvement	Average	355%	94%	228%
	Max	485%	128%	254%
	Min	224%	62%	201%

Table 4-17 and Figure 4-18 provide a summary of the effects of coagulation with the three coagulants on membrane resistance for each trial. In Table 4-17 the values are expressed as a percentage change with respect to the non-dosed effluent. It can be seen from Table 4-17, that ferric chloride out-performed the two other coagulants since it had the highest efficiencies in increasing the flux and decreasing reversible and irreversible fouling and had more consistent results considering the variation in effluent characteristics.

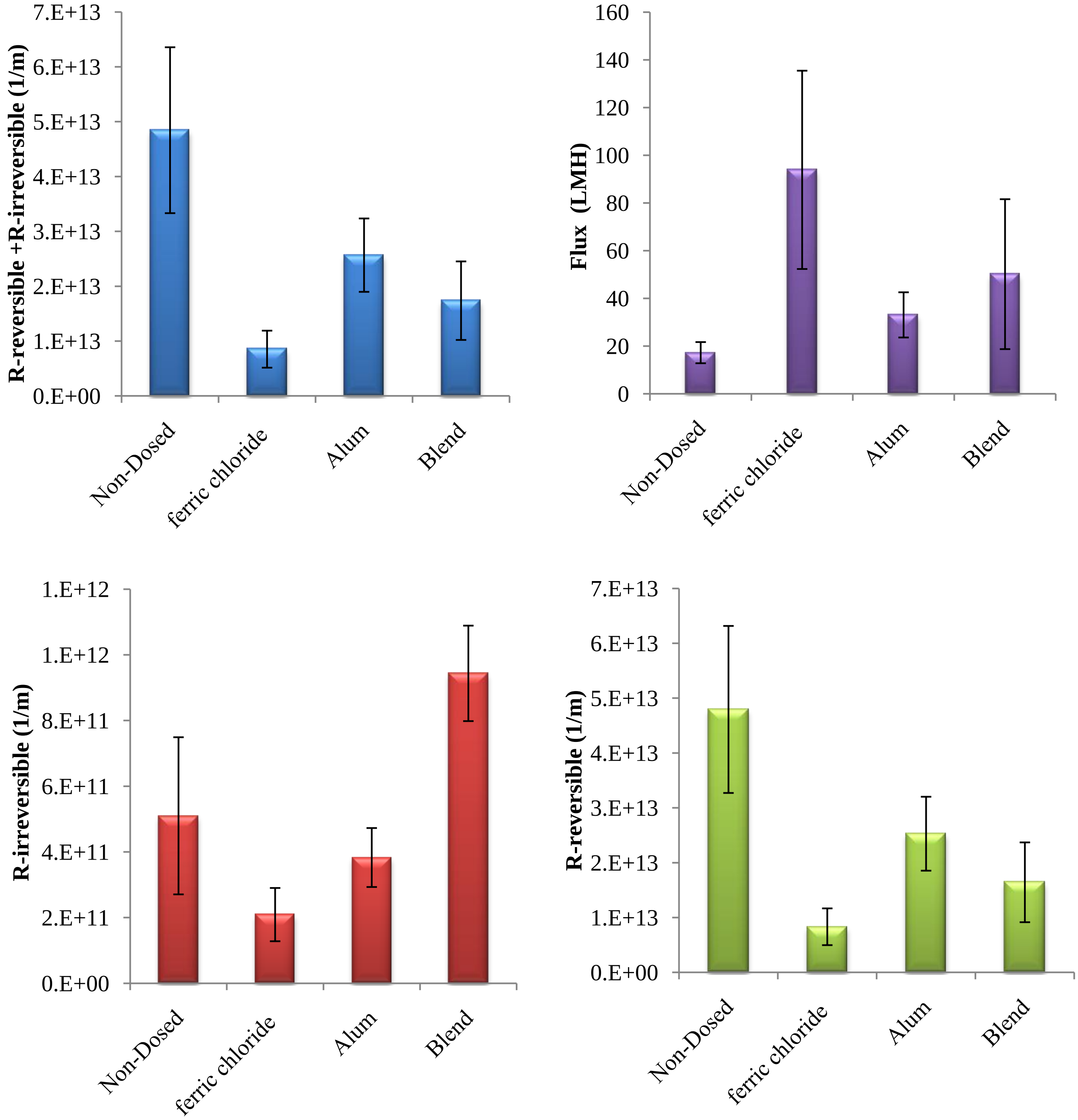


Figure 4-18 Summary of effect of coagulant on total, reversible, irreversible fouling and flux for ultra-filtration of pre-coagulated and non-coagulated samples

In this study, the dominant fouling mechanism was cake formation which contributed to more than 90% of total fouling and the changes in irreversible fouling were negligible. This was probably due the small membrane pore sizes and operating conditions of the experiments.

The blend had slightly lower efficiency in decreasing the reversible fouling than ferric chloride. The blend had higher efficiency than alum in increasing the flux, however its effect on irreversible fouling was variable and may have been due to the effect of residual polyamine in the samples. It can be concluded that the addition of coagulants incorporates colloidal materials that do not pass through the membrane into larger flocs and this decreases the fouling since the cake layer becomes more porous and pore blockage is decreased. The results of the COD fractionation and permeate COD measurements showed that FFCOD removal and COD removal of the UF membrane was not increased by addition of the coagulant. Hence it was concluded that low molecular weight particles which pass through the membrane were not affected by coagulant addition. As a result, coagulation did not affect the COD removal of the whole system tested. This may be due in part to the pH at which tests were carried out. It should be noted that the coagulation was optimized based on turbidity removal and not COD removal. On the other hand, the HRT of the MBBR is an important parameter which can significantly affect the COD removal efficiency of the MBBR-MR systems.

Chapter 5

Conclusions and Recommendations

5.1 CONCLUSION

A review of the literature found few publications on MBBR-MR and no studies that have been performed with pretreatment of MBBR effluent with coagulation for membrane fouling reduction. In this research preliminary studies that investigated the feasibility and potential of the MBBR-MR process were conducted. The performance of a MBBR-MR system for industrial wastewater treatment (starch line from a potato chip factory) was assessed with respect to membrane fouling and COD removal efficiency. The effect of pre-coagulation of MBBR effluent by different types of coagulant (alum, a blend of polyamine and poly aluminum chloride, and ferric chloride) on fouling of membrane and COD removal efficiency of the whole system (MBBR-MR) was investigated. Based on the effluents tested and conditions of these experiments, the findings of this research can be summarized as:

1- Over the operating period the MBBR effluent demonstrated variable characteristics that corresponded to influent feed fluctuations. However, membrane filtration minimized these fluctuations and a consistent high quality permeate that is suitable for water reuse purposes was obtained at relatively high loading rates.

2- The loading to the MBBR-MR was found to affect treatment efficiency and the membrane performance. Operation under the elevated loading conditions (HRT = 2.6 hours) resulted in an increase in the irreversible fouling of the membranes (60% on average). The increased fouling was likely due to the residual foulants from the raw wastewater that were not removed in the MBBR due to hydraulic limitations. Correspondingly, a lower removal efficiency of total COD (13%) was observed.

3- Fouling of the membrane by the wastewater was found to be substantially reduced by treatment with the MBBR. The reversible and irreversible fouling of the MBBR effluent were 56 and 63%, respectively of that observed with the raw wastewater. The higher fouling with the raw wastewater was likely due to elevated concentrations of colloidal and dissolved matter which were removed in the MBBR.

4- Coagulation did not remove FFCOD from the MBBR effluent and as a result, pre-coagulation of the membrane feed did not improve the treatment efficiency of the MBBR-MR with respect to COD removal.

5- The addition of coagulants was found to improve membrane permeability. All coagulants decreased reversible fouling, presumably by changing the structure of flocs which resulted in increased cake layer porosity and the observed improved performance. The non-coagulated samples likely produce a less porous structure on the membrane than the coagulated samples due to the smaller particle sizes.

6- The extent of the pre-coagulation effect on membrane fouling was found to strongly dependent on the type and dosage of the coagulant and the MBBR effluent characteristics. All the coagulants had significantly higher efficiency at their optimal dosages as determined in preliminary jar tests.

7- Ferric chloride performed the best as a pre-treatment coagulant when compared to alum and the coagulant blend with reductions in both reversible and irreversible fouling (43-86% and 51-71%, respectively) and increased consistency as compared to the other coagulants. The reduced irreversible fouling may have been due to lower pore blockage of the membrane that resulted from a reduction in colloidal matter with $FeCl_3$ addition.

8- Alum had no significant effect on irreversible fouling and the coagulant blend significantly increased irreversible fouling in some trials (up to 196% or by a factor of

3 when overdosed). The increase in fouling may have been due to residual polyamine that might have acted as foulant. Additionally, alum and the blend were, on average, 29% and 7%, less effective than ferric chloride in reducing reversible fouling.

5.2 RECOMMENDATIONS

The application of the combination of MBBR and ultra-filtration system for treatment of potato processing wastewater showed promising results. Recommendations for further study of the MBBR-MR system include:

1- Operation of the MBBR at higher HRTs than 4.6 (which was the highest HRT that the MBBR could be operated at in this project due to rotameter restrictions) to investigate its effect on membrane fouling and removal efficiency and find an optimal HRT for the MBBR-MR process

2- Investigation of the MBBR-MR with a pilot scale membrane unit which allows obtaining a more realistic assessment of the pre-coagulation and MBBR-MR process. The scale dependent factors (such as flocculation), contribution of each MLSS factor to membrane fouling, and identification of the dominant fouling mechanisms can be better assessed in pilot scale membrane units which are equipped with physical (aeration and back washing) and chemical membrane cleaning. More realistic values will be obtained for reversible and irreversible fouling resistances and flux. Additionally, the long term effect of pre-coagulation and operational factors such as HRT on membrane performance can be assessed.

3- Assessment COD fractions in various stages of the process since the characteristics of the flocs changes at different stages. In this study COD fractionation was performed on MBBR effluent before and after coagulation, however, COD fractionation of samples from the pilot scale membrane and retentate (settled sludge) would be more helpful for fouling characterization.

4- Analysis of particle size distribution and characteristics (such as Zeta potential/ hydrophobicity) of MLSS constituents can provide insight to membrane fouling. The use of fluorescence spectroscopy to characterize and quantify various components of natural organic matter might be employed for this purpose. This technique can be helpful to investigate the contribution of various constituents of MLSS on fouling and the effect of coagulation on these constituent.

5- Assessment of settling, dewatering and filtering characteristics of the retentate by sludge volume index (SVI), capillary suction time (CST) and time-to-filtrate (TTF) which may be helpful for explaining the MLSS concentrations in the membrane unit and provides an insight to sludge characteristics which this information is helpful for sludge disposal considerations

6- Investigation of the nutrient removal (nitrogen and phosphorous) of the whole pre-coagulation and MBBR-MR system

7- Investigation of the possible effects of the defoamer (KFO™ 6450FL) employed in this study on the performance of the whole pre-coagulation and MBBR-MR system and use of an alternative non-toxic defoamer if required

8- Investigation of feasibility and benefits of application of an equalization tank at the facility investigated. An equalization tank would decrease MBBR effluent fluctuations and hence a more consistent permeate quality could be obtained and the operational costs would likely decrease

9- On the basis of the results obtained in this study, it is recommended that ferric chloride and PACl be compared both in bench scale and pilot scale ultra-filtration tests. Additionally, there are other coagulants that remain to be tested.

10- Investigation of pre-coagulation/sedimentation and inline coagulation and comparison of these two pre-coagulation methods with respect to fouling of the membrane, phosphorous and COD removal of the whole process, and their capital and operational costs

11- Provision of cost estimates is required to assess the system economically. For example, considering the high dosages of coagulant which were required to effectively reduce membrane fouling, consideration of the expenses for coagulant addition and additional expenses for membrane cleaning and replacement which are required in the absence of pre-coagulation can indicate if pre-coagulation is an economical pre-treatment method in this study.

5.2.1 Recommendations for the pilot MBBR:

1- Increase the number of MBBR compartments in order to increase the loading rates and achieve higher and more consistent COD removal efficiencies
2- Improve the MBBR aeration system to obtain uniform dissolved oxygen concentration throughout the tank and prevent solids settlement at the bottom of the tank
3- Install a digital flow-meter for MBBR influent which does not get clogged by high concentrations of starch
4- Install a smaller line for the effluent to prevent solids settlement in the tube
5- Install an inline DO transmitter/controller and application of a flow meter which can provide higher airflow rates than 20 SCFM
6- Consider an enhanced defoamer system

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Appendices

Appendix A

ACTIVECELL AREAL BIOMASS DENSITY TEST (AGST)

Purpose:

While suspended growth may be readily measured, the amount of attached growth is more difficult to quantify on a daily basis. The procedure to determine the mass of biomass on the ActiveCell biofilm carriers is termed the biomass areal density test.

Procedure:

1. Use a clean beaker to scoop water (with carrier) from the bioreactor (suggested minimum # of carrier pieces = 10, recommended 20).
2. Using gloved hands, extract the carrier pieces, being careful not to dislodge any significant amount of biofilm (touch the exteriors of the carrier only) and place the pieces into a large beaker with fresh water. Let stand for 5 minutes (this should dislodge any loose biofilm that may cling to the carrier)
3. Touching only the exterior of the carrier, remove the carrier pieces from the beaker, place them in a pre-weighed crucible (or aluminum weigh dish) and place the crucible in an oven at a temperature of 100°C for 24 hours.
4. Remove the dried carrier pieces from the oven and put in a desiccator for > 1 hour and note the weight (in grams) (A).
5. Put the dried carrier pieces in individual 100 ml vials/beaker (5 pieces/vial) or all pieces in a larger vial, fill the vials with domestic bleach and cap them tightly.
6. Shake the contents of each vial 4-5 times for 1-2 minutes each. Place a stir bar in the vial/beaker and let them stir overnight.
7. Use a strainer to thoroughly wash the carrier pieces under running tap water and dry the carrier pieces on a towel paper for 15 minutes.
8. Put the carrier pieces in a pre-weighed crucible and place the crucible in an oven at a temperature of 100°C for 24 hours.
9. Remove the dried carrier pieces from the oven and put in a desiccator for 1 hour and note the weight (in grams) (B).

Calculations:

The results of the test and the calculation of the biomass density are shown below:

Weight of dried carrier =A

Weight of dried and cleaned carrier = B

# of test pieces = N

Weight of biomass = A – B

Weight of biomass per unit of carrier = (A – B) / (N)

Surface area per unit of carrier = 0.003792 m^2

Biomass Areal Density (g/m^2) = weight per unit carrier / surface area per unit carrier

Reference:

Headworks Bio Canada Inc. Victoria, BC

Appendix B

ZETAG®8125

Technical Information

Product name:

CIBA®ZETAG®8125 Flocculant
Cationic Polyelectrolyte incorporating Unique Molecular Architecture
A Product of Ciba Specialty Chemicals

Description:

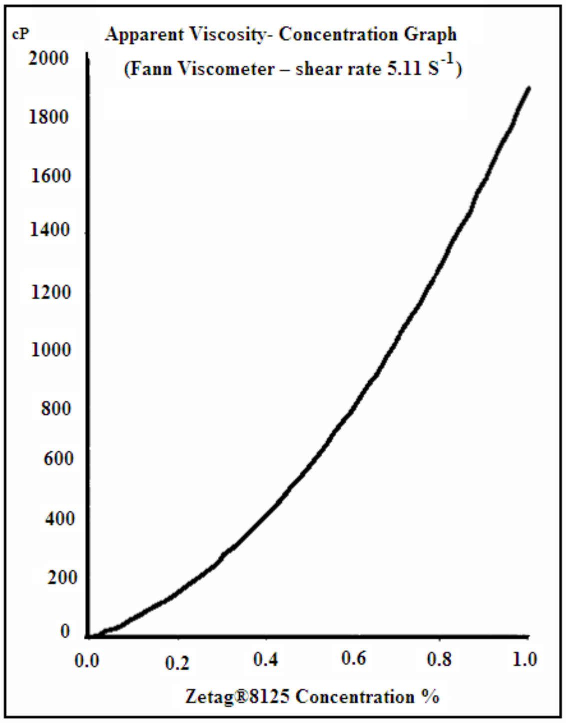
Zetag®8125 is a synthetic high molecular weight polyacrylamide. It is supplied as a free flowing white powder. Zetag®8125 is of low cationic charge.

Principle Uses:

Zetag®8125 has been specifically designed to operate on organic industrial and municipal sludges where such wastes are thickened or dewatered using mechanical equipment such as centrifuges, gravity belt thickeners etc.

Typical Properties: Appearance	Off-white granular solid
Molecular weight	High
Particle size	98% < 1750 microns
Bulk density	0,7 g/cm^3
pH of 0,5% solution	approx 4,3
Viscosity at 25°C	See graph

Viscosity Curve:



Application & Storage:

Recommended solution concentrations	
Stock solution	0,20 – 0,50% max.
Feed solution	0,05 – 0,20% max.

Recommended storage periods	
Dry product	up to two years
Stock solution	2 – 5 days
Feed solution	1 – 3 days

Storage of the dry product and solutions for longer than the recommended periods may be acceptable under the correct conditions but could result in some loss of product efficiency. Storage of the solids should be in a cool, dry place and conditions of high temperature and high humidity should be avoided. Under such conditions the hygroscopic nature of the product may result in excessive moisture up-take and resultant caking. Packages should be kept sealed when not in use.

Corrosive properties: Corrosion towards most standard materials of construction is very low. Stainless steel, fibreglass, polyethylene, polypropylene and rubberised surfaces are recommended as ideal. In some cases aluminium surfaces can be adversely affected.

Packaging:

Zetag®8125 is supplied in 25 kg nett weight plastic bags in palletised shrink wrapped units of total nett weight 900 kg. Zetag®8125 is also available in semi-bulk palletised “Big Bags” of 700 kg nett weight.

Spillages:

Spillages of Zetag®8125 should be contained and disposed of in accordance with local regulations. Discharges of neat product or solutions of product to watercourses should be avoided as Zetag®8125 may adversely affect the mucous membranes on fish gills. Solutions of Zetag®8125 are extremely slippery and caution should be exercised.

Health & Safety:

Zetag®8125 exhibits a very low order of oral toxicity and does not present any abnormal problems in its handling or general use. However, as with all cationic polyelectrolytes the product exhibits toxicity towards fish. It is important that precautions are taken where the product may come into direct contact with fresh water courses, streams and rivers. Detailed information on handling and any precautions to be observed in the use of the product(s) described in this leaflet can be found in our relevant Materials Safety Data Sheet.

Reference:

http://www.acat.com/_files/datasheets/701/ZETAG_8125%28TMB-EN%29.pdf