Comparison between Hybrid Moving Bed Membrane Bioreactor and Conventional Membrane Bioreactor Processes in Municipal Wastewater Treatment

by

Sasha Michael Rollings-Scattergood

A Thesis presented to The University of Guelph

In partial fulfilment of requirements for the degree of Master of Applied Science in Environmental Engineering

Guelph, Ontario, Canada

© Sasha Michael Rollings-Scattergood, November, 2011
ABSTRACT

COMPARISON BETWEEN HYBRID MOVING BED MEMBRANE BIOREACTOR AND CONVENTIONAL MEMBRANE BIOREACTOR PROCESSES IN MUNICIPAL WASTEWATER TREATMENT

Sasha Michael Rollings-Scattergood
University of Guelph, 2011

Advisor:
Professor Hongde Zhou

A conventional membrane bioreactor (MBR) and two moving bed bioreactors coupled with ultrafiltration membrane filtration were operated for close to six months to investigate biological nutrient removal and potential fouling inducing parameter mitigation. Unique to one of the moving bed membrane bioreactors (MBMBR) was a newly designed media that incorporated a hydrodynamic exterior carrier with a highly porous interior packing. Preliminary investigation indicates that nitrogen compounds were superiorly removed in the two MBMBRs when compared with the MBR. This is a result of denitrification processes occurring in anoxic micro-zones found within the depths of the biofilm affixed to media. Fouling propensity was found to be increased by over four times in the MBMBR systems as compared to the MBR. Mixed liquor, permeate and filtrate analysis, membrane fibre examination and permeability tests indicated that colloidal organic carbon, as well as soluble microbial products were the dominant fouling inducing compounds.
I would firstly like to acknowledge my graduate advisor Dr. Hondge Zhou, P.Eng., for his thoughtful insight and support throughout my graduate career. His mentorship extended beyond the walls of the University and his support allowed me to obtain several prestigious awards and compete in environmental engineering design competitions. I would also like to extend my appreciation towards Dr. Sheng Chang who provided insight throughout the duration of my experimentation.

Laboratory support was provided by Joanne Ryks, Dr. Victor Zhang and Chris Potvin and for that I am indebted. Furthermore, I acknowledge Dr. Liangfei Dong, who during a six month sabbatical helped set-up and begin operation of the pilot plant.

I would lastly like to make personal acknowledgements to my family and friends. To my mother, father and older sister who throughout my life always encouraged higher education and a quest for knowledge. To my best man Scott Hillaby, together we have endured trials and tribulations in both our undergraduate and graduate careers to which we prevailed. Finally, to my wife and best friend Melissa McKeown, who has always wholeheartedly supported me throughout my scholarly achievements and in our journey through life together. Je t'aimerai toujours!
# TABLE OF CONTENTS

Chapter 1 Introduction ........................................................................................................... 1

Literature Review ................................................................................................................... 6
  Moving Bed Bioreactor Technologies in Wastewater .................................................. 6
  Membrane Technologies in Wastewater ................................................................. 8
  Mechanisms of Fouling ................................................................................................. 9
  Foulants of Concern ....................................................................................................... 12
  Colloidal and Submicron Particles .............................................................................. 12
  Integrated Flocculation Zone for Enhanced Particle Coagulation ......................... 17
  Bio-Polymeric Substances ......................................................................................... 18

Abbreviations ....................................................................................................................... 28

Chapter 2 Operation of two Hybrid Moving Bed Membrane Bioreactors and a
Conventional Membrane Bioreactor for Biological Nutrient Removal of Real Municipal
Wastewater ....................................................................................................................... 30

Abstract ................................................................................................................................ 30

Introduction ....................................................................................................................... 31

Materials and Methods .................................................................................................... 35

Hybrid Membrane Pilot Plant ......................................................................................... 35

Analysis .............................................................................................................................. 39

Results and Discussion ................................................................................................. 41
Temperature ............................................................................................................... 65
Bulk Parameter Effects on Fouling ........................................................................... 66
Chemical Oxygen Demand ......................................................................................... 69
Total Organic Carbon ............................................................................................... 69
Mean Oxidation State of Carbon .............................................................................. 72
Soluble Microbial Products ....................................................................................... 73
Solid Retention Time ................................................................................................. 75
Particle Size Distribution .......................................................................................... 76
Membrane Fibres ....................................................................................................... 78
Resistance Model ....................................................................................................... 78
FT-IR .......................................................................................................................... 80
CLSM .......................................................................................................................... 84
Conclusions ................................................................................................................ 88
Chapter 4 Conclusions and Recommendations ........................................................ 90
Conclusions of Results ............................................................................................... 90
Future Research Potential ......................................................................................... 92
Engineering Significance ........................................................................................... 93
Chapter 5 References ............................................................................................... 95
LIST OF TABLES

Table 1-1 – Current state of the research for the moving bed membrane bioreactor technology

Table 1-2 – Reported concentration of EPS and SMP for the MBR process

Table 1-3 – Reported concentrations of EPS and SMP for the MBMBR process

Table 1-4 - EPSp/EPSc ratios for parallel operating MBMBRs and CMBRs

Table 2-1 - Summary of test apparatus and key experimental parameters

Table 2-2 - Measured quality of the influent, reactor, permeate and filtrate

Table 2-3 - Percent of carrier volume utilized for biofilm growth

Table 3-1 - Summary of test apparatus and key experimental parameters

Table 3-2 - The stains used in membrane fibre analysis

Table 3-3 - Bulk liquid parameters for influent wastewater and the three bioreactors

Table 3-4 - Estimated fouling rate

Table 3-5 - Pearson correlation coefficient with respect to fouling rate and other suspected bulk liquid parameters

Table 3-6 - Paired statistical analysis of COD and TOC concentrations

Table 3-7 - Value of the filtration resistance

Table 3-8 - Fractions contributing to filtration resistance
LIST OF FIGURES

Figure 1-1 - Typical diagram showing operation of (a) a submerged membrane bioreactor; (b) a moving bed biofilm reactor with solid liquid separation using a clarifier; and (c) a moving bed membrane bioreactor ........................................ 4

Figure 1-2 - Illustration of the exponential growth of TMP after sustainable flux is exceeded (Nywening & Zhou, 2009) ................................................................. 11

Figure 1-3 - Illustration of the protection mechanism of the dynamic membrane (Lee et al., 2001) ........................................................................................................... 13

Figure 1-4 - Comparison of EPS concentrations in studies with MBMBRs operating parallel to MBRs .............................................................................................. 21

Figure 1-5 - Comparison of SMP concentrations in studies with MBMBRs operating parallel to MBRs (‡ Fixed carrier attached growth system) ....................... 21

Figure 2-1 - Schematic for experimental setup ........................................................................ 37

Figure 2-2 - MBMBR C contained a novel fibrous media packed inside a polyethylene carrier ............................................................................................................. 38

Figure 2-3 - COD concentration and removal rates for the three bioreactors. ................. 43

Figure 2-4 - Total Nitrogen (TN) and nitrate concentration in the three reactors. ........ 46

Figure 3-1 - Schematic of the moving bed membrane bioreactor concept ....................... 55

Figure 3-2 - Temporal variation of TMP for the three bioreactors; MBMBR B and MBMBR C required chemical cleaning after 48 and 43 days of operation respectively. ......................................................................................... 63

Figure 3-3 - Critical flux analysis for MBR A ........................................................................ 64
Figure 3-4 - Temporal variation of temperature for the influent wastewater and three bioreactors ................................................................. 66

Figure 3-5 - TOC concentration for (a) filtrate; (b) permeate; and (c) colloidal samples from the three bioreactors and the filtered influent................................. 71

Figure 3-6 - Correlation of humic acids in mixed liquor supernatant and colloidal TOC 72

Figure 3-7 – Mixed liquor supernatant concentrations of SMP (number of measurements: n = 16) ......................................................................................... 74

Figure 3-8 – Permeate concentrations of SMP (number of measurements n = 8).......... 74

Figure 3-9 – The D10, D50 and D90 particle size for mixed liquor from the three reactors during the developmental phase ............................................................ 77

Figure 3-10 – Average FTIR output for fouled membranes after close to 6 months of operation and an unused membrane fibre (sample size: 6 locations per reactor, 256 scans per location) .......................................................... 82

Figure 3-11 – Average FT-IR output for membrane fibres after recovery cleaning with 1,000 ppm NaOCl (sample size: 6 locations per reactor, 256 scans per location) ......................................................................................... 83

Figure 3-12 – Average FT-IR output for membrane fibres after recovery cleaning with 2,000 ppm citric acid (sample size: 6 locations per reactor, 256 scans per location) ......................................................................................... 83

Figure 3-13 – 375 μm × 375 μm CLSM images of an unused membrane sample taken tangential to the fibre. ................................................................................. 85

Figure 3-14 - CLSM imaging of a fouled membrane fibre from MBR A. ................. 85

Figure 3-15 - CLSM imaging of a fouled membrane fibre from MBMBR B. ........... 85
Figure 3-16 - CLSM imaging of a fouled membrane fibre from MBMBR C. ................. 86

Figure 3-17 - CLSM imaging of membrane fibres to show cleaning efficacy of NaOCl and citric acid ........................................................................................................................................... 87

Figure 3-18 - Biofilm thickness and filtration resistance for a dirty fibre, after NaOCl recovery cleaning and after citric acid recovery cleaning........................................... 87
Chapter 1 Introduction

Hybrid membrane technologies in which conventional processes are integrated with solid-liquid separation through membrane filtration are advancing water and wastewater processes. Of primary interest in the field of wastewater treatment and water reuse is the membrane bioreactor (MBR). The conventional MBR uses suspended biomass to degrade wastewater constituents and membrane filtration to separate biomass typically through microfiltration (MF) or ultrafiltration (UF) (Zhou & Smith, 2002). Through MF and UF membranes (pore sizes in the range of 0.05 μm to 0.4 μm), complete physical retention of bacterial flocs and confinement of virtually all suspended solids to within the bioreactor can be achieved (Le-Clech et al., 2006).

Conventional wastewater treatment is superseded by MBR treatment attributable to several advantages including smaller footprint, higher effluent quality, good disinfection capability and the capacity for higher volumetric loading rates (Le-Clech et al., 2006). Unfortunately, a major obstacle for the broad application of MBRs is the rapid decline of membrane permeability. More commonly known as membrane fouling, the loss of permeability in conventional MBRs has been extensively reviewed by notable researchers including Judd (2006), Le-Clech et al. (2006) and Drews (2010).

The moving bed biofilm reactor (MBBR) represents a different spectrum in advanced wastewater treatment. MBBRs are operated similarly to the activated sludge process with the addition of freely moving carrier media (Ødegaard, 2006). More specifically, in the MBBR process, biofilm grows attached on small carrier elements suspended in constant
motion throughout the entire volume of the reactor and is constrained to the bioreactor through sieve arrangements at the reactor outlet (Mannina & Viviani, 2009). Advantages of the MBBR process over the conventional activated sludge (CAS) process include better oxygen transfer, shorter hydraulic residence time (HRT), higher organic loading rates, a higher nitrification rate and a larger surface area for mass transfer (Sombatsompop et al., 2006; Chan et al., 2009).

According to Ivanovic & Leiknes (2008) and Ahl et al. (2006) MBBRs can process high organic loading rates at relatively short HRTs (in the range of 4 hours) while producing consistently high quality effluent with respect to BOD, TN and TSS. Ødegaard (2000) reported BOD removal in the range of 95% to 85% for loading rates of 15 g BOD/m²⋅d to 60 g BOD/m²⋅d (roughly equivalent to a volumetric loading rate of 5 kg BOD/m³⋅d to 20 kg BOD/m³⋅d).

Within the MBBR operation there exists three main phases according to Chan et al. (2009): (i) the discrete solid phase of inert carriers with immobilized microbial cells, (ii) the discrete air bubbles and (iii) the continuous aqueous phase. The immobilized microbial cells offer an additional advantage of seamlessly integrated simultaneous nitrification and denitrification (SND) (Yang et al., 2009b). The main physical explanation for SND within microbiological flocs is dissolve oxygen (DO) concentration gradients as a result of diffusion limitations from the aqueous phase into the immobilized biofilm. The aerobic bulk liquid provides an oxidizing environment where soluble BOD is removed and ammonia is nitrified. The nitrite and nitrate produced during nitrification diffuses to the inner parts of the biofilm where there exists an anoxic micro-zone that
harbors heterotrophic denitrifiers which produce nitrogen gas in the traditional manner (Yang et al., 2009b).

Due to the higher loading rates achievable with the MBBR system, smaller footprint bioreactors are often feasible. Unfortunately, the production of filamentous bacteria and poorly settling biomass often hinder solid separation in secondary clarifier operations. According to Ødegaard (2000), settleability of biosolids remains the largest challenge in MBBR design.

Recently proposed, a hybrid membrane and moving bed biofilm reactor process aims to partially mitigate the aforementioned fouling concerns consistent with membranes and the settleability issues consistent with MBBRs. Originally introduced by Leiknes & Ødegaard (2007), the moving bed membrane bioreactor (MBMBR) or the biofilm-MBR (BF-MBR) process has shown good treatment efficiencies with production of consistently high-quality effluent. Comparing with other hybrid membrane bioreactors, an MBMBR could optimistically operate at 10 – 15 times higher volumetric loading at 10 – 30 times shorter HRT (Sombatsompop et al., 2006; Leiknes & Ødegaard, 2007). For visual reference, typical schematics for membrane bioreactor, moving bed biofilm reactor and hybrid moving bed membrane bioreactor processes are presented in Figure 1-1.

Bio-polymeric substances and submicron particles are of paramount concern in the control of long-term irreversible membrane fouling. Successful application of membrane operations in full-scale wastewater treatment is hindered by the costly and energy intensive cleaning processes required for the removal of the aforementioned foulants. Determining the applicability of the MBMBR at controlling these foulants could provide
invaluable strategies for fouling control. Unfortunately research into the feasibility of the MBMBR to mitigate fouling potential has been dominated by synthetic wastewater studies with limited studies using real municipal wastewater. Furthermore, inconsistent results have been presented in terms of major foulant production and the potential reduction of fouling rates in parallel conventional MBR and MBMBR operations.

Figure 1-1 - Typical diagram showing operation of (a) a submerged membrane bioreactor; (b) a moving bed biofilm reactor with solid liquid separation using a clarifier; and (c) a moving bed membrane bioreactor. Wastewater passes from left to right undergoing biological degradation in bioreactors. In moving bed operations, the media fluidizes the reaction tank through force provided by aeration.
The basis of the presented research is to provide a more thorough understanding of moving bed membrane bioreactors in terms of foulant production, system performance and media geometry, material and complexity while operated with real municipal wastewater. A summary of the current state of the literature as well as the contributions from this research is presented in Table 1-1.

**Table 1-1 – Current state of the research for the moving bed membrane bioreactor technology**

<table>
<thead>
<tr>
<th>Hybrid MBBR Membrane Research</th>
<th>Wastewater Type</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Effect of membrane aeration and colloidal fraction on fouling rate</td>
<td>Municipal after primary clarifier (COD: 275 mg/L)</td>
<td>Ivanovic &amp; Leiknes (2008)</td>
</tr>
<tr>
<td>Flocculation zone for submicron particle control installed in membrane tank</td>
<td>Municipal after primary clarifier (COD: 243 - 312 mg/L)</td>
<td>Ivanovic et al. (2008)</td>
</tr>
<tr>
<td>Fouling rate as a function of HRT and particle size distribution</td>
<td>Municipal combined sewer (COD: 242 mg/L)</td>
<td>Leiknes &amp; Ødegaard (2007)</td>
</tr>
<tr>
<td>Optimize relaxation, scouring aeration and UV dose for membrane fouling control</td>
<td>Semi-synthetic food-processing (COD: 480 mg/L)</td>
<td>Phattaranawik et al. (2011)</td>
</tr>
<tr>
<td>Optimized membrane and MBBR compartment aeration rate</td>
<td>Synthetic (COD: 944 mg/L)</td>
<td>Rahimi et al. (2011)</td>
</tr>
<tr>
<td>Fouling mechanisms at varying biomass concentrations</td>
<td>Synthetic (COD: 500 mg/L)</td>
<td>Sombatsompop et al. (2006)</td>
</tr>
<tr>
<td>Salinity effect on fouling propensity</td>
<td>Semi-synthetic shipboard (COD: 259 mg/L)</td>
<td>Sun et al. (2010a)</td>
</tr>
<tr>
<td>Shipboard treatment using dead-end and recycle side-stream configurations</td>
<td>Semi-synthetic shipboard (COD: 209 mg/L)</td>
<td>Sun et al. (2010b)</td>
</tr>
<tr>
<td>Filtration resistance and fouling mechanisms</td>
<td>Synthetic (COD: 800 mg/L)</td>
<td>Yang et al. (2009a)</td>
</tr>
<tr>
<td>Organic carbon and nitrogen removal at various COD/TN ratios</td>
<td>Synthetic (varying COD)</td>
<td>Yang et al. (2009b)</td>
</tr>
<tr>
<td>Organic carbon, nitrogen and phosphorous removal comparing a novel media</td>
<td>Municipal after 1 mm screen (COD: 527 mg/L)</td>
<td>Chapter 2</td>
</tr>
<tr>
<td>Fouling rate as a function of liquid foulants and foulants attached to membrane fibres</td>
<td>Municipal after 1 mm screen (COD: 527 mg/L)</td>
<td>Chapter 3</td>
</tr>
</tbody>
</table>

Logistically, the thesis is presented in manuscript format based on a compilation of two scientific articles. Firstly, a thorough review of the literature is presented to describe the
state-of-the-technology. Chapter 2 contains a scientific article entitled *Operation of two Hybrid Moving Bed Membrane Bioreactors and a Conventional Membrane Bioreactor for Biological Nutrient Removal of Real Municipal Wastewater* which discusses the efficacy of a MBR and two MBMBR systems at removing organic carbon, nitrogenous compounds and phosphorous with further discussion on the performance of the newly developed media as compared to the industry standard finned media. The second scientific article in Chapter 3 is entitled *Comparison of two Hybrid Moving Bed Membrane Bioreactors and a Conventional Membrane Bioreactor for Ultrafiltration Membrane Fouling Control* which discusses the long term fouling propensity, bulk liquid fouling substances and foulants attached to fibres for the three membrane reactors. Since the articles are in publication format, small portions of the literature review are repeated in the two scientific articles. Finally, conclusions from both articles are summarized with their engineering significance discussed in Chapter 4 and references presented in Chapter 5.

**Literature Review**

Moving Bed Bioreactor Technologies in Wastewater Treatment

In an effort to control stricter effluent limits or upgrade existing overloaded activated sludge plants, emerging technologies have been proposed that incorporate attached and suspended biomass to enhance carbon and nitrogen removal in activated sludge basins (Mannina & Viviani, 2009). Commonly, carrier material is incorporated into activated sludge basins and retained through various screen arrangements in the moving bed biofilm reactor (MBBR) process (also known as integrated fixed-film activated sludge
(IFAS) process). The conventional activated sludge wastewater process scheme is virtually unchanged in both systems with primary sedimentation and secondary clarification unchanged. The foremost difference between the MBBR and IFAS systems is the presence of a return activated sludge stream that remains central to the IFAS process. In the MBBR process, biomass is retained in the bioreactor through attachment to suspended carrier material and retention of carrier material using sieves.

Biofilm reactors have been successfully used for treatment of dairy wastewater (Andreottola et al., 2002), landfill leachate (Canziani et al., 2006), petrochemical wastewater (Whang et al., 2009), thermomechanical pulping whitewater (Jahren et al., 2002) and municipal wastewater (Falletti & Conte, 2007; Rusten et al., 1994; Ødegaard, 2006).

Carrier media geometry to promote attached growth has included smooth cylinders (Andreottola et al., 2002; Yang et al., 2010), cylinders with internal crosses and external fins (Ødegaard, 2006), rectangles and cubes (Golla et al., 1994; Valdivia et al., 2007) and spheres (Valdivia et al., 2007). Furthermore, various materials have been employed for biomass support including porous ceramic (Valdivia et al., 2007), reticulated foam (Golla et al., 1994; Valdivia et al., 2007), polyvinyl alcohol (PVA) (Levstek & Plazl, 2009), polyurethane (Ngo et al., 2008; Yang et al., 2006a), plastic foam (Valdivia et al., 2007) and high density polyethylene (Ødegaard, 2006).

Mixed relationships have been presented in the literature in terms of the recommended filling fraction (carrier volume versus total bioreactor volume). Ødegaard (2006) recommends a filling fraction below 70% for cylindrical plastic carriers to allow for
smooth unimpeded suspension of moving bed media. Studies by Di Trapani et al. (2008) and Mannina & Viviani (2009) analyzed the nutrient removing performance of moving bed bioreactors at 33% and 66% filling ratio and noticed little performance variation in terms of wastewater constituent removal. Canziani et al. (2006) successfully used plastic media at a filling fraction of 37.5% for landfill leachate post-denitrification treatment after membrane filtration. For enhanced nitrification/denitrification of a municipal wastewater treatment plant, Falletti & Conte (2007) recommended a 43% filling fraction with plastic cylindrical media. Levstek & Plazl (2009) found similar nitrification rates and required basin volume for plastic cylindrical media at a filling fraction of 37% and for PVA-gel carriers at a filling fraction of 9.6%. This highlights the potential that specific surface area may also be an important design parameter. Xiao & Ganczarczyk (2006) found that at a filling fraction of 70% the attached growth density is 5 to 13 times higher and responds more strongly to COD influent as compared to that of activated sludge flocs found in suspended growth CAS systems. Obviously there exists a large disconnect in the research community concerning media geometry, material and filling fraction. Future research should focus on the effect of these parameters for nutrient removal, microbial biocenosis and fouling propensity in moving bed bioreactors and hybrid membrane processes.

Membrane Technologies in Wastewater

Applications of membrane processes for the treatment of municipal wastewater, industrial wastewater including food-processing waste, slaughterhouse wastewater and landfill leachates have been well documented in the literature (Yang et al., 2006b). MBR processes have been favoured for industrial wastewater treatment due to the tolerance to
high pollutant loading and relatively small footprint. For municipal wastewater treatment, hybrid membrane processes become economically attractive when compact technology is required to accommodate space constraints or stringent effluent quality requirements are mandatory (Yang et al., 2006b). More widespread use of membrane processes has been limited due to the fouling propensity and energy requirements for recirculating mixed liquor and air scrubbing (Zhou & Smith, 2002).

Mechanisms of Fouling

Sombatsompop et al. (2006) reported the causes of fouling in MBRs to be sludge particle deposition on membrane surfaces, adhesion of macromolecules such as extracellular polymeric substances (EPS) and soluble microbial products (SMP) and pore clogging due to the submicron particles. In an extensive review of the state-of-the-technology, Le-Clech et al. (2006) confirmed these foulants and added a temporal component to define the progression of membrane fouling. Under constant flux conditions a three stage fouling process is observed; stage 1 - conditional fouling, stage 2 - steady fouling and stage 3 - transmembrane pressure (TMP) jump.

Stage 1 fouling is initiated through strong interactions between the membrane surface and the EPS present in the mixed liquor. Even in the absence of convection (i.e., zero flux conditions), Zhang et al. (2006) observed passive adsorption of colloids and organics onto the membrane surface. Under normal operation, crossflow conditions are capable of removing the biomass, however a residual footprint of small flocs or EPS still remains on the membrane surface. This footprint lays the foundation for further irreversible
attachment of larger bioflocs and colonization of the membrane leading to stage 2 fouling (Zhang et al., 2006).

Modest operation of membranes between the critical flux and sustainable flux is widely accepted as a method to achieve sustainable filtration while maintaining the permeate flux as high as possible (Nywening & Zhou, 2009). Although even in MBRs operated below the critical flux bioflocs may still randomly land and contribute to the stage 2 fouling (Le-Clech et al., 2006). As a consequence of stage 1, the membrane surface is mostly covered by polymeric substances, leading to a higher propensity for attachment of biomass particles and colloids (Zhang et al., 2006). Cake formation occurs as adsorption of organics begins to occur on the surface and within the pores of the membrane. The cake formation may develop without effecting permeability of the membrane, however over time biological flocs agglomerate and block pores leading to subsequently stage 3 fouling (Le-Clech et al., 2006).

During stage 3 fouling, localized regions fouled more than others are expected to experience a significant decrease in flux. Under constant TMP operation, this fouling leads to a decline in production. However, operation at constant flux yields localized regions of high flux through less fouled pores. The localized increase in flux exceeds the sustainable flux and a self-accelerating process of exponential TMP growth occurs (Cho & Fane, 2002; Le-Clech et al., 2006; Nywening & Zhou, 2009). An illustration of this occurrence is presented in Figure 1-2.

Once a critical TMP has been reached, cleaning processes will be attempted to remove foulants accumulated during the stages of fouling. A portion of the foulants can be
removed through physical cleaning methods such as membrane relaxation, air scouring and backwash. This fraction of membrane foulants is categorized as reversible fouling (Judd, 2006). A more tightly integrated fraction referred to as long-term foulants (categorized as irreversible fouling) requires chemical cleaning for removal (Drews, 2010). A final fraction categorized as irrecoverable fouling cannot be removed by any cleaning and occurs over long periods of time. As later discussed, it is the long-term foulants that most dramatically affect membrane operations.

Figure 1-2 - Illustration of the exponential growth of TMP after sustainable flux is exceeded (Nywening & Zhou, 2009)
Foulants of Concern

*Colloidal and Submicron Particles*

It is well documented in the literature that there exists a strong correlation between submicron particles and fouling in hybrid membrane operations (Chang *et al.*, 2002; Defrance *et al.*, 2000; Le-Clech *et al.*, 2006; Leiknes *et al.*, 2006). However, the relative degree of fouling associated with the colloidal and submicron range is undefined. Defrance *et al.* (2000) reported that the relative contributions of suspended solids, colloids, and dissolved matter to filtration resistance caused by fouling were 65%, 30%, and 5%, respectively. The same study reported by Chang *et al.* (2002) revealed relative contribution on fouling to be 24%, 50%, and 26% for suspended solids, colloids, and solutes, respectively. Fan *et al.* (2006) found that fouling was controlled almost exclusively by colloidal total organic carbon (TOC) and MLSS was shown to have little impact. Le-Clech *et al.* (2006) reports a more broad range from 17% to 81% for the contributions of soluble and colloids to overall membrane fouling.

To further exasperate the discrepancies, the incorporation of a biofilm and a varying concentration of MLSS in the MBBR facilitate comparisons with conventional MBRs more difficult. Systems operating at high MLSS concentrations have been shown to produce a cake layer that shields the membrane surface from direct attachment of foulants. Lee *et al.* (2001) identified the phenomena as dynamic membrane formation and explained its importance in suspended growth processes. The researchers reported a 7 times higher fouling rate (presumably associated with long-term foulants) for biofilm operations with attached biomass as compared to suspended biomass. The increased
fouling propensity was defined by the lack of dynamic membrane formation in attached growth systems operating with lower suspended solids concentrations. A conceptual illustration of the membrane fouling is presented in Figure 1-3 for both attached growth and suspended growth bioreactors.

![Illustration of the protection mechanism of the dynamic membrane (Lee et al., 2001)](image)

**Figure 1-3 - Illustration of the protection mechanism of the dynamic membrane (Lee et al., 2001)**

In a study comparing fouling mechanisms in conventional MBR and MBMBR operation, Sombatsompop *et al.* (2006) concluded that membrane fouling was controlled by physical characteristics of the biomass (particle size distribution). The study was unable to link membrane fouling to biological characteristics such as bound and soluble EPS. Operation of the MBMBR at steady state yielded higher fractions of colloidal (<5 μm) particles and lower mean particle sizes as compared to the conventional MBR. Strangely however, results from Sombatsompop *et al.* (2006) indicated that MBMBRs operating parallel to conventional MBRs developed less fouling even though EPS concentrations were similar and there was an increased presence of submicron particles in the MBMBR. Sombatsompop *et al.* (2006) alluded to the fact that the presence of smaller particles improved the porosity and reduced the thickness of the cake layer. Moreover, the reduced cake layer thickness produced a lower specific cake layer resistance according to the
Kozeny-Carman relationship. Interestingly, fouling resistance caused by solute adsorption into the membrane pore measured using chemical cleaning was higher in the MBMBR system as compared to the MBR. This would indicate that although short-term fouling due to cake layer development was higher in the MBR, the MBMBR has a higher propensity for long-term fouling. This was confirmed by the Lee et al. (2001) study that compared attached growth fouling to suspended growth fouling. Although the attached growth system produced lower cake layer resistance compared to suspended growth, resistance due to fouling was considerably higher in the attached growth system.

A study by Huang et al. (2008) revealed that suspended carriers had two effects on membrane fouling: one was the positive effect of mechanical scouring induced on the membrane surface when carriers were allowed to interact with membrane fibres and the second was the negative effect of breaking up the sludge floc. Huang and co-workers found that suspended carrier filling fractions as low as 5% had a dramatic affect on particle size distribution and as well the EPS and supernatant TOC concentrations. In two parallel operated MBRs one without carriers and one with carriers, both with a MLSS concentration of 5 g/L, the median diameter of mixed liquor without suspended carriers was approximately 95 μm, whereas with a carrier dose of 5% the median diameter of mixed liquor decreased to 68.3 μm after 72 hours of operation. This occurrence indicates that the circulating suspended carriers disrupt the suspended biomass and continuously fragment flocculating sludge (Huang et al., 2008). The effect of shifting particle size diameter towards the macromolecule range caused more particles to deposit on the membrane surface therefore increasing the rate of TMP rise and decreasing the critical flux value. Ahl et al. (2006) and Melin et al. (2005) reported similar shifts in mean
particle size towards smaller particles associated with a decreasing HRT in MBBR operations. The foregoing researchers also noted an increased fouling rate associated with a shift towards smaller particles. This phenomenon can be described by the critical flux or the inertial lift theory as later discussed (AWWA, 1996; Huang et al., 2008).

In a critical flux model developed by Vigneswaran et al. (2000) using crossflow MF for separation of uniform polystyrene latex particles, critical flux values decreased sharply to a minimum flux that corresponded with a 0.45 μm particle size and then increased with increasing particle size thereafter. According to the inertial lift theory, particle transport is governed by two opposing forces: permeation drag force (permeation flux) and lateral inertial lift force. The former moves particles towards the membrane whereas the later shifts particles away from the membrane. While in equilibrium (i.e., the permeation flux equals the inertial lift velocity) the particles are in a balanced state and no deposition on the membrane occurs. When permeation drag force is greater than the lateral inertial lift force, particle deposition and membrane fouling occurs. Alternatively, when permeation drag force is less than the lateral inertial lift force particle deposition does not occur. At the minimum critical flux value, the total lift force represented by the summation of shear induced, lateral migration and Brownian diffusion is at a minimum and particle deposition leading to membrane fouling occurs (Vigneswaran et al., 2000). This is explained by the fact that filtration of particles below a size range of several tenths of a micrometer is more strongly affected by Brownian force whereas above this range shear induced forces prevail (AWWA, 1996).

In other work done by Leiknes et al. (2006) particle size distribution (PSD) revealed that submicron particles can be well correlated to membrane fouling rate in MBMBR.
Leiknes and co-workers found that when the differential number percentage of submicron particles is high an increase in the membrane fouling rate was observed. Similar work by Defrance et al. (2000) concluded that membrane permeability was decreased with filtration of smaller flocs in the colloidal range. These results are supported by Huang et al. (2008) who reported lower critical flux with decreasing particle size but contradicts results previously presented by Sombatsompon et al. (2006) that reported improved permeability in MBMBR operation.

Melin et al. (2005) investigated the effect of loading rate on particle size and subsequently fouling potential. A clear shift towards smaller particles was exhibited in systems operating at high loading rates (lower HRTs). In high-rate systems (HRT < 1 hr), 10% of the particles were within the submicron range (0.1 – 1 μm). Conversely, low-rate operation (HRT > 3 hr) produced 3% of particles in the submicron range. As a result the initial TMP development in the high-rate system was much more rapid than that of the low-rate operation. This occurrence is synonymous with the hypothesis of AWWA (1996) and Vigneswaran et al. (2000) who reported particles in the tenth of a micron range to adversely affect membrane permeability.

Oddly, in the experiments of Melin and co-workers the TMPs of each production cycle were in the same range towards the end of the experiment. Interestingly, the initial TMP after backpulse was lower in low-rate operation as compared to the high-rate system suggesting that the submicron particles may lead to issues with long-term fouling (Melin et al., 2005). Le-Clech et al. (2006) confirms that colloidal materials are partially responsible for the irreversible pore blockage of the membrane. The deposition of organic and inorganic materials into the membrane pores is the main cause of poor long-term
performances and irreversible fouling. Unfortunately, in the study by Melin and co-workers long term operation of the membrane was not achieved and therefore definite confirmation of this hypothesis is impossible.

*Integrated Flocculation Zone for Enhanced Particle Coagulation*

Several authors (Leiknes *et al.*, 2006; Ji & Zhou, 2006; Ivanovic *et al.*, 2008) have investigated the potential of an integrated flocculation zone to enhance submicron particle coagulation. The flocculation zone or floc-zone is typically installed between the MBBR effluent and membrane basin influent; however Ivanovic *et al.* (2008) integrated a floc-zone by extending the bottom of the membrane tank and placing the inlet to the membrane tank under the membrane aeration system.

In parallel operation of MBMBRs with and without floc-zones, Leiknes *et al.* (2006) observed a direct link between a decrease in the differential number percentage of submicron particles and a decrease in the membrane fouling rate. Furthermore, operation with a floc-zone achieved lower submicron particle concentration around the membrane, better solids settling and better dewatering characteristics.

In a similar study by Ivanovic *et al.* (2008), integration of a floc-zone into a ZW-10 submerged module reduced the submicron particles around the membrane from 8.2% to 6.9% (as differential number percentage). Also, the size of the most abundant particle fraction increased from 0.70 μm to 0.84 μm. Moreover, operation with floc-zone was capable of 16 days of operation before 0.45 bar TMP was achieved whereas operation without floc-zone reached 0.45 bar TMP after 12 days. In the study by Ivanovic and co-workers, short term fouling was controlled with continuous air scouring and temporal
backwashing. Therefore increase in production longevity can be predominantly associated with long-term fouling prevention.

Many authors agree that fouling in MBMBR systems is controlled by the submicron particles (Leiknes et al., 2006; Leiknes & Ødegaard, 2007; Ivanovic et al., 2006). Furthermore, it is accepted that the MBMBR as compared to the conventional MBR may shift the particle differential number percentage towards the submicron range (Leiknes et al., 2006; Sombatsompop et al., 2006). Therefore, for the range of the literature examined it can be concluded that the MBMBR generates a higher degree of fouling associated with submicron particles than does the conventional MBR.

**Bio-Polymeric Substances**

Bio-polymeric substances found within wastewater bioreactors can be mainly differentiated into two categories, bound EPS extracted artificially from the biological cell floc and soluble EPS present in the supernatant not associated with the cell (Le-Clech et al., 2006). EPS consist of a wide range of molecular weight species with a high concentration of small hydrophilic aromatic compounds. SMP are generally larger macromolecules with the majority of molecular weight bands within the range of >5 kDa, 3 – 4 kDa and 0.5 – 1 kDa (Brookes et al., 2003). For the purpose of this review, the bound EPS is referred to simply as EPS and the soluble fraction is referred to as SMP.

The products of cell lysis and hydrolysis naturally secreted by the bacteria and related to EPS are polysaccharides, lipids, proteins, humic substances and nucleic acids (Laspidou & Rittmann, 2002). Conversely, SMP are the soluble cellular components released by the cell during cell synthesis, cell lysis or excreted for some purpose and most notably
reported by the relative concentration of proteins, carbohydrates or more rarely polysaccharides contained within the reactor supernatant. To distinguish between the protein and carbohydrate products, EPS and SMP are herein referred to as protein extracellular polymeric substances (EPSp), carbohydrate extracellular polymeric substances (EPSc), protein soluble microbial products (SMPp) and carbohydrate soluble microbial products (SMPc).

It is well founded that TOC in the biomass supernatant (i.e., SMP) has a deleterious effect on membrane fouling. Ng et al. (2005) operated a dual compartment MBR pilot plant in which biomass was pre-settled before membrane filtration and found that a higher filtration resistance occurred while filtering supernatant as compared to filtration of mixed liquor with 4 g/L SS. This supports the conclusion that macromolecule substances in the supernatant have a more significant contribution to membrane fouling and lower TOC concentration in the supernatant could alleviate fouling propensity. This same hypothesis is confirmed by Lee et al. (2001) in which the formation of a dynamic membrane at higher levels of MLSS shielded the membrane from adsorption of SMP onto the surface of the membrane and gel formation leading to fouling. Since the dynamic layer contains bioactive organisms and the soluble components are themselves biodegradable it is not unfathomable that the dynamic layer formation may consume the soluble foulants further preventing permeability decline (Brookes et al., 2003).

In MBMBR operation, Huang et al. (2008) reported that one effect of carrier material was the destruction of biomass and bound EPS and the formation of biomass-associated products (BAP). A suspended carrier dose of 5% reduced EPSp and EPSc concentrations from 24.2 mg/g SS and 16.6 mg/g SS to 14.0 mg/g SS and 12.3 mg/g SS respectively.
Furthermore, the supernatant TOC as dissolved organic carbon (DOC) and colloidal organic carbon (COC) increased from 6.0 mg/L and 4.6 mg/L to 11.8 mg/L and 33.1 mg/L respectively. Huang et al. (2008) reasons that EPS were released and converted into supernatant TOC when sludge flocs were broken up by the suspended carriers. Effluent TOC from biological treatment processes is ubiquitously present and usually consists of primarily SMP. Therefore supernatant TOC is a suitable surrogate for SMP concentration (Laspidou & Rittmann, 2002). In research by Huang and co-workers, supernatant TOC was the dominant substance responsible for gel layer formation and membrane pore blockage. Therefore, an increase in supernatant TOC has a negative effect on membrane fouling. At lower carrier media dosages (1% filling fraction) the increase in supernatant TOC was weak; roughly 30% as compared to 325% at filling fractions of 5%. Although this reactor cannot accurately represent a pure biofilm-MBR, the relationship between carrier material and microbial colonies that are presented are still applicable.

Other articles have highlighted the importance of EPS and SMP control as a means to prevent long-term membrane fouling (Zhang et al., 2006; Meng et al., 2009; Wang et al., 2009; Farquharson & Zhou, 2010). Furthermore, certain studies have made efforts to compare the production of EPS and SMP in parallel conventional MBR and MBMBR operation. Table 1-2 and Table 1-3 present EPS and SMP concentrations from various MBR and MBMBR set-ups respectively. Parallel operation of MBMBR and MBR are directly compared in Figure 1-4 and Figure 1-5 for EPS and SMP respectively.
Figure 1-4 - Comparison of EPS concentrations in studies with MBMBRs operating parallel to MBRs

Figure 1-5 - Comparison of SMP concentrations in studies with MBMBRs operating parallel to MBRs (‡ Fixed carrier attached growth system)
<table>
<thead>
<tr>
<th>EPSp (mg/g SS)</th>
<th>EPSc (mg/g SS)</th>
<th>SMPp (mg/L)</th>
<th>SMPc (mg/L)</th>
<th>Other</th>
<th>Extraction Method</th>
<th>Details</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>-</td>
<td>0.84</td>
<td>1.7*</td>
<td>TOC: 5.9 mg C/L</td>
<td>SMPC: phenol-sulpheric acid (std. glucose) SMPP: Spectrophotometric (std. BSA)</td>
<td>MLSS: 3,000 mg/L Synthetic wastewater</td>
<td>Lee, Ahn &amp; Lee (2001)</td>
</tr>
<tr>
<td>59.5</td>
<td>24.3</td>
<td>3.3</td>
<td>12.9</td>
<td>Avg Particle: 226 μm $\mu_{mud}$: 244 mPa s</td>
<td>EPS extraction: Heating method SMPC: phenolic-sulpheric acid (std. glucose) SMPP: Lowry method (std. BSA)</td>
<td>MLSS: 6,000 mg/L HRT: 2 hr Synthetic wastewater</td>
<td>Sombatsompop et al. (2006)</td>
</tr>
<tr>
<td>68.2</td>
<td>29</td>
<td>4</td>
<td>7.4</td>
<td>Avg Particle: 116 μm $\mu_{mud}$: 970 mPa s</td>
<td>EPS extraction: Heating method SMPC: phenolic-sulpheric acid (std. glucose) SMPP: Lowry method (std. BSA)</td>
<td>MLSS: 10,000 mg/L HRT: 2 hr Synthetic wastewater</td>
<td>Sombatsompop et al. (2006)</td>
</tr>
<tr>
<td>22.6</td>
<td>7.9</td>
<td>-</td>
<td>-</td>
<td>Viscosity: 1.9 mPa s</td>
<td>EPS extraction: Cation ion exchange resin</td>
<td>MLSS: 8,750 mg/L Synthetic wastewater</td>
<td>Yang, Yang, Fu, &amp; Lei (2009)</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>18.2</td>
<td>10.1</td>
<td>TOC$<em>{filter}$: 7.5 mg C/L TOC$</em>{unfilter}$: 7.9 mg C/L</td>
<td>SMPC: Anthrone method (std. glucose) SMPP: Lowry method (std. BSA)</td>
<td>MLSS: 3,000 mg/L HRT: 12 hr &amp; SRT: 15 d Synthetic wastewater</td>
<td>Ng et al. (2010)</td>
</tr>
<tr>
<td>100.9 ± 21</td>
<td>24.1 ± 2.8</td>
<td>6 ± 2.2</td>
<td>4.5 ± 0.9</td>
<td>pol: 627 ± 43 mg/ gSS</td>
<td>EPS extraction formaldehyde-NaOH method SMPC: anthrone method (std. glucose) SMPP: corrected Lowry method (std. BSA) pol: formaldehyde-NaOH method</td>
<td>MLSS: ~3,250 mg/L HRT: 11.3 hr &amp; SRT: 20 d J: 8 LMH &amp; AR: 120 L/hr Synthetic wastewater</td>
<td>Ji &amp; Zhou (2006)</td>
</tr>
<tr>
<td>116.1 ± 13</td>
<td>21.9 ± 2.7</td>
<td>4.5 ± 2.5</td>
<td>4.2 ± 1.9</td>
<td>pol: 680 ± 44 mg/ gSS</td>
<td>EPS extraction formaldehyde-NaOH method SMPC: anthrone method (std. glucose) SMPP: corrected Lowry method (std. BSA) pol: formaldehyde-NaOH method</td>
<td>MLSS: ~2,750 mg/L HRT: 11.3 hr &amp; SRT: 20 d J: 8 LMH &amp; AR: 80 L/hr Synthetic wastewater</td>
<td>Ji &amp; Zhou (2006)</td>
</tr>
<tr>
<td>105.6 ± 30</td>
<td>22.0 ± 3.5</td>
<td>4.4 ± 2.0</td>
<td>3.7 ± 1.0</td>
<td>pol: 701 ± 94 mg/ gSS</td>
<td>EPS extraction formaldehyde-NaOH method SMPC: anthrone method (std. glucose) SMPP: corrected Lowry method (std. BSA) pol: formaldehyde-NaOH method</td>
<td>MLSS: ~1,800 mg/L HRT: 11.3 hr &amp; SRT: 20 d J: 8 LMH &amp; AR: 40 L/hr Synthetic wastewater</td>
<td>Ji &amp; Zhou (2006)</td>
</tr>
<tr>
<td>25-30</td>
<td>7-8</td>
<td>8</td>
<td>25</td>
<td>Humic EPS: 12-13 Humic SMP: 36</td>
<td>-</td>
<td>SRT: 10 d Real wastewater</td>
<td>La-Clech et al. (2006)</td>
</tr>
</tbody>
</table>

BAS - bovine serum albumin, std. - substance used for standard, $\mu_{mud}$ - Sludge Viscosity, AR - aeration rate, pol - Sum of the Polymers (proteins & carbohydrates) in cell floc

* Reported as polysaccharides
<table>
<thead>
<tr>
<th>EPS&lt;sub&gt;p&lt;/sub&gt; (mg/g SS)</th>
<th>EPS&lt;sub&gt;c&lt;/sub&gt; (mg/g SS)</th>
<th>SMP&lt;sub&gt;p&lt;/sub&gt; (mg/L)</th>
<th>SMP&lt;sub&gt;c&lt;/sub&gt; (mg/L)</th>
<th>Other</th>
<th>Extraction and Analysis Method</th>
<th>Details</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>_</td>
<td>_</td>
<td>18.83</td>
<td>12.33</td>
<td>Oil: 4.15 mg/L FCOD: 75 mg/L</td>
<td>SMP&lt;sub&gt;c&lt;/sub&gt;: phenol-sulpheric acid (std. glucose)</td>
<td>Dead-end side-stream MLSS: 20-200 mg/L HRT: 4 hr Shipboard wastewater</td>
<td>Sun et al. (2010)</td>
</tr>
<tr>
<td>_</td>
<td>_</td>
<td>12.45</td>
<td>10.19</td>
<td>Oil: 1.04 mg/L FCOD: 52 mg/L</td>
<td>SMP&lt;sub&gt;c&lt;/sub&gt;: phenol-sulpheric acid (std. glucose) SMP&lt;sub&gt;p&lt;/sub&gt;: Foline method (std. BSA)</td>
<td>Recycle side-stream HRT: 4 hr MLSS: 20-200 mg/L Shipboard wastewater</td>
<td>Sun et al. (2010)</td>
</tr>
<tr>
<td>_</td>
<td>_</td>
<td>0.75</td>
<td>1.65&lt;sup&gt;*&lt;/sup&gt;</td>
<td>TOC: 5.4 mg C/L</td>
<td>SMP&lt;sub&gt;c&lt;/sub&gt;: phenol-sulpheric acid (std. glucose)</td>
<td>MLSS: 100 mg/L</td>
<td>Lee, Ahn &amp; Lee (2001)</td>
</tr>
<tr>
<td>90</td>
<td>124*</td>
<td>_</td>
<td>_</td>
<td>Avg Particle: 50 μm</td>
<td>EPS extraction: Heating method SMP&lt;sub&gt;c&lt;/sub&gt;: phenol-sulpheric acid (std. glucose) SMP&lt;sub&gt;p&lt;/sub&gt;: Lowry method (std. BSA)</td>
<td>MLSS: 5,000 mg/L Biomass: 17,000 mg/L HRT: 10 hr &amp; SRT: 10 d Synthetic wastewater</td>
<td>Lee, Kang &amp; Lee (2006)</td>
</tr>
<tr>
<td>_</td>
<td>_</td>
<td>4.1</td>
<td>4.3</td>
<td>TOC&lt;sub&gt;filter&lt;/sub&gt;: 3.0 mg C/L TOC&lt;sub&gt;biofilter&lt;/sub&gt;: 3.3 mg C/L</td>
<td>SMP&lt;sub&gt;c&lt;/sub&gt;: Anthrone method (std. glucose) SMP&lt;sub&gt;p&lt;/sub&gt;: Lowry method (std. BSA)</td>
<td>Biomass: 11,000 mg/L HRT: 12 hr &amp; SRT: 300 d Synthetic wastewater</td>
<td>Ng et al. (2010)&lt;sup&gt;†&lt;/sup&gt;</td>
</tr>
<tr>
<td>62.3</td>
<td>19.7</td>
<td>2.2</td>
<td>11.7</td>
<td>Avg Particle: 33 μm μ&lt;sub&gt;sludge&lt;/sub&gt;: 277 mPa s</td>
<td>EPS extraction: Heating method SMP&lt;sub&gt;c&lt;/sub&gt;: phenolic-sulpheric acid (std. glucose) SMP&lt;sub&gt;p&lt;/sub&gt;: Lowry method (std. BSA)</td>
<td>MLSS: 6,000 mg/L HRT: 2 hr Synthetic wastewater</td>
<td>Sombatsompop et al. (2006)</td>
</tr>
<tr>
<td>78.7</td>
<td>31.9</td>
<td>7.7</td>
<td>7.6</td>
<td>Avg Particle: 27 μm μ&lt;sub&gt;sludge&lt;/sub&gt;: 705 mPa s</td>
<td>EPS extraction: Heating method SMP&lt;sub&gt;c&lt;/sub&gt;: phenolic-sulpheric acid (std. glucose) SMP&lt;sub&gt;p&lt;/sub&gt;: Lowry method (std. BSA)</td>
<td>MLSS: 10,000 mg/L HRT: 2 hr Synthetic wastewater</td>
<td>Sombatsompop et al. (2006)</td>
</tr>
<tr>
<td>76.7</td>
<td>19.8</td>
<td>_</td>
<td>_</td>
<td>μ&lt;sub&gt;sludge&lt;/sub&gt;: 3.6 mPa s</td>
<td>EPS extraction: Cation ion exchange resin</td>
<td>MLSS: 4,030 mg/L Biomass: 1,030 mg/L Synthetic wastewater</td>
<td>Yang, Yang, Fu, &amp; Lei (2009)</td>
</tr>
</tbody>
</table>

<sup>BAS</sup> - bovine serum albumin, <sup>stdn.</sup> - substance used for standard, μ<sub>sludge</sub> - Sludge Viscosity

<sup>*</sup> Reported as polysaccharides

<sup>†</sup> Fixed carrier biological system
With regard to Figure 1-4, when comparing results from MBMBR and MBR, observed differences for EPSp, EPSc, SMPp and SMPc in MBMBR and MBR were found not to be statistically significant at the 95% confidence level using the paired t-test. This would indicate that EPS and SMP are not a major source of variation between MBMBR and MBR processes. A caveat to these conclusions is that synthetic wastewater was used in the aforementioned studies. Le-Clech et al. (2006) alludes to the reduction in SMP and EPS formation in systems operating with synthetic wastewater. Furthermore, complex bio-polymeric conjugates present in real wastewater influent are poorly synthesized by a glucose surrogate. Cho et al. (2005) concluded that fouling in MBRs fed with synthetic wastewater was affected more by the bound EPS of the sludge floc rather than the dissolved organic matter. SUVA measurements of supernatant fed with synthetic wastewater confirmed the presence of a portion of larger, more aromatic, more hydrophobic, double-bond-rich organics, which originate from the decayed biomass rather than the feed (Le-Clech et al., 2006). This confirms that there are minimal substrate residuals from glucose biodegradation and the majority of SMP measured in synthetic wastewater based supernatant is the result of cell lysis or cell release alone; described by Laspidou & Rittmann (2002) as biomass-associated products (BAP) or utilization associated products (UAP). Therefore, to authenticate comparisons between MBMBR and conventional MBR in terms of bio-polymeric substances real wastewater studies are required.

With regard to Table 1-2, the range of EPSp for the MBR system is between 22.6 mg/g SS and 116.1 mg/g SS. In terms of EPSc, the range is 7 mg/g SS and 24.3 mg/g SS for the MBR system. The EPSp concentration was consistently larger than EPSc
concentration for the results studied. The range of SMP for MBR systems has also been presented in Table 1-2; SMPp is within the range of 0.84 mg/L and 18.2 mg/L, while SMPP is within a range of 1.7 mg/L and 25 mg/L.

Table 1-3 presents the range of EPSp, EPSc, SMPp and SMPc for MBMBR systems. The reported minima and maxima concentrations for EPSp are 62.3 mg/g SS and 90 mg/g SS respectively; whereas the minima and maxima for EPSc are 19.7 mg/g SS and 124 mg/g SS respectively. Similarly to MBR, in most cases the EPSp concentration was greater than EPSc; this pattern was also confirmed by Le-Clech et al (2006) for a range of MBR set-ups. In terms of SMPp, the range is 2.2 mg/L to 18.8 mg/L; whereas the range for SMPc is 1.7 mg/L to 12.3 mg/L.

It is difficult to draw parallels between various MBR and MBMBR set-ups due to the inherent variability in the operation details and extraction methods. A potential method for broad comparison between membrane operations is the protein/carbohydrate (P/C) ratio. In a comprehensive study using synthetic wastewater with varying influent EPSp and EPSc ratios, Arabi & Nakhla (2008) found that fouling increased with increasing P/C ratios. Within the biomass concentration range studied of 5,200 – 6,100 mg/L, membrane fouling rate increased with increasing P/C ratio in the influent. The highest membrane permeability was achieved at a P/C ratio of 2/1 and the lowest at a P/C ratio of 8/1 (Arabi & Nakhla, 2008). Although the influent ratios were not strictly conserved through to the bulk MBR liquid the general trend was. Arabi & Nakhla (2008) observed decreased permeability at increasing P/C ratios within the MBR supernatant.
The average paired P/C ratio for conventional MBR and MBMBR systems presented in Table 1-2 and Table 1-3 are 3.5/1 and 2.5/1 respectively. With reference to results from Arabi & Nakhla (2008), these ratios would suggest that the MBMBR is less prone to EPS fouling as compared to conventional MBRs (CMBRs). Therefore, the EPS P/C ratio is either not relevant to MBMBR membrane fouling or the dominant mechanism of MBMBR fouling is not EPS and more likely related to the concentration of soluble microbial products in the sludge supernatant. Further research should focus on membrane fouling as a function of P/C ratio in MBMBRs to conclude whether extrapolation of Arabi & Nakhla (2008) results is appropriate.

<table>
<thead>
<tr>
<th>MBMBR P/C Ratio</th>
<th>CMBR P/C Ratio</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.2</td>
<td>2.4</td>
<td>Sombatsompop et al. (2006)</td>
</tr>
<tr>
<td>2.5</td>
<td>2.4</td>
<td>Sombatsompop et al. (2006)</td>
</tr>
<tr>
<td>3.9</td>
<td>2.9</td>
<td>Yang et al. (2009a)</td>
</tr>
</tbody>
</table>

Further mixed results are presented in Table 1-4 for P/C ratios. Consistently the MBMBR has a higher P/C ratio as compared to a parallel operated CMBR. However, Sombatsompop et al. (2006) reported a lower fouling propensity in the MBMBR whereas Yang et al. (2009a) reported a higher fouling propensity in the MBMBR. This further confirms the fact that either the P/C ratio is not relevant to MBMBR membrane fouling or the dominant mechanism of MBMBR fouling is not EPS.

A more broad approach in qualitatively describing the presence of EPS and SMP is the use of the mean oxidation state of the organic carbon (MOC). Originally presented by
Stumm & Morgan (1981) for surface water analysis, in which COD is expressed in mol O\textsubscript{2} \cdot liter\textsuperscript{-1} and TOC in mol C \cdot liter\textsuperscript{-1}.

\[
MOC = \frac{4(TOC - COD)}{TOC}
\]

Wang et al. (2009) found that the major components of the bound EPS was proteins and carbohydrates from the estimation protocol reported by Stumm & Morgan (1981). Wang and co-workers confirmed the estimation of EPS components based on MOC analysis was consistent with the composition quantification results obtained through the phenol-sulfuric acid method (Dubois et al., 1956), the modified Lowry method (Hartree, 1972) and Fourier transform infrared (FT-IR) spectroscopy (Maruyama et al., 2001) and was observed to have a positive correlations with membrane fouling.

Lee et al. (2001) compared attached growth reactors and suspended growth reactors in terms of MOC in the mixed liquor and on the membrane surface. Qualitatively, the mixed liquor was shown to contain mainly organic acids from metabolic by-products or end products of biodegradation. The membrane fibres were found to be covered by proteins and polysaccharides due to their hydrophobic interactions. Quantitative analysis for proteins using Coomassie brilliant blue dye-binding method with BSA as the standard (Holme & Pect, 1998) and for polysaccharides using phenol-sulfuric acid method (Dubois et al., 1956) verified the presence of the aforementioned substances. Lee and co-workers were unable to find a correlation between MOC and fouling and rather found that decreasing MLSS concentrations caused an increasing fouling rate.
**Abbreviations**

- ATR – attenuated total reflectance;
- BOD – biochemical oxygen demand;
- BSA – bovine serum albumin;
- CLSM – confocal laser scanning microscopy;
- COD – chemical oxygen demand;
- DIC – dissolved inorganic carbon;
- DO – dissolved oxygen;
- DOC – dissolved organic carbon;
- DSVI – diluted sludge volume index;
- EPS – extracellular polymeric substances;
- FT-IR – Fourier transform infrared;
- HRT – hydraulic retention time;
- IC – inorganic carbon;
- MBBR – moving bed bioreactor;
- MBMBBR – moving bed membrane bioreactor;
- MBR – membrane bioreactor;
- MF – microfiltration;
- MLSS – mixed liquor suspended solids;
- MLVSS – mixed liquor volatile suspended solids;
- MOC – mean oxidation state of the organic carbon;
- pCOD – particulate chemical oxygen demand;
• sBOD – soluble biochemical oxygen demand;
• sCOD – soluble chemical oxygen demand;
• SMP – soluble microbial products;
• SRT – sludge residence time;
• SS – suspended solids;
• SVI – sludge volume index;
• TMP – transmembrane pressure;
• TN – total nitrogen;
• TOC – total organic carbon;
• TP – total phosphorous;
• TSS – total suspended solids;
• TTF – time to filter;
• UF – ultrafiltration;
• VSS – volatile suspended solids.
Chapter 2 Operation of two Hybrid Moving Bed Membrane Bioreactors and a Conventional Membrane Bioreactor for Biological Nutrient Removal of Real Municipal Wastewater

Abstract

A conventional membrane bioreactor (MBR) and two hybrid moving bed membrane bioreactors (MBMBR) using submerged solid liquid separation were tested for municipal wastewater treatment and biological nutrient removal. Unique to this study was the advent of a novel biofilm carrier that incorporated a high porosity fibrous packing inside a spherical high density polyethylene carrier. To test the validity of the media against another carrier, the industry standard finned cylindrical media was used as a control MBMBR system. To investigate biofilm growth as a function of media size three spherical diameters were developed; 21 mm, 27 mm and 33 mm. Preliminary results for the range tested indicates that the 21 mm media has the highest capacity to accumulate biomass with 47% of the available volume colonized by biomass, whereas a standard finned cylindrical media only capitalized on 18% of available volume and the 27 mm spherical and 33 mm spherical both colonized 28% of available volume. In addition to media performance, the three bioreactors were assessed by analyzing mixed liquor suspended solids (MLSS), mixed liquor volatile suspended solids (MLVSS), attached biomass, biochemical oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC), total nitrogen (TN), ammonia nitrogen, nitrate nitrogen and total phosphorous. Organic carbon removal was consistent in all three reactors with average BOD and COD removal exceeding 98% and 94% respectively. Preliminary biological
nutrient removal results indicate that nitrogen compounds were superiorly removed in the MBMBR systems when compared to the MBR system due to the attached growth denitrification.

**Keywords:** moving bed bioreactor (MBBR); moving bed membrane bioreactor (MBMBR); membrane bioreactor (MBR); nutrient removal; wastewater; biofilm; carrier.

**Introduction**

Increasing pressure exerted on watersheds from the proliferation of eutrophication caused by enrichment from anthropological nutrient inputs coupled with the increasing demand for safe drinking water supplies has invigorated the need to protect marine ecosystems. As a result of nitrogen and phosphorous overenrichment, hypoxia in coastal marine ecosystems where dissolved oxygen (DO) falls below 2 mg/L has been reported in more than 400 systems globally including the Black Sea, Gulf of Mexico, East China Sea and Chesapeake Bay (Diaz & Rosenberg, 2008). These “dead zones” alter migration pathways, reduce marine biomass and subsequently deliteriously affect fishery resources (Breitburg et al., 2009). A primary cause of watershed pollution is the discharge of inadequately treated municipal and industrial wastewater. Given the aforementioned concerns, increasingly strict regulations and pollution control strategies are being implemented by governmental bodies.

Attached-growth (biofilm) systems have been used successfully for biological nutrient removal of wastewater (Chan et al., 2009; Falletti & Conte, 2007). The moving bed biofilm reactor (MBBR) represents a spectrum in advanced wastewater treatment that incorporates a biofilm process into the suspended growth reactor. MBBRs are operated
similarly to the activated sludge process with the addition of freely moving carrier media (Ødegaard, 2006). More specifically, in the MBBR process, biofilm grows attached on small carrier elements suspended in constant motion throughout the entire volume of the reactor and is constrained to the bioreactor through sieve arrangements at the reactor outlet (Mannina & Viviani, 2009). Advantages of the MBBR process over the conventional activated sludge (CAS) process include better oxygen transfer, shorter hydraulic residence time (HRT), higher organic loading rates, a higher nitrification rate and a larger surface area for mass transfer (Sombatsompop et al., 2006; Chan et al., 2009).

Within the MBBR operation there exists three main phases according to Chan et al. (2009): (i) the discrete solid phase of inert carriers with immobilized microbial cells, (ii) the discrete air bubbles; and (iii) the continuous aqueous phase. The immobilized microbial cells offer an additional advantage of seamlessly integrated simultaneous nitrification and denitrification (SND). The main physical explanation for SND within microbiological flocs is DO concentration gradients as a result of diffusion limitations from the aqueous phase into the immobilized biofilm. The aerobic bulk liquid provides an oxidizing environment where soluble BOD is removed and ammonia is nitrified. The nitrite and nitrate produced during nitrification diffuses to the inner parts of the biofilm where there exists an anoxic micro-zone that harbors heterotrophic denitrifiers which produce nitrogen gas in the traditional manner (Yang et al., 2009b).

MBBR reactors have been successfully used for treatment of dairy wastewater (Andreottola et al., 2002), landfill leachate (Canziani et al., 2006), petrochemical wastewater (Whang et al., 2009), thermomechanical pulping whitewater (Jahren et al.,
2002) and municipal wastewater (Falletti & Conte, 2007; Ødegaard, 2006; Rusten et al., 1994).

Due to the higher loading rates achievable with the MBBR system, smaller footprint bioreactors are often feasible. Unfortunately, the production of filamentous bacteria and poorly settling biomass often hinder solid separation in secondary clarifier operations. According to Ødegaard (2000), settleability of biosolids remains the largest challenge in MBBR design.

Recently proposed a hybrid membrane and moving bed biofilm reactor process aims to partially mitigate the aforementioned settleability issues consistent with MBBRs while also potentially addressing fouling concerns consistent with membranes. Originally introduced by Leiknes & Ødegaard (2007), the moving bed membrane bioreactor (MBMBR) or the biofilm-MBR process has shown good treatment efficiencies with production of consistently high-quality effluent. Comparing with other hybrid membrane bioreactors, a moving bed membrane bioreactor could optimistically operate at 10 – 15 times higher volumetric loading at 10 – 30 times shorter HRT (Sombatsompop et al., 2006; Leiknes & Ødegaard, 2007).

The geometry of the biofilm carrier media that stays fluidized inside the MBBR compartment has included smooth cylinders (Andreottola et al., 2002; Yang et al., 2010), cylinders with internal crosses and external fins (Ødegaard, 2006), rectangles and cubes (Golla et al., 1994; Valdivia et al., 2007) and spheres (Valdivia et al., 2007). Furthermore, various materials have been employed for biomass support including porous ceramic (Valdivia et al., 2007), reticulated foam (Golla et al., 1994; Valdivia et
Mixed relationships have been presented in the literature in terms of the recommended filling fraction (carrier volume versus total bioreactor volume). Ødegaard (2006) recommends a filling fraction below 70% for cylindrical plastic carriers to allow for smooth unimpeded suspension of moving bed media. Studies by Di Trapani et al. (2008) and Mannina & Viviani (2009) analyzed the nutrient removing performance of moving bed bioreactors at 33% and 66% filling ratio and noticed little performance variation in terms of wastewater constituent removal. Canziani et al. (2006) successfully used plastic media at a filling fraction of 37.5% for landfill leachate post-denitrification treatment after membrane filtration. For enhanced nitrification/denitrification of a municipal wastewater treatment plant, Falletti & Conte (2007) recommended a 43% filling fraction with plastic cylindrical media. Levstek & Plazl (2009) found similar nitrification rates and required basin volume for plastic cylindrical media at a filling fraction of 37% and for PVA-gel carriers at a filling fraction of 9.6%. This highlights the potential that specific surface area may also be an important design parameter. Xiao & Ganczarczyk (2006) found that at a filling fraction of 70% the attached growth density is 5 to 13 times higher and responds more strongly to COD influent as compared to that of activated sludge flocs.

The research presented within aims to further broaden the understanding of the MBMBR system with emphasis on nutrient removal in hybrid biofilm systems coupled with membrane separation. Furthermore, a novel biofilm growth media is proposed that
incorporates a hydrodynamic spherical carrier filled with a highly porous packing for enhanced biofilm growth. To evaluate the mechanisms of biofilm attachment as a function of media size, the media were prepared in three diameters from 21 mm to 33 mm. The three novel media sizes were compared with the industry standard finned cylindrical media for biofilm growth and volume utilization.

**Materials and Methods**

Hybrid Membrane Pilot Plant

Three pilot scale bioreactors with membrane separation were installed to treat municipal wastewater at the City of Guelph wastewater treatment plant (WWTP) in Ontario, Canada. The three bioreactors tested were a conventional MBR (MBR A) and two moving bed membrane bioreactors (MBMBR B and MBMBR C). Figure 2-1 shows the process flow diagram for the three trains. The bioreactors were open top polyethylene with a length, width and depth of 76 cm, 30 cm and 107 cm respectively and a 42 cm freeboard. The total volume of the system was 150 L, of which 40 L is the screened membrane zone and 110 L is the suspended or biofilm zone where biomass consumes substrate. A summary of the test apparatus and the key operational parameters are presented in Table 2-1. Raw municipal wastewater was sieve pre-treated using a 1 mm brush-type rotating drum filter (Type C, Or-Tec Inc., USA) to remove hair and other large debris and delivered by pump to ball float valves for level control (BFB005-HF, Chemline Plastics Limited, Canada). Membrane filtration was achieved by a submerged ZeeWeed-10 (ZW-10) hollow fibre ultrafiltration (0.04 μm pore size) membrane modules (GE Water & Process Technologies, Oakville, Canada) withdrawn using variable speed
magnetic drive gear pumps (Micropump Inc., USA) at a constant permeate flux target of 14 l/m²/hr (LMH). Course bubble cyclic aeration of the membrane (10 seconds ON/10 seconds OFF) was achieved using a solenoid valve (Skinner Electric Valves, USA) controlled by a digital timer (Model 655, Gralab, Dimco-Gray Co., USA). A gas rotameter was used to control the specific aeration demand per membrane area (SADₘ) to 2.1 m³ₐir · m⁻²membrane · h⁻¹. Fine bubble aeration was provided to the bioreactor for biological respiration and to maintain media in suspension using a single 229 mm diameter fine pore flexible membrane disk diffuser (Environmental Dynamics Inc., USA) at a rate of 1.7 m³ · h⁻¹. To prevent membrane/carrier physical interactions the membrane zone was separated from the MBBR zone by welded 304 Stainless steel wire mesh (6 mm x 6 mm) with 76% open area. To reduce the variance caused by bubble coalescence that occurs on the mesh parallel to the membrane module the MBR system was also equipped with wire mesh to separate the membrane zone and the pseudo MBBR zone. Transmembrane pressure was recorded using a data acquisition system equipped with a logging unit on 15 second sampling intervals (Model AD128C-T2, Omega, USA) and pressure transducers (Model 68075, Cole-Parmer, USA). Bioreactor and wastewater influent temperature were recorded using a four channel datalogging digital thermometer at 120 second sampling intervals (Model 800024, Sper Scientific, USA) with Type K PTFE insulated probe with PTFE-coated tip (Model EW-08113-23, Cole-Parmer, USA).
Two separate carrier types and materials were analyzed in MBMBR B and MBMBR C systems. MBMBR B carriers are made of high density polyethylene (SG = 0.95) and are cylindrical in shape. The length and diameter are 7 mm and 10 mm respectively, they contain a cross on the inside and a series of fins on the outside to provide sheltered biofilm growth. The carriers were maintained at a filling fraction of 40% in the MBBR compartment providing an effective surface area of 200 m$^2 \cdot$ m$^{-3}$. Figure 2-2 shows the MBMBR C media which was a hybrid high density polyethylene carrier with a high specific surface area fibrous packing. The carrier shell was spherical in shape formed by two thin cylinders forming a cross at the top and bottom. To investigate biofilm development as a function of carrier diameter, three outside diameters were developed,
21 mm, 27 mm and 33 mm. The total filling fraction was maintained at 20% in the MBBR compartment with a contribution to volume of 5%, 45% and 50% by the 21 mm, 27 mm and 33 mm media respectively.

Figure 2-2 - MBMBR C contained a novel fibrous media packed inside a polyethylene carrier

For starting the process, the three reactors were filled with mixed liquor from aeration tank B of a large-scale submerged ZeeWeed 500 MBR pilot plant located at the City of Guelph WWTP (see Farquharson & Zhou, 2010 for ZeeWeed 500 process specifications). The filtration cycle was a 9.5 minute permeation period followed by 30 seconds of relaxation. The SRT of the suspended growth portion was maintained in steady-state at 15 days, 5 days and 5 days for the entire duration of the experiment by wasting 10 L, 30 L and 30 L mixed liquor from the membrane zone of MBR A, MBMBR B and MBMBR C respectively. The average HRT and the corresponding flux for MBR A, MBMBR B and MBMBR C are 5.2±0.37 hr, 5.1±0.23 hr and 5.5±0.44 hr and 14.6±1.06 LMH, 14.8±0.62 LMH and 13.7±1.10 LMH.
A single container composite sampler was used for influent wastewater collection. The daily composite sample was formed by automatically taking a sample every hour from the influent delivery line after screen using an electronic timer (Model 451, Gralab, Dimco-Gray Co., USA). The sample container had an insulated exterior with built-in ice packs to keep composite cool between sampling.

Analysis

The collected samples were taken in 1 L fluorinated high-density polyethylene bottles and transported inside an ice-packed insulated bag to the Environmental Engineering Laboratory of the University of Guelph for analysis within 2 hours of collection. Activated sludge samples were taken from the membrane zone at mid-depth, permeate samples were taken from the permeate storage tanks and raw influent samples were taken from the composite influent sampler. For a filtrate sample, activated sludge was

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>MBR A</th>
<th>MBMBR B</th>
<th>MBMBR C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacity</td>
<td>m³/d</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>Membrane zone volume</td>
<td>L</td>
<td>40</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>Bioreactor zone volume</td>
<td>L</td>
<td>110</td>
<td>110</td>
<td>110</td>
</tr>
<tr>
<td>Nominal pore size</td>
<td>μm</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>Fibre outer diameter</td>
<td>mm</td>
<td>1.9</td>
<td>1.9</td>
<td>1.9</td>
</tr>
<tr>
<td>Fibre internal diameter</td>
<td>mm</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
</tr>
<tr>
<td>Total membrane area per pilot</td>
<td>m²</td>
<td>1.86</td>
<td>1.86</td>
<td>1.86</td>
</tr>
<tr>
<td>Number of membrane modules per plant</td>
<td></td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Suspended growth SRT</td>
<td>d</td>
<td>15</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>HRT (mean ± s.d.)</td>
<td>hrs</td>
<td>5.2 ± 0.37</td>
<td>5.1 ± 0.23</td>
<td>5.5 ± 0.44</td>
</tr>
<tr>
<td>MLSS (mean ± s.d.)</td>
<td>g/L</td>
<td>5.9 ± 0.89</td>
<td>2.8 ± 0.82</td>
<td>2.5 ± 0.74</td>
</tr>
<tr>
<td>Attached Biomass (mean ± s.d.)</td>
<td>g/L</td>
<td>2.6 ± 0.78</td>
<td>1.3 ± 0.15</td>
<td></td>
</tr>
<tr>
<td>Net Flux (mean ± s.d.)</td>
<td>L/m²/h</td>
<td>14.6 ± 1.06</td>
<td>14.8 ± 0.62</td>
<td>13.7 ± 1.10</td>
</tr>
<tr>
<td>Temperature mean (min-max)</td>
<td>°C</td>
<td>13.4 (7.6-21.0)</td>
<td>13.6 (9.3-20.2)</td>
<td>13.5 (8.8-20.1)</td>
</tr>
<tr>
<td>Fouling Rate</td>
<td>kPa/day</td>
<td>-0.12</td>
<td>-0.50</td>
<td>-0.56</td>
</tr>
</tbody>
</table>
immediately processed at the pilot plant by vacuum filtering through a 1.5 μm glass microfiber filter (Whatman 934-AH, GE Healthcare, USA) to produce a 100 mL filtrate sample.

Activated sludge samples were analyzed for MLSS and MLVSS according to the *Standard Methods* (APHA *et al.*, 2005). Dissolved oxygen and pH were measured in situ using a portable DO meter (Model 52, YSI Incorporated, USA) with DO probe (Model 5239, YSI Incorporated, USA) and a portable pH/conductivity meter with platinum pH electrode (sensION156, Hach, USA). The DO meter and probe were air calibrated daily in 100% relative humidity and the FEP Teflon membrane and KCl electrolyte solution replaced bi-weekly. The pH meter and probe were calibrated with a three point calibration curve weekly using 4.01, 7.00 and 10.01 pH calibration solutions.

The amount of biomass fixed to the cylindrical media with fins was determined by subtracting the average weight of 50 clean media dried at 105°C from the weight of 50 media taken from MBMBR B and dried to 105°C. For the biomass fixed into the hybrid media, 6, 10 and 5 of the 21 mm, 27 mm and 33 mm media were taken from MBMBR C and dried to 105°C overnight. The dried media were weighed by group and then cleaned in a solution of 1,000 mg/L NaOCl to remove biofilm, rinsed with de-ionized water and dried to 105°C overnight before reweighing. The average mass of biofilm as attached growth was extrapolated to the entire reactor volume to estimate the attached biomass as mg/L.

Raw wastewater was analyzed for total suspended solids (TSS) and volatile suspended solids (VSS) according to *Standard Methods*. Total phosphorus (TP), ammonia nitrogen
and biochemical oxygen demand (BOD) were measured according to the ascorbic acid method, phenate method and 5-day method from *Standard Methods* respectively. COD was measured using digestion vials compliant with the closed reflux, colorimetric method 5220D of *Standard Methods* (Method 8000, Hach, USA). Nitrate nitrogen was measured using cadmium reduction (Method 8039, Hach, USA). Total organic carbon (TOC), total nitrogen (TN) and inorganic carbon (IC) was measured using a TOC analyzer (TOC_VCSH, Shimadzu, Japan).

**Results and Discussion**

Performance of the MBR and MBMBR

Table 2-2 presents the average concentrations with standard deviation for the major wastewater constituents throughout the experimental procedure. Of primary interest when comparing moving bed membrane bioreactor and conventional membrane bioreactor processes is the mixed liquor suspended solids concentration and the attached biomass concentration. Notice that although the mixed liquor concentration is significantly lower in the MBMBR process, the total biomass, estimated as the sum of volatile suspended solids and attached biomass are relatively similar. A unique trait to the MBMBR process is the possibility to establish total biomass concentrations larger than that of the MLSS concentration.

Further to this point, the presence of carriers increases the aeration efficiency by; (i) decreasing MLSS which increases the oxygen transfer efficiency; (ii) increasing the gas-liquid interfacial area; and (iii) improving the shear stress induced by coarse bubble coalescence on the surface of the membrane.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Influent</th>
<th>MBR A</th>
<th>MBMBR B</th>
<th>MBMBR C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Influent</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>527 ± 137</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>sCOD (mg/L)</td>
<td>139 ± 60</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pCOD (mg/L)</td>
<td>388 ± 113</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BOD (mg/L)</td>
<td>178 ± 21</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>sBOD (mg/L)</td>
<td>93 ± 16</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DOC (mg/L)</td>
<td>26.5 ± 7.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IC (mg/L)</td>
<td>94.1 ± 6.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PO₄ - P (mg/L)</td>
<td>7.0 ± 1.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TN (mg/L)</td>
<td>25.4 ± 6.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH₄ - N (mg/L)</td>
<td>18.5 ± 5.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO₃ - N (mg/L)</td>
<td>5.4 ± 3.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TSS (mg/L)</td>
<td>344 ± 96</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VSS (mg/L)</td>
<td>266 ± 66</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>7.70 ± 0.11</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bioreactor</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MLSS (mg/L)</td>
<td>5,900 ± 885</td>
<td>2,800 ± 822</td>
<td>2,475 ± 738</td>
<td></td>
</tr>
<tr>
<td>MLVSS (mg/L)</td>
<td>4,475 ± 701</td>
<td>2,175 ± 637</td>
<td>1,900 ± 565</td>
<td></td>
</tr>
<tr>
<td>Attached Biomass (mg/L)</td>
<td>2,575 ± 775</td>
<td>1,275 ± 150</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DO (mg/L)</td>
<td>7.5 ± 1.8</td>
<td>7.5 ± 1.5</td>
<td>7.6 ± 1.3</td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>7.59 ± 0.20</td>
<td>7.65 ± 0.18</td>
<td>7.65 ± 0.20</td>
<td></td>
</tr>
<tr>
<td>Permeate</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>24.0 ± 9.1</td>
<td>25.2 ± 8.1</td>
<td>28.7 ± 10.1</td>
<td></td>
</tr>
<tr>
<td>BOD (mg/L)</td>
<td>1.36 ± 1.02</td>
<td>1.82 ± 1.10</td>
<td>1.87 ± 1.44</td>
<td></td>
</tr>
<tr>
<td>TOC (mg/L)</td>
<td>5.67 ± 1.63</td>
<td>6.36 ± 1.32</td>
<td>7.74 ± 1.23</td>
<td></td>
</tr>
<tr>
<td>PO₄ - P (mg/L)</td>
<td>1.22 ± 0.61</td>
<td>0.89 ± 0.26</td>
<td>0.79 ± 0.27</td>
<td></td>
</tr>
<tr>
<td>TN (mg/L)</td>
<td>25.8 ± 6.5</td>
<td>21.9 ± 4.5</td>
<td>21.8 ± 4.4</td>
<td></td>
</tr>
<tr>
<td>NH₄ - N (mg/L)</td>
<td>0.03 ± 0.02</td>
<td>0.25 ± 0.26</td>
<td>0.37 ± 0.29</td>
<td></td>
</tr>
<tr>
<td>NO₃ - N (mg/L)</td>
<td>15.9 ± 4.6</td>
<td>13.4 ± 3.3</td>
<td>12.8 ± 3.1</td>
<td></td>
</tr>
<tr>
<td>Filtrate</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>56.2 ± 21.3</td>
<td>45.0 ± 10.0</td>
<td>64.0 ± 14.6</td>
<td></td>
</tr>
<tr>
<td>TOC (mg/L)</td>
<td>11.5 ± 2.3</td>
<td>11.5 ± 2.3</td>
<td>17.4 ± 3.3</td>
<td></td>
</tr>
</tbody>
</table>
Organic Substrate Removal

Figure 2-3 presents the removal of COD throughout the whole operating period. The three reactors, MBR A, MBMBR B and MBMBR C all showed excellent performance in organic carbon removal throughout varying influent COD concentrations with removal efficiencies of 95.2±2.4%, 95.0±2.3% and 94.2±2.7% respectively. The results for organic substrate removal exceed previous results of 91% and 87% presented by Ivanovic et al. (2008) and Ahl et al. (2006) respectively for similar operating MBMBR systems treating municipal wastewater.

Figure 2-3 - COD concentration and removal rates for the three bioreactors.

Symbols: (■) influent; (○) permeate MBR A; (×) permeate MBMBR B; (◄) permeate MBMBR C; (◇) MBR A removal; (+) MBMBR B removal; (►) MBMBR C removal.
Using the paired student’s t-test at the 0.05 significance level it was found that the permeate from reactor MBR A and MBMBR B was significantly lower than that of MBMBR C however no significant difference could be found between MBR A and MBMBR B. The lower organic substrate removal could be attributed to the lower combined biomass (sum of MLVSS and attached biomass) found in MBMBR C. The average combined biomass with standard deviation of MBR A, MBMBR B and MBMBR C was found to be 4,475±701 mg/L, 4,900±1,189 mg/L and 3,325±751 mg/L respectively.

Biochemical oxygen demand removal was also consistently high with carbonaceous BOD removals for MBR A, MBMBR B and MBMBR C of 99.2±0.63%, 98.9±0.70% and 98.2±2.2% respectively. Applying the paired t-test at the 0.05 significance level, biological removal in the three reactors was found to not be statistically different.

**Nitrogen and Phosphorous Removal**

Removal of nitrogen was classified through measuring total nitrogen (TN), nitrate and ammonia of the filtered influent and the permeate samples. Figure 2-4 presents the TN and nitrate concentration throughout the experimental process. Nitrogen parameters were compared at the significance level $\alpha = 0.05$ using the one-sided paired t-test. It was shown that TN and nitrate concentrations were significantly lower in the MBMBR reactors as compared to the MBR reactor whereas there was not enough statistical evidence to differentiate nitrate and TN removal between MBMBR B and MBMBR C. Conversely, it was shown that MBR A had significantly better removal of ammonia when compared to MBMBR B and MBMBR C, while there was not enough statistical evidence
to differentiate ammonia removal between MBMBR B and MBMBR C. The average ammonia concentration for reactor A, B and C respectively are 0.033±0.022 mg/L as N, 0.25±0.26 mg/L as N and 0.37±0.29 mg/L as N.

Dissolved oxygen concentrations and pH were monitored throughout the duration of the test protocol. It is well recognized that biological nutrient removal is sensitive to both the DO concentration and pH of the bulk liquid and is often controlled as a method to enhance nutrient removal (Chan et al., 2009). Statistical analysis indicates that there was no significant difference of the bulk liquid DO or pH between reactors and therefore cannot be used to explain variations in nitrification and denitrification rates between reactors.

The increased nitrate removal is more likely a result of anoxic micro-zones that developed in the inner regions of the biofilm attached to carrier material. Within the anoxic micro-zones, DO concentrations are not controlled by the bulk liquid DO that was considerably higher than the conditions required for denitrification (less than 0.5 mg/L DO). Instead, interior regions of the biofilm oxidize ammonia nitrogen and carbonaceous substances consuming dissolved oxygen. The reductive environment established by higher nitrate concentrations produced during nitrification further consumes organic carbon releasing nitrogen gas in the traditional denitrification process. The improved removal of TN can be explained by the increased capacity of MBMBRs to perform nitrate removal.

Although the concentration of oxidized nitrogen was statistically lower in the MBMBBR systems, further denitrification could be realized through reactor improvements. Utilizing
coarse bubble aeration within the MBBR compartment would lower bulk liquid DO concentration producing larger anoxic micro-zones through further diffusion limitations. Further to this point, a dedicated anoxic zone in which mixers as opposed to aeration maintain media in suspension would ensure nitrate is reduced by denitrifying biomass.

Figure 2-4 - Total Nitrogen (TN) and nitrate concentration in the three reactors.

Symbols: (■) filtered influent NO$_3$; (○) NO$_3$ permeate MBR A; (∗) NO$_3$ permeate MBMBR B; (◄) NO$_3$ permeate MBMBR C; (◇) TN permeate MBR A; (+) TN permeate MBMBR B; (►) TN permeate MBMBR C; (□) TN filtered influent.
The decreased nitrification process in the biofilm reactors is most likely attributed to the lower SRT (5 days in MBMBR B and MBMBR C). At the reduced SRT, the suspended population of nitrifying bacteria was not preferential selected. Artiga et al. (2005) reported similar results when the suspended biomass SRT of a hybrid biofilm reactor was reduced from 10 days to 1 day and subsequently the ammonia conversion decreased from 97% to 76%. This contradicts research previously suggested by Ødegaard (2006) that the MBBR system is superior in nitrification and nitrifiers colonize carrier as attached growth.

Total phosphorous removal was found to be 81%, 86% and 88% with average total phosphorous concentrations in the permeate of 1.22 mg/L, 0.89 mg/L and 0.79 mg/L for reactors A, B and C respectively. While enhanced phosphorous removal is achieved in the MBMBR systems, it can be explained by the lower SRT of these systems. Although lower MLSS concentrations were achieved in the MBMBR systems the higher volumetric wasting resulted in higher quantities of volatile solids being wasted from the MBMBR systems. Phosphorous accumulating organisms (PAOs) may contain 0.30 g P/g VSS and non-PAOs may contain 0.02 g P/g VSS. Given the high MLVSS concentrations ubiquitous to membrane bioreactors, this represents a significant phosphorous removal mechanism. It is not believed that considerable anaerobic zones were established in the MBMBR reactors which would contribute to increased PAO concentrations and enhanced removal of phosphorous.
Performance of the Novel Hybrid Carrier

The novel hybrid media were tested for biofilm carrying capacity as a function of the volume of sheltered packing. It was found that the smallest of the three media achieved the highest specific biomass accumulation with 40±12 g/cm³, 24±7.2 g/cm³ and 24±5.4 g/cm³ attached on the 21 mm, 27 mm and 33 mm carriers respectively.

Timmermans & Van Haute (1984) presented an estimate of the density of dry biofilms in fluidized bed reactors treating wastewater with a range from 0.055 g/cm³ to 0.11 g/cm³ and an average dry biofilm density of 0.085 g/cm³ over a range of biofilm thicknesses. This range is consistent with similar research presented by Ro & Neethling (1991) and Boaventura & Rodrigues (1988). The average dry density was used to estimate the utilized carrier volume as presented in Table 2-3 using the following:

\[
\% \text{ Utilized} = \frac{M_{biofilm}}{\rho_{biofilm} \cdot V_{sheltered}}
\]

where \(M_{biofilm}\) is the mass of biofilm attached to a single media, \(\rho_{biofilm}\) is the density of dry biofilm and \(V_{sheltered}\) is the volume available for biomass growth in a single media.

For the dimensions and media tested, the 21 mm spherical media produced the highest capacity for biofilm growth and as a result could be used to optimize the filling fraction for attached biomass development. Furthermore, for all of the dimensions tested the novel media provided a higher utilized volume for biofilm developed when compared to the finned industry standard cylindrical media. The increased biomass density in the novel media can be attributed to the superior porous packing that provides enhanced sheltered surface area. The 27 mm and 33 mm novel media did not develop biomass densities as high as the 21 mm media as a result of the interior regions of the media not being
colonized do to either physical restraints due to sieving or diffusion limitations resulting in inhospitable growth conditions.

An observed drawback of the fibrous packing was the detachment of fibres from the carrier which through advection force became entangled with the membrane fibres. Such extensive agglomeration, generally comprising of cellulosic fibre, hair or other stranded material, is referred to as ‘ragging’, ‘matting’ or ‘braiding’ (Judd, 2006). The ragging was not broadly observed during early stages of the experiment (<45 days), but was significantly observable after 6 months of operation. The most significant accumulation was observed where the membrane lumen connects to the top and bottom header and within the potting resin due to restricted aeration intensity to these regions. A more tightly bound porous packing such as non-woven foam could alleviate these concerns.

### Table 2-3 - Percent of carrier volume utilized for biofilm growth

<table>
<thead>
<tr>
<th>Carrier Type</th>
<th>Average mass of biofilm (g/media)</th>
<th>Sheltered Volume (cm³)</th>
<th>Biofilm density (g/cm³)</th>
<th>Utilized volume (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cylindrical media (MBMBR B)</td>
<td>0.0086</td>
<td>0.550</td>
<td>0.085</td>
<td>18</td>
</tr>
<tr>
<td>21 mm (MBMBR C)</td>
<td>0.043</td>
<td>1.07</td>
<td>0.085</td>
<td>47</td>
</tr>
<tr>
<td>27 mm (MBMBR C)</td>
<td>0.085</td>
<td>3.62</td>
<td>0.085</td>
<td>28</td>
</tr>
<tr>
<td>33 mm (MBMBR C)</td>
<td>0.21</td>
<td>8.58</td>
<td>0.085</td>
<td>28</td>
</tr>
</tbody>
</table>

An interesting observation was the highly porous packing material became colonized by worm-like organisms (helminths) during the prolonged temperature spike experienced during the final 12 days of operation. The helminths preferred the carrier phase over the liquid phase and no helminths were observed in the mixed liquor. MBR A and MBMBR B were not shown to contain helminths; however helminths have been reported in the
large ZeeWeed 500 pilot plant in the past. To prevent erroneous biofilm estimates, attached biomass measurements of MBMBR C were not taken during this period.

**Conclusions**

- Organic carbon removal was excellent in all three bioreactors with total COD removals of 95.2±2.4%, 95.0±2.3% and 94.2±2.7% respectively in MBR A, MBMBR B and MBMBR C;
- Total nitrogen and nitrate concentrations were superiorly removed in the MBMBR systems as compared to the MBR system due to anoxic micro-zones within the carrier material;
- Better removal of ammonia occurred in the MBR system as compared to the MBMBR systems as a result of the increased suspended growth SRT;
- Over the dimensions of media tested, the smallest media, the spherical 21 mm diameter carrier had the highest capacity to accumulate biofilm;
- A new approach to verify biofilm growth, named here volume percent utilized, represents a good method to determine the validity of carrier performance due to design dependence on reactor filling fraction.
Chapter 3 Comparison of two Hybrid Moving Bed Membrane Bioreactors and a Conventional Membrane Bioreactor for Ultrafiltration Membrane Fouling Control

Abstract

A new type of membrane bioreactor was tested for municipal wastewater treatment and fouling control. Assigned the title of moving bed membrane bioreactor (MBMBR), suspended growth was augmented with attached growth through biofilm development on media in constant suspension and directly compared against a conventional membrane bioreactor (MBR). Unique to this study was the advent of a novel biofilm carrier that incorporated a high porosity fibrous packing inside a spherical high density polyethylene carrier. Although the MBMBR systems were capable of producing lower mixed liquor suspended solids concentrations, long term fouling control of ultrafiltration membranes was not achievable and in fact the fouling rate was surprisingly more than 4 times higher in the two MBMBR systems as compared to the conventional MBR system. Colloidal TOC was found to be a primary fouling inducing parameter and was significantly higher in both MBMBR systems. Carbohydrate substances were poorly rejected by the membrane and did not produce significant fouling propensity whereas proteins and humic acids were well rejected by the membrane (~50%) and were found to be fouling influencing substances.

Fourier transform infrared spectrometry (FT-IR) was performed to analyze the foulant layer. Biopolymers including polysaccharides, humic acids, proteins and carbohydrate as well as fluorinated organic halogens associated with the membrane module functional
groups were observed on the membrane fibre. FT-IR analysis confirmed the higher degree of fouling with higher reported absorbance in biopolymer regions found on the surface of MBMBR membrane fibres. Confocal laser scanning microscopy (CLSM) confirmed the presence of carbohydrates and proteins as well as living cells, dead cells and lipids on the surface of all membrane fibres. Again applying CLSM, the thickness of biofilm attached to membrane fibres were measured and found to be higher in the MBMBR systems with depths ranging from 10.8±4.4 μm to 33.3±8.0 μm, whereas the MBR membrane had a biofilm 4.6±1.0 μm thick. Permeability studies revealed that cake layer resistance associated with the MBR was significantly higher than that of the MBMBR systems, while fouling resistances due to pore blocking and gel layer formation were higher in the MBMBR systems as compared to the MBR.

**Keywords:** moving bed bioreactor (MBBR); moving bed membrane bioreactor (MBMBR); membrane bioreactor (MBR); membrane fouling; wastewater; biofilm; carrier; FT-IR; CLSM.

**Introduction**

Hybrid membrane technologies in which conventional processes are integrated with solid-liquid separation through membrane filtration are advancing water and wastewater processes. Of primary interest in the field of wastewater treatment and water reuse is the membrane bioreactor. The conventional MBR uses suspended biomass to degrade wastewater constituents and membrane filtration to separate biomass typically through microfiltration (MF) or ultrafiltration (UF) (Zhou & Smith, 2002). Through MF and UF membranes (pore sizes in the range of 0.05 μm to 0.4 μm), complete physical retention of
bacterial flocs and confinement of virtually all suspended solids to within the bioreactor can be achieved (Le-Clech et al., 2006).

Conventional wastewater treatment is superseded by MBR treatment attributable to several advantages including smaller footprint, hygienic effluent and the capacity for higher volumetric loading rates (Kraume & Drews, 2010). Unfortunately, a major obstacle for the broad application of MBRs is the rapid decline of membrane permeability. More commonly known as membrane fouling, a loss of permeability results in either a steady decline in permeate flux (operation at constant pressure) or a steady increase in transmembrane pressure (TMP) (operation at constant flux). Notable researchers including Judd (2006), Le-Clech et al. (2006) and Drews (2010) have extensively reviewed the status and trends of membrane fouling in mainly conventional MBR operation. More recently, hybrid membrane systems that incorporate biofilm growth, anaerobic-aerobic treatment, biological nutrient removal and promise to decrease fouling proliferation have been proposed (Chan et al., 2009; Leiknes & Ødegaard, 2007; Phattaranawik & Leiknes, 2010).

A moving bed biofilm reactor (MBBR) coupled with a membrane separation process aims to partially mitigate the aforementioned fouling concerns consistent with membranes while also performing enhanced biological nutrient removal. Originally introduced by Leiknes & Ødegaard (2007), the moving bed membrane bioreactor (MBMBR) or the biofilm-MBR (BF-MBR) process has shown good treatment efficiencies with production of consistently high-quality effluent. Comparing with other hybrid membrane bioreactors, an MBMBR could optimistically operate at 10 – 15 times
higher volumetric loading at 10 – 30 times shorter HRT (Leiknes & Ødegaard, 2007; Sombatsompop et al., 2006).

In the MBBR process, biofilm grows attached on small carrier elements suspended in constant motion throughout the entire volume of the reactor and is constrained to the bioreactor through sieve arrangements at the reactor outlet. Advantages of the MBMBR process over the conventional activated sludge process include better oxygen transfer, shorter hydraulic residence time (HRT), higher organic loading rates, a higher nitrification rate and a larger surface area for mass transfer (Mannina & Viviani, 2009; Sombatsompop et al., 2006).

The research presented here applies a novel biofilm growth media that incorporates a hydrodynamic spherical carrier filled with a highly porous packing for enhanced biofilm growth. The novel media was tested against the industry standard biofilm carrier material and a control MBR system. The three hybrid membrane pilot plants were operated for close to 6 months treating real municipal wastewater. Fouling inducing parameters were continuously monitored with membrane fibre analysis performed at the end of system operation.

**Materials and Methods**

Hybrid Membrane Pilot Plant

A summary of the test apparatus and the key operational parameters is presented in Table 3-1. As shown in Figure 3-1, the bioreactors were open top polyethylene with a length, width and depth of 76 cm, 30 cm and 107 cm respectively and a 42 cm freeboard. A
process flow diagram can be found above in Figure 2-1. Modules were operated at the same constant flux operation with a set point flux of 14 l/m$^2$/hr (LMH).

![Schematic of the moving bed membrane bioreactor concept](image)

**Figure 3-1 - Schematic of the moving bed membrane bioreactor concept**

**Table 3-1 - Summary of test apparatus and key experimental parameters**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>MBR A</th>
<th>MBMBR B</th>
<th>MBMBR C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacity</td>
<td>m$^3$/d</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>Membrane zone volume</td>
<td>L</td>
<td>40</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>Bioreactor zone volume</td>
<td>L</td>
<td>110</td>
<td>110</td>
<td>110</td>
</tr>
<tr>
<td>Nominal pore size</td>
<td>μm</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>Fibre outer diameter</td>
<td>mm</td>
<td>1.9</td>
<td>1.9</td>
<td>1.9</td>
</tr>
<tr>
<td>Fibre internal diameter</td>
<td>mm</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
</tr>
<tr>
<td>Total membrane area per pilot</td>
<td>m$^2$</td>
<td>1.86</td>
<td>1.86</td>
<td>1.86</td>
</tr>
<tr>
<td>Number of membrane modules per plant</td>
<td></td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Suspended growth SRT</td>
<td>d</td>
<td>15</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>HRT (mean ± s.d.)</td>
<td>hrs</td>
<td>5.2 ± 0.37</td>
<td>5.1 ± 0.23</td>
<td>5.5 ± 0.44</td>
</tr>
<tr>
<td>MLSS (mean ± s.d.)</td>
<td>g/L</td>
<td>5.9 ± 0.89</td>
<td>2.8 ± 0.82</td>
<td>2.5 ± 0.74</td>
</tr>
<tr>
<td>Attached Biomass (mean ± s.d.)</td>
<td>g/L</td>
<td>2.6 ± 0.78</td>
<td>1.3 ± 0.15</td>
<td></td>
</tr>
<tr>
<td>Net Flux (mean ± s.d.)</td>
<td>L/m$^2$/h</td>
<td>14.6 ± 1.06</td>
<td>14.8 ± 0.62</td>
<td>13.7 ± 1.10</td>
</tr>
</tbody>
</table>

The same carrier types and materials were analyzed in MBMBR B and MBMBR C systems as presented previously. MBMBR B carriers were maintained at a filling fraction
of 40% in the MBBR compartment providing an effective surface area of 200 m²⋅m⁻³. MBMBR C media had a total filling fraction of 20%.

Analysis

Samples were collected in 1 L fluorinated high-density polyethylene bottles and transported inside an ice-packed insulated bag to the Environmental Engineering Laboratory of the University of Guelph for immediate analysis. Activated sludge samples were taken from the membrane zone at mid-depth, permeate samples were taken from the permeate storage tanks and raw influent samples were taken from the composite influent sampler. Filtrate samples were processed immediately at the pilot plant by vacuum filtering 100 mL of mixed liquor through 1.5 μm glass microfiber filter paper (Whatman 934-AH, GE Healthcare, USA).

Activated sludge samples were analyzed for time to filter (TTF) according to the Standard Methods (APHA et al., 2005). Due to the high concentrations of suspended solids in the MBR A system, the samples were diluted four times for the diluted sludge volume index measurements (DSVI), whereas MBMBR B and MBMBR C were measured without dilution for SVI according to Standard Methods.

Particle size distribution was measured using a laser diffraction particle size analyzer with de-ionized water as the dispersant (Mastersizer 2000, Malvern Instruments Ltd., UK). Zeta potential was measured using a Malvern Nano Zetasizer in clear polycarbonate folded capillary cells (Malvern Instruments, UK). To eliminate large particle interference, the supernatant of the activated sludge was used for zeta potential measurements (Chang et al., 2001).
The mean oxidation state of the organic carbon (MOC) was calculated from the concentration of TOC and COD expressed as mol C ⋅ liter\(^{-1}\) and mol O\(_2\) ⋅ liter\(^{-1}\) respectively and according to:

\[
MOC = \frac{4(TOC - COD)}{TOC}
\]

The soluble extracellular polymeric substances (EPS) or so-called SMP were extracted from the mixed liquor through centrifugation at 3,000 g and 4°C for 30 minutes. The decanted supernatant was filtered through Whatman GF/F filter (0.7 μm particle retention) for polishing. The modified anthrone method presented by Raunkjaer \textit{et al.} (1994) based on modifications to work by Gaudy (1962) was used to measure the concentration of carbohydrate with glucose as the standard reference. The modified Lowry method proposed by Hartree (1972), modified from Lowry \textit{et al.} (1951), was used for protein and humic acid determination with bovine serum albumin (BSA) and humic acid salt (Na+-HA) as the standard reference solutions respectively. Protein colour development was achieved in the presence of CuSO\(_4\) whereas it was omitted for humic acid measurements (Frølund \textit{et al.}, 1996). To prevent false estimates of the protein and humic acid concentrations and based on recommendations by Avella \textit{et al.} (2010) for low protein concentrations (<50 mg/L) the corrected Lowry method presented by Frølund \textit{et al.}(1995) was not adopted. Fresh standard solutions and standard curves for glucose, BSA and humic acids were prepared daily and tested identically to samples.
Resistance Analysis

Through application of Darcy’s law and the resistance in series model, the components contributing to total filtration resistance can be determined according to:

\[ J = \frac{\Delta P}{\mu R_T} = \frac{\Delta P}{\mu(R_M + R_F + R_C)} \]

where \( J \) is the permeate flux, \( \Delta P \) is the transmembrane pressure, \( \mu \) is the dynamic viscosity of the permeate and \( R_T \) is total membrane resistance. Components of \( R_T \) include \( R_M \) which is the intrinsic membrane resistance, \( R_F \) the fouling resistance which can be subdivided into an inorganic fraction \( (R_{F_{Inor}}) \) and an organic fraction \( (R_{F_{Org}}) \) and \( R_C \) which is the cake resistance. Temperature correction was performed to account for the dependence of permeate viscosity on temperature.

Total membrane resistance was calculated at the end of system operation by carefully transferring modules into pure water and permeating. Filtration of pure water after a two stage ex situ chemical cleaning gave intrinsic membrane resistance. Filtration of pure water between chemical cleaning stages provided the fouling resistance from the organic fraction. Cake layer resistance was the difference between total membrane resistance and the resistance measured after removing the cake layer by backwashing with pure water at twice the permeate flux for 120 seconds with continuous air scouring.

Cleaning Protocol

For chemical recovery cleaning, the membrane was systematically cleaned by first soaking the module ex situ in 1,000 mg/L sodium hypochlorite for 24 hours followed by
another 24 hour immersion in 2,000 mg/L citric acid solution (pH 2.5). Between caustic and acid immersion, the membranes were well rinsed with tap water.

The focus of this study was on irreversible fouling and therefore residual fouling was not controlled with routine maintenance cleaning. Furthermore, following the trend of pilot plant and full-scale operations, physical cleaning was controlled by relaxation rather than backflushing (Judd, 2006).

**Critical Flux**

To ensure that the permeate flux was selected within the sustainable flux region, the flux stepping method presented by Le-Clech et al. (2003) was adapted. A step length of 9 minutes with a 60 second relaxation between flux steps was selected. In situ testing was performed with a single ZW-10 module to provide more reliable information about reactor specific critical flux (de la Torre et al., 2008). Permeation was achieved using a variable speed magnetic drive gear pump.

**FT-IR Analysis**

Membrane fibres taken for Fourier transform infrared spectroscopy (FT-IR) analysis were air dried in Petri dishes covered by watch glasses in a biological safety cabinet. Dry fibres of approximately 40 mm were examined in a Varian FT-IR spectrometer coupled with a Pike MIRacle ATR (attenuated total reflectance) accessory equipped with a Diamond/ZnSe crystal plate. To reduce interference of water vapour and CO$_2$, the sample compartment of the FT-IR apparatus was purged throughout the experiment with dry N$_2$ gas.
Baseline correction was achieved using air as a background, as later discussed a clean unused fibre was not a suitable baseline due to membrane functional groups producing higher absorbance at lower wavenumbers. Two fibres were sampled from each bioreactor and each fibre was tested at a minimum of three locations with 4 cm\(^{-1}\) resolution and 256 scans per location. The spectrum was calculated from the average of all scans with ATR correcting. Between membrane samples, the crystal plate was swabbed with Ethanol alcohol, rinsed three times with milli-Q and finally dried with a Kimwipe.

**CLSM Analysis**

Membrane fibres were carefully extracted from the membrane modules and immediately placed in labeled Petri dishes upon Kimwipes moistened with milli-Q water. Analysis was performed within 6 hours of sampling to preserve the bio-structure attached to membrane fibres. A five-fluorescence-dye staining procedure was adapted from Chen *et al.* (2007) to study total cells, dead cells, lipids, proteins and carbohydrates. As presented in Table 3-2, five fluorescence dyes were prepared (Invitrogen, Canada) at varying concentrations in 0.1 M NaHCO\(_3\) aqueous solution. The 50 mm fibre samples were immersed into the dye solution in 2 ml plastic centrifuge tubes for 30 minutes in darkness at room temperature. The fibres were stained in series beginning with Syto 63 and followed by FITC, ConA, Nile Red and finally Sytox Blue. Between dye immersions, residuals were gently rinsed with 5 mL of 1× phosphate buffered saline solution with a Pasteur pipette.

Membrane samples were scanned on a Leica TCS SP2 confocal laser scanning microscope (Leica Microsystems Heidelberg GmbH, Germany). Samples were
submerged in milli-Q water, anchored to a Petri dish and observed using a 40× water-immersion lens at 400× magnification. Fibres were scanned in series at the target wavelengths provided in Table 3-2.

Table 3-2 - The stains used in membrane fibre analysis

<table>
<thead>
<tr>
<th>Targets (presented in staining order)</th>
<th>Dye</th>
<th>Excitation (nm)</th>
<th>Emission (nm)</th>
<th>Staining Solution Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total cells</td>
<td>Syto 63</td>
<td>633</td>
<td>650-670</td>
<td>20 μM</td>
</tr>
<tr>
<td>Proteins, amino sugars</td>
<td>FITC</td>
<td>488</td>
<td>510-550</td>
<td>100 μg/ml</td>
</tr>
<tr>
<td>Carbohydrates</td>
<td>ConA-tetramethylrhodamine</td>
<td>543</td>
<td>560-600</td>
<td>50 μg/ml</td>
</tr>
<tr>
<td>Lipids, hydrophobic sites</td>
<td>Nile Red</td>
<td>514</td>
<td>625-700</td>
<td>10 μg/ml</td>
</tr>
<tr>
<td>Dead cells</td>
<td>Sytox Blue</td>
<td>458</td>
<td>465-500</td>
<td>10 μM</td>
</tr>
</tbody>
</table>

For determination of biofilm thickness the lens was focused on top dead center of the membrane sample and scanned towards the fibre interior. The lens depth was recorded at the first instance of fluorescence from Syto 63 dye and again at the first instance of the membrane substructure. The difference in depth represented the biofilm thickness plus membrane thickness. A single 50 mm unused membrane segment was stained and observed identically to determine the membrane thickness and subtracted from the aforementioned measurement to yield biofilm thickness. Two fibres were sampled from each bioreactor and each fibre was tested at a minimum of three locations for biofilm thickness.

**Results and Discussion**

During the entire test program, which lasted 154 days, the temperature and transmembrane pressure were continuously logged with bulk liquid parameters frequently
sampled. Membrane fibre samples were withdrawn on operating days 140 and 154 with permeability tests for resistance analysis performed on the final day.

Temporal Components

TMP

The development of transmembrane pressure is shown in Figure 3-2. Average fouling rate was estimated as the total increase in transmembrane pressure, including that regained through recovery cleaning, divided by the total days of operation. MBR A was capable of achieving long term stable operation with an average fouling rate of ~0.12 kPa/day. MBMBR B and MBMBR C experienced a TMP jump after 48 and 43 days of operation respectively. Permeability was regained by ex situ chemical cleaning and the remainder of the experiment was completed without further chemical cleaning. The average rate of fouling over the entire duration of study was found to be ~0.50 kPa/day and ~0.56 kPa/day for MBMBR B and MBMBR C in that order, which were over 4 times higher than experienced in MBR A. The fouling rates are compatible with results reported elsewhere (Rosenberger et al., 2006; Sun et al., 2010a). Furthermore, the higher fouling rate encountered in the MBMBR systems as compared to the MBR system is similar to values reported elsewhere by Yang et al. (2009a). Lee et al. (2001) described the formation of a dynamic membrane comprising of larger suspended solids that form a barrier between the bulk liquid membrane foulants and the membrane surface. Resistance analysis of the membranes indicated that higher cake layer resistance was achieved in MBR A, whereas higher irreversible fouling resistance was accumulated on the membrane in MBMBR B and MBMBR C. This further supports the formation of the said
dynamic membrane, which in this research shielded MBR A from adsorption of foulants into the pores of membrane fibres and gel layer formation on the surface.

![Temporal variation of TMP for the three bioreactors; MBMBR B and MBMBR C required chemical cleaning after 48 and 43 days of operation respectively.](image)

Figure 3-2 - Temporal variation of TMP for the three bioreactors; MBMBR B and MBMBR C required chemical cleaning after 48 and 43 days of operation respectively.

Modest operation of membranes between the critical flux and sustainable flux is widely accepted as a method to achieve sustainable filtration while maintaining the permeate flux as high as possible (Nywening & Zhou, 2009). To estimate the region on the critical flux curve in which the selected flux appeared, a critical flux analysis was performed on the MBR system (Figure 3-3). The strictest definition of the critical flux characterized by
$d\text{TMP}/dt = 0$ was never achieved. The weak form of critical flux, described by Le-Clech et al. (2003) as the point in which fouling starts to become significant, occurred around 12 l/m²/hr. The selected flux of 14 l/m²/hr was above this critical flux value, which by definition would explain the steady decrease in membrane permeability throughout the test period as experienced by MBR A. The selected flux was below the sustainable flux, as described by Nywening & Zhou (2009) which was found to be 22 l/m²/hr. Critical flux analysis was not performed on the MBMBR systems and therefore unfortunately cannot be used to explain the dramatic loss of permeability experienced in those systems.

![Figure 3-3 - Critical flux analysis for MBR A](image-url)
Temperature

It is well understood that permeate flux is inversely proportional to permeate viscosity and as a result inversely proportional to temperature. In other reviews, decreasing bioreactor temperature has been shown to; (i) increase sludge viscosity; (ii) decrease shear stress induced by coarse bubble coalescence on the surface of the membrane; (iii) cause defloculation of the biomass and release EPS into solution; (iv) decrease Brownian diffusion, hindering particle back transport velocity; and (v) decrease biological kinetics creating higher concentrations of soluble COD and colloidal COD inside the bioreactor (Belfort et al., 1994; Le-Clech et al., 2006). A linear relationship was tested using the Pearson correlation coefficient. Results indicated that fouling rate was loosely dependent on temperature with increasing fouling rate at decreasing temperatures. Although statistically significant ($\alpha = 0.05$), the relationship contained significant noisiness showing a lack of dependence (data not shown). A more complex relationship of a myriad of the aforementioned temperature dependent effects is more probable (i.e., EPS release or hindered COD removal) which are further discussed in later sections.

Figure 3-4 presents the temporal variations of temperature within the bioreactors and influent. Average bioreactor temperature for MBR A, MBMBR B and MBMBR C were 13.4°C, 13.6°C and 13.5°C respectively, whereas average influent temperature was 11.3°C.
Figure 3-4 - Temporal variation of temperature for the influent wastewater and three bioreactors

Bulk Parameter Effects on Fouling

Table 3-3 presents the average performance parameters with standard deviation for the MBR and two MBMBR systems over the entire test period. Pearson correlation analysis was performed on key fouling influencing parameters with respect to fouling rate ($d\text{TMP}/dt$) with results presented in Table 3-5. Briefly, the Pearson’s correlation indicates the relationship of two random variables, in this instance fouling inducing parameters and the rate of fouling. A Pearson correlation of +1 indicates perfect positive correlation and a −1 indicates perfect decreasing correlation. Values close to +1 and −1 reveal the variables are closely related. To correct for the variations in fouling rate, the temporal
variation of TMP for the three reactors were subdivided according to the range presented in Table 3-4.

Table 3-3 - Bulk liquid parameters for influent wastewater and the three bioreactors

<table>
<thead>
<tr>
<th>Parameter</th>
<th>mean ± standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Influent</td>
</tr>
<tr>
<td>Influent</td>
<td></td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>527 ± 137</td>
</tr>
<tr>
<td>sCOD (mg/L)</td>
<td>139 ± 60</td>
</tr>
<tr>
<td>pCOD (mg/L)</td>
<td>388 ± 113</td>
</tr>
<tr>
<td>BOD (mg/L)</td>
<td>178 ± 21</td>
</tr>
<tr>
<td>sBOD (mg/L)</td>
<td>93 ± 16</td>
</tr>
<tr>
<td>DOC (mg/L)</td>
<td>26.5 ± 7.8</td>
</tr>
<tr>
<td>DIC (mg/L)</td>
<td>94.1 ± 6.5</td>
</tr>
<tr>
<td>TSS (mg/L)</td>
<td>344 ± 96</td>
</tr>
<tr>
<td>VSS (mg/L)</td>
<td>266 ± 66</td>
</tr>
<tr>
<td>pH</td>
<td>7.70 ± 0.11</td>
</tr>
<tr>
<td>Bioreactor</td>
<td></td>
</tr>
<tr>
<td>MLSS (mg/L)</td>
<td>5,900 ± 885</td>
</tr>
<tr>
<td>MLVSS (mg/L)</td>
<td>4,475 ± 701</td>
</tr>
<tr>
<td>Attached Biomass (mg/L)</td>
<td>2,575 ± 775</td>
</tr>
<tr>
<td>SVI (mL/g) (*DSVI 4× dilution)</td>
<td>*171.8 ± 34.5</td>
</tr>
<tr>
<td>TTF (s)</td>
<td>46.2 ± 30.6</td>
</tr>
<tr>
<td>DO (mg/L)</td>
<td>7.5 ± 1.8</td>
</tr>
<tr>
<td>pH</td>
<td>7.59 ± 0.20</td>
</tr>
<tr>
<td>Permeate</td>
<td></td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>24.0 ± 9.1</td>
</tr>
<tr>
<td>BOD (mg/L)</td>
<td>1.36 ± 1.02</td>
</tr>
<tr>
<td>TOC (mg/L)</td>
<td>5.67 ± 1.63</td>
</tr>
<tr>
<td>Filtrate</td>
<td></td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>56.2 ± 21.3</td>
</tr>
<tr>
<td>TOC (mg/L)</td>
<td>11.5 ± 2.3</td>
</tr>
<tr>
<td>Colloidal</td>
<td></td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>32.8 ± 19.9</td>
</tr>
<tr>
<td>TOC (mg/L)</td>
<td>4.2 ± 2.7</td>
</tr>
<tr>
<td>Supernatant</td>
<td></td>
</tr>
<tr>
<td>Zeta Potential (mV)</td>
<td>-11.1 ± 2.0</td>
</tr>
<tr>
<td>SMP&lt;sub&gt;carbohydrate&lt;/sub&gt; (mg/L as glucose)</td>
<td>60.7 ± 25.0</td>
</tr>
<tr>
<td>SMP&lt;sub&gt;protein&lt;/sub&gt; (mg/L as BSA)</td>
<td>31.9 ± 16.2</td>
</tr>
<tr>
<td>SMP&lt;sub&gt;humic acid&lt;/sub&gt; (mg/L as humic acid)</td>
<td>57.7 ± 11.3</td>
</tr>
</tbody>
</table>
Based on the definition of the Pearson’s correlation, several of the water quality parameters are closely related to fouling rate. In particular, the colloidal TOC is significant in all three reactors and could represent a key process parameter in the reduction of fouling propensity. In this research, colloidal TOC is defined as particles in the range of 0.04 μm to 1.5 μm. Vigneswaran et al. (2000) suggests that microfiltration of particles of 0.45 μm sharply decreases membrane permeability. The total lift force represented by the summation of shear induced, lateral migration and Brownian diffusion is at a minimum and particle deposition leading to membrane fouling occurs. This is explained by the fact that filtration of particles below a size range of several tenths of a micrometer is more strongly affected by Brownian force whereas above this range shear induced forces prevail (AWWA, 1996).

<table>
<thead>
<tr>
<th>Unit</th>
<th>Operation Period (day)</th>
<th>(d\text{TMP}/d\text{t}) (kPa/day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MBR A</td>
<td>0 to 61</td>
<td>-0.23</td>
</tr>
<tr>
<td></td>
<td>61 to 153</td>
<td>-0.034</td>
</tr>
<tr>
<td></td>
<td>0 to 39</td>
<td>-0.70</td>
</tr>
<tr>
<td></td>
<td>39 to 48</td>
<td>-2.54</td>
</tr>
<tr>
<td>MBMBR B</td>
<td>48 to 63</td>
<td>-1.95</td>
</tr>
<tr>
<td></td>
<td>63 to 76</td>
<td>1.60</td>
</tr>
<tr>
<td></td>
<td>76 to 153</td>
<td>-0.22</td>
</tr>
<tr>
<td>MBMBR C</td>
<td>0 to 43</td>
<td>-1.27</td>
</tr>
<tr>
<td></td>
<td>43 to 71</td>
<td>-1.46</td>
</tr>
<tr>
<td></td>
<td>71 to 76</td>
<td>4.15</td>
</tr>
<tr>
<td></td>
<td>76 to 153</td>
<td>-0.17</td>
</tr>
</tbody>
</table>
Table 3-5 - Pearson correlation coefficient with respect to fouling rate and other suspected bulk liquid parameters

<table>
<thead>
<tr>
<th>Unit</th>
<th>Pearson Correlation</th>
<th>( \frac{d}{dt} ) TMP</th>
<th>Colloidal COD</th>
<th>Filtered COD</th>
<th>Permeate COD</th>
<th>Colloidal TOC</th>
<th>Filtered TOC</th>
<th>Permeate TOC</th>
<th>SMP(_C)</th>
<th>SMP(_P)</th>
<th>SMP(_H)</th>
<th>Zeta Potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>MBR A</td>
<td>Correlation</td>
<td>1</td>
<td>-0.781</td>
<td>-0.775</td>
<td>-0.154</td>
<td>-0.662</td>
<td>-0.347</td>
<td>0.642</td>
<td>-0.436</td>
<td>-0.164</td>
<td>-0.705</td>
<td>0.264</td>
</tr>
<tr>
<td>MBR A</td>
<td>Significance</td>
<td>--</td>
<td>0.000</td>
<td>0.000</td>
<td>0.357</td>
<td>0.000</td>
<td>0.041</td>
<td>0.000</td>
<td>0.092</td>
<td>0.559</td>
<td>0.003</td>
<td>0.342</td>
</tr>
<tr>
<td>MBMBRB B</td>
<td>Correlation</td>
<td>1</td>
<td>-0.104</td>
<td>-0.008</td>
<td>-0.093</td>
<td>-0.433</td>
<td>-0.317</td>
<td>0.368</td>
<td>-0.342</td>
<td>-0.785</td>
<td>-0.437</td>
<td>-0.190</td>
</tr>
<tr>
<td>MBMBRB B</td>
<td>Significance</td>
<td>--</td>
<td>0.559</td>
<td>0.964</td>
<td>0.599</td>
<td>0.011</td>
<td>0.064</td>
<td>0.030</td>
<td>0.195</td>
<td>0.001</td>
<td>0.104</td>
<td>0.497</td>
</tr>
<tr>
<td>MBMBRB C</td>
<td>Correlation</td>
<td>1</td>
<td>-0.373</td>
<td>0.068</td>
<td>-0.196</td>
<td>-0.832</td>
<td>-0.727</td>
<td>0.199</td>
<td>-0.340</td>
<td>-0.149</td>
<td>-0.897</td>
<td>0.678</td>
</tr>
<tr>
<td>MBMBRB C</td>
<td>Significance</td>
<td>--</td>
<td>0.030</td>
<td>0.685</td>
<td>0.267</td>
<td>0.000</td>
<td>0.000</td>
<td>0.252</td>
<td>0.198</td>
<td>0.595</td>
<td>0.000</td>
<td>0.006</td>
</tr>
</tbody>
</table>

Chemical Oxygen Demand

Referring to Table 3-6, COD does not sufficiently explain the fouling that occurred in MBMBRB. As presented in Chapter 2, excellent organic substrate removal was achieved in all reactors, with COD reductions of 95.2±2.4%, 95.0±2.3% and 94.2±2.7% in MBR A, MBMBRB and MBMBRC respectively.

Table 3-6 - Paired statistical analysis of COD and TOC concentrations

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Result of paired T-test (Prob&lt;(t))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permeate COD (DF = 33)</td>
<td>n.s. (0.087)</td>
</tr>
<tr>
<td>Filtered COD (DF = 33)</td>
<td>n.s. (0.99)</td>
</tr>
<tr>
<td>Colloidal COD (DF = 33)</td>
<td>n.s. (0.99)</td>
</tr>
<tr>
<td>Permeate TOC (DF = 34)</td>
<td>A &lt; B (1.2E-5)</td>
</tr>
<tr>
<td>Filtered TOC (DF = 34)</td>
<td>A &lt; B (5.5E-8)</td>
</tr>
<tr>
<td>Colloidal TOC (DF = 34)</td>
<td>A &lt; B (7.7E-5)</td>
</tr>
</tbody>
</table>

n.s.: not significantly different at \(\alpha = 0.05\); DF: degrees of freedom

Total Organic Carbon

Table 3-6 confirms that all TOC parameters (permeate, filtrate and colloidal) are significantly higher in concentration in ranking order of MBMBRC, MBMBRB and MBR A. Figure 3-5 presents a plot of the temporal variation of TOC providing clear
evidence of MBR A producing the lowest concentrations. It is well accepted that TOC can be used as a surrogate for other fouling inducing parameters \( (i.e., \text{SMP or EPS}) \) and may be indicative of the presence of carbohydrates, proteins or other carbonaceous organic solutes (Dong & Jiang, 2009; Drews, 2010; Laspidou & Rittmann, 2002). A possible explanation for the elevated TOC concentration may be the attached growth carriers found in the MBBR system inducing shear stress on biomass causing the formation of biomass-associated products (BAP) which occur upon hydrolyzation of bound EPS. The BAP, subsequently measured as TOC, contributed to gel layer formation on the membrane surface and pore blockage which was ultimately responsible for increased fouling propensity. Huang et al. (2008) reported a reduction of bound EPS and a direct increase in the dissolved and colloidal organic carbon concentration with the addition of suspended carriers at a dose as low as 5% filling fraction.

Although the MBR consistently produced lower TOC concentrations for filtrate, permeate and colloidal samples, only the colloidal fraction produced a linear relationship with significance below a level of 0.05 in all three reactors. Fan et al. (2006) found that the concentration of colloidal TOC (measured as the difference between the TOC of filtrate passing through 1.5 μm filtration paper and the TOC of permeate which passed through 0.04 μm membrane) almost exclusively controlled the critical flux and permeability decline in a MBR system. In work by Wang & Li (2008) the colloidal TOC was classified as biopolymer clusters (BPC) and were found to have a profound effect on membrane fouling.

Lyko and co-workers (2008) used DOC as a fouling indicator and found a correlation between soluble carbohydrates and DOC in the supernatant \( (R^2 = 0.407) \) whereas no
correlation between DOC and protein or humic acids was tangible. In this work, a very weak linear relationship was found for colloidal TOC and carbohydrates ($R^2 = 0.156$) and colloidal TOC and proteins ($R^2 = 0.183$). A stronger linear relationship was found for humic acid compounds and colloidal TOC with $R^2 = 0.530$ (presented in Figure 3-6).

Figure 3-5 - TOC concentration for (a) filtrate; (b) permeate; and (c) colloidal samples from the three bioreactors and the filtered influent.

Symbols: (■) filtered influent; (○) filtrate MBR A; (∆) filtrate MBMBR B; (◄) filtrate MBMBR C; (◊) permeate MBR A; (+) permeate MBMBR B; (►) permeate MBMBR C; (□) colloidal MBR A; (●) colloidal MBMBR B; (▲) colloidal MBMBR C.
Mean Oxidation State of Carbon

In an effort to characterize the origin of the organic carbon, the mean oxidation state of carbon was tested. The MOC of the filtrate from reactors A, B and C were found to be \(-2.25\), \(-2.26\) and \(-2.09\) respectively, whereas the permeate MOC were \(-1.12\), \(-1.39\) and \(-1.41\) respectively. From the Stumm & Morgan (1981) estimation protocol the filtrate samples may dominantly contain fats and hydroxyl functional groups possibly associated with lipids and polysaccharides or humic substances. Using the same estimation procedure, the permeate samples contained mainly products of bacteria, proteins and polysaccharides typical to membrane bioreactors. Nonetheless, the mean oxidation state of the organic carbon appeared to be almost the same in both the filtrate and permeate samples for all reactors and could not be used to further characterize the origin of the
organic carbon. Further to this, the MOC could not provide an explanation for the increased propensity of fouling observed in the MBMBR systems.

**Soluble Microbial Products**

The majority of effluent COD in biological treatment processes is attributable to soluble microbial products (de Silva & Rittmann, 2000). Furthermore, the contribution of SMP towards membrane fouling propensity has been well reported in prominent literature reviews (*i.e.*, Drews 2010; Le-Clech *et al.*, 2006). Results of SMP analysis for supernatant and permeate samples are presented in Figure 3-7 and Figure 3-8 respectively. The relative concentrations were statistically analyzed using the paired t-test at $\alpha = 0.05$ significance level. Of importance, the MBMBR systems showed a significantly higher level of protein as compared to the MBR system whereas there was no significant difference in carbohydrate concentration between MBMBR systems and the MBR system. Humic acids were shown to be significantly higher in MBMBR C as compared to MBR A and MBMBR B.

Referring to Figure 3-7 and Figure 3-8, carbohydrates are not a suitable indicator of fouling. No statistically significant difference could be found between the three reactors tested. Moreover, the proportions of carbohydrates in supernatants from mixed liquor and in permeates were almost identical, implying that membrane sieving did not affect carbohydrates. A similar statement cannot be made for proteins and humic substances, proteins were rejected by the membrane at a fraction of 51.6%, 52.1% and 60.8% whereas humic substances were rejected at a rate of 55.8%, 56.2% and 44.9% in reactors A, B and C respectively.
Figure 3-7 – Mixed liquor supernatant concentrations of SMP (number of measurements: n = 16)

Figure 3-8 – Permeate concentrations of SMP (number of measurements n = 8)
The accumulation of proteins and humic substances could be attributed to sieving of organic matter larger than the molecular weight cut-off of the membrane or some other SMP characteristics (i.e., hydrophobic/hydrophilic interactions, charge properties). This serves to enhance the argument that fouling is caused by the higher concentration of proteins in MBMBR B and MBMBR C and the higher concentration of humic acids in MBMBR C.

Although the quantity of certain soluble microbial products were found to be statistically higher in MBMBR systems, other distinguishing characteristics of the carbohydrates, proteins and humic acids in attached and suspended growth systems may exist. It is reasonable to suggest that the bulk liquid in MBMBR and MBR systems should contain different biomass-associated products, which would lead to different filtration behaviour. Liang et al. (2007) concluded that in a comparative study with MBRs operating with SRTs ranging from 10 to 40 days, fouling potential was affected by differentiating SMP characteristics more than SMP concentration. While filtering equivalent DOC concentrations of 5 mg/L, SMP products from a bioreactor with a 10 day SRT produced fouling potential 4 times higher than SMP products from a 40 day SRT reactor. Liang and co-workers concluded that SMP generated at short SRTs produced higher proportions of hydrophilic neutrals and therefore the key foulants of supernatant SMP.

**Solid Retention Time**

The fouling associated with a lower SRT has been well reported by other authors (i.e., Drews, 2010; Farquharson & Zhou, 2010). Lower SRT has been shown to produce higher colloidal TOC (Fan et al., 2006; Grelier et al., 2006) and higher polysaccharide, protein
and organic colloid concentrations (Rosenberger et al., 2006). Interestingly in this research, the SRT of the attached growth phase was controlled only by biofilm detachment mechanisms and said to be infinite whereas the SRT of the suspended growth portion was controlled manually at 15 days, 5 days and 5 days in MBR A, MBMBR B and MBMBR C respectively. This would indicate that assimilation of colloidal substances and SMP is more productively achieved through more slowly growing suspended biomass as compared to biofilm based systems. Moreover, the metabolic rate of biomass may be diminishing at longer SRTs, reducing the production of utilization-associated products (UAP) produced directly during substrate metabolism and captured in the analysis of SMP or TOC (Laspidou & Rittmann, 2002).

**Particle Size Distribution**

With respect to Figure 3-9 and using the student’s t-test (α = 0.05 significance level), no significant difference was found between reactors in the D90 range. Interestingly though, MBMBR C had statistically larger particles in both the D50 range and the D10 range. The more hydrodynamic geometry of the novel carrier media found in MBMBR C seemed to handle the mixed liquor more delicately than the finned media of MBMBR B that seemed to chop up bio-flocs shifting the particle size distribution towards smaller particles. However, for the particle size range tested, no clear relationship could be found between fouling rate and PSD.
Figure 3-9 – The D10, D50 and D90 particle size for mixed liquor from the three reactors during the developmental phase.

Symbols: (○) MBR A; (×) MBMBR B; (◆) MBMBR C.

Table 3-3 presents results for SVI, TTF and zeta potential. Zeta potential was not found to be significantly different in any of the reactors and cannot be used as an indicator of fouling. SVI and TTF were found to be the lowest by order of MBMBR C, MBMBR B and MBR A, which was also found to be the order of increasing fouling rate. SVI is an excellent indicator of sludge settleability and for sludge bulking control in activated sludge processes, but does not appear to be an indicator of fouling. This was also confirmed by Fan et al. (2006) and Farquharson & Zhou (2010).
Lower time to filter in the MBMBR systems can be explained by the lower suspended solid mixed liquor concentration. Interestingly, this short term filterability cannot be extrapolated to long term fouling rates. Ng et al. (2005) operated a dual compartment MBR pilot plant in which biomass was pre-settled before membrane filtration and found that a higher fouling rate occurred while filtering supernatant as compared to filtration of mixed liquor with 4,000 mg/L. This further supports the conclusion that macromolecule substances in the supernatant have a more significant contribution to membrane fouling than mixed liquor suspended solids and lower colloidal TOC concentration in the supernatant could alleviate fouling propensity. This same hypothesis is confirmed by Lee et al. (2001) in which the formation of a dynamic membrane at higher levels of MLSS shielded the membrane from adsorption of SMP onto the surface of the membrane and gel formation leading to fouling. Since the dynamic layer contains bioactive organisms and the soluble components are themselves biodegradable it is not unfathomable that the dynamic layer formation may consume the soluble foulants further preventing permeability decline (Brookes et al., 2003; Laspidou & Rittmann, 2002).

Membrane Fibres

Resistance Model

In theory, the attached growth system reduces overall mixed liquor concentration and as a result should reduce the cake layer resistance ($R_C$). Furthermore, in its design the moving bed membrane bioreactor promises to reduce fouling resistance ($R_F$) (Leiknes & Ødegaard, 2007; Sombatsompop et al., 2006; Yang et al., 2009a). Refering to Table 3-7, the later of the aforementioned statements is correct and average $R_C$ for MBR A,
MBMBR B and MBMBR C are $1.14 \times 10^{12} \text{ m}^{-1}$, $0.18 \times 10^{12} \text{ m}^{-1}$ and $0.22 \times 10^{12} \text{ m}^{-1}$ respectively. The later of the statements however was not confirmed in this study and the average irreversible fouling ($R_F = R_{F \text{ Org}} + R_{F \text{ Inor}}$) was found to be significantly higher in the MBMBR systems with results of $2.9 \times 10^{12} \text{ m}^{-1}$, $5.41 \times 10^{12} \text{ m}^{-1}$ and $8.1 \times 10^{12} \text{ m}^{-1}$ for MBR A, MBMBR B and MBMBR C respectively.

### Table 3-7 - Value of the filtration resistance

<table>
<thead>
<tr>
<th>Membrane Tank</th>
<th>Module No</th>
<th>$R_M$ ($10^{12} \text{ m}^{-1}$)</th>
<th>$R_C$ ($10^{12} \text{ m}^{-1}$)</th>
<th>$R_{F \text{ Org}}$ ($10^{12} \text{ m}^{-1}$)</th>
<th>$R_{F \text{ Inor}}$ ($10^{12} \text{ m}^{-1}$)</th>
<th>$R_T$ ($10^{12} \text{ m}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MBR A</td>
<td>1</td>
<td>1.72 ± 0.017</td>
<td>1.74 ± 0.14</td>
<td>1.98 ± 0.21</td>
<td>0.91 ± 0.16</td>
<td>6.42 ± 0.30</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.21 ± 0.12</td>
<td>0.53 ± 0.067</td>
<td>2.21 ± 0.064</td>
<td>0.68 ± 0.14</td>
<td>4.62 ± 0.34</td>
</tr>
<tr>
<td>MBMBR B</td>
<td>3</td>
<td>1.40 ± 0.16</td>
<td>0.16 ± 0.061</td>
<td>5.11 ± 0.40</td>
<td>0.53 ± 0.11</td>
<td>7.09 ± 0.24</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>1.92 ± 0.21</td>
<td>0.20 ± 0.23</td>
<td>4.73 ± 0.29</td>
<td>0.44 ± 0.055</td>
<td>7.33 ± 0.24</td>
</tr>
<tr>
<td>MBMBR C</td>
<td>5</td>
<td>1.69 ± 0.21</td>
<td>0.73 ± 0.25</td>
<td>6.25 ± 0.23</td>
<td>1.04 ± 0.093</td>
<td>9.83 ± 0.45</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>2.02 ± 0.35</td>
<td>-0.29 ± 0.95</td>
<td>7.93 ± 1.12</td>
<td>1.01 ± 0.22</td>
<td>11.04 ± 1.49</td>
</tr>
</tbody>
</table>

$R_T = R_M + R_C + R_{F \text{ Org}} + R_{F \text{ Inor}}$ Lee et al. (2001)

The above discussed filtration resistances, are further supported by the fractions with $R_C$ and $R_F$. The average contribution of $R_C$ towards fouling for MBR A, MBMBR B and MBMBR C were 18.7%, 2.5% and 2.2% whereas average proportion of $R_F$ towards fouling was 55.2%, 75.5% and 79.7% respectively. The results presented here are in agreement with work done by Sombatsompop and co-workers (2006) in which attached and suspended growth membrane bioreactors were maintained at 6 g/L. In their work, $R_C$ contributed 95.4% and 31.6% to $R_T$, whereas $R_F$ contributed 2.8% and 39.2% to $R_T$ in a suspended growth and an attached growth reactor respectively. Conversely, the results presented here are in contradiction with results from Yang et al. (2009a). Their research found that cake layer resistance contributed 57.8% and 83.7% to total resistance in a MBR and MBMBR respectively; while pore blocking resistance was 12.9% and 7.4% in a MBR and MBMBR respectively. Yang and co-authors (2009a) reported an overgrowth
of filamentous bacteria in their MBMBR system that may have produced a dense cake layer or biofilm that was irremovable by conventional air scouring which potentially fouled their results.

Table 3-8 - Fractions contributing to filtration resistance

<table>
<thead>
<tr>
<th>Membrane Tank</th>
<th>Module No</th>
<th>$R_M$ (%)</th>
<th>$R_C$ (%)</th>
<th>$R_{F,Org}$ (%)</th>
<th>$R_{F,Inor}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MBR A</td>
<td>1</td>
<td>26.9 ± 1.0</td>
<td>27.7 ± 2.4</td>
<td>31.4 ± 3.1</td>
<td>14.4 ± 1.9</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>26.7 ± 0.9</td>
<td>9.6 ± 1.5</td>
<td>49.4 ± 1.7</td>
<td>15.2 ± 1.7</td>
</tr>
<tr>
<td>MBMBR B</td>
<td>3</td>
<td>20.1 ± 2.9</td>
<td>2.3 ± 0.9</td>
<td>71.7 ± 3.3</td>
<td>7.6 ± 1.7</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>26.5 ± 2.2</td>
<td>2.7 ± 3.2</td>
<td>65.5 ± 4.3</td>
<td>6.1 ± 0.8</td>
</tr>
<tr>
<td>MBMBR C</td>
<td>5</td>
<td>17.5 ± 1.5</td>
<td>7.5 ± 2.5</td>
<td>64.8 ± 2.6</td>
<td>10.8 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>19.6 ± 3.1</td>
<td>-3.1 ± 9.7</td>
<td>75.2 ± 8.5</td>
<td>8.5 ± 0.6</td>
</tr>
</tbody>
</table>

**FT-IR**

The depositions of biopolymers on the membrane surface were characterized through Fourier transform infrared spectrometry which confirmed several regions where membrane fibre samples vary between membrane systems. A broad absorbance in the range of 3600 – 3000 cm$^{-1}$ (peak 3290 cm$^{-1}$) is associated with O–H stretching in hydroxyl functional groups which could be attributed to polysaccharides or humic substances (Howe et al., 2002; Kumar et al., 2006). A medium peak in the general region of 3000 – 2840 cm$^{-1}$ (peak 2924 cm$^{-1}$) was observed arising from C–H stretching in the alkanes. Referring to Figure 3-10 MBMBR C produced the highest absorbance with MBMBR B following and MBR A produced the lowest absorbance. Due to the diamond top Zinc Selenide crystal plate, examination in the 2500 – 1800 cm$^{-1}$ range is ill advised.

Many sharp peaks are observed in the region of 1800 – 620 cm$^{-1}$. The strong peak between 1650 cm$^{-1}$ and 1640 cm$^{-1}$ are attributed to C=O adsorption in primary amides.
and simple, open-chain, secondary amides in solid samples respectively (Silverstein et al., 2005; Wang et al., 2008). The medium peak in the region of 1570 – 1510 cm\(^{-1}\) is caused by interactions between the N–H bending and the C–N stretching of the C–N–H group in secondary amides. These bands are unique to protein secondary structures, indicating that the membrane surface is fouled by proteins (Maruyama et al., 2001). Furthermore, an absence of a peak near 1720 cm\(^{-1}\) indicates a lack of acidic content (i.e., carboxylic acid anhydrides or amino acid hydrochlorides) further justifying that the fraction is entirely proteinaceous (Croue et al., 2003; Silverstein et al., 2005). From Figure 3-10, MBMBR C is the most dramatically affected by protein adsorption with MBMBR B following and MBR A the least affected. This ranking trend was also observed in the bulk liquid SMP analysis, indicating that filtration of higher SMP concentration mixed liquors does result in membrane foulant adsorption.

A shoulder peak at 1045 cm\(^{-1}\) is the result of C–O stretching vibrations associated with alcohols, ethers and polysaccharides. The peak has been attributed to both polysaccharide membrane foulants and silicate impurities in humic substances (Meng et al., 2008).

In the fingerprint region (1300 – 900 cm\(^{-1}\)), the membrane functional groups are most robustly expressed. The strong peaks at 1172 cm\(^{-1}\) and 1404 cm\(^{-1}\) are attributable to stretching modes of C–F whereas strong peaks at 1275 cm\(^{-1}\), 1234 cm\(^{-1}\), 1072 cm\(^{-1}\), 878 cm\(^{-1}\) and 838 cm\(^{-1}\) are within the characteristic frequency of the CF\(_2\) groups respectively (Silverstein et al., 2005). This is to be expected for Polyvinylidene Fluoride (PVDF) membranes and has been shown in other work (Li et al., 2010). Interestingly, the functional groups of the membrane surface are more intensely expressed in the MBR system as compared to the MBMBR systems. This is a result of a thicker foulant layer.
covering the membrane surface causing a reduction in absorbance. The thicker biofilm layer was confirmed using CLSM imaging, further supporting this claim.

As shown in Figure 3-11, the fibres are returned to near unused condition after chemical cleaning with NaOCl. Evidence of the polysaccharides and humic substances observed in the range of 3600 – 3000 cm\(^{-1}\) still exists, but is dramatically reduced. Following the aforementioned hypochlorite cleaning, recovery cleaning with citric acid was performed which successfully removed all but trace artifacts of the O–H stretching in hydroxyl functional groups (Figure 3-12).
Figure 3-11 – Average FT-IR output for membrane fibres after recovery cleaning with 1,000 ppm NaOCl (sample size: 6 locations per reactor, 256 scans per location)

Figure 3-12 – Average FT-IR output for membrane fibres after recovery cleaning with 2,000 ppm citric acid (sample size: 6 locations per reactor, 256 scans per location)
CLSM

The surface topography of the membrane fibres were analyzed using CLSM for the presence of living and dead cells, lipids, proteins and carbohydrates which were ubiquitously found. The thicknesses of the biofilm were found to be 4.6±1.0 μm, 10.8±4.4 μm and 33.3±8.0 μm for MBR A, MBMBR B and MBMBR C respectively. This layer was a tightly bound gel not possible to remove through mechanical methods (i.e., relaxation, air scouring). MBR A had a loosely compacted bio-structure that was fully penetrable through the entire spectrum of the biofilm thickness. All of the membrane fibres taken from MBMBR B had very dense bio-structure that made visualization of the membrane support structure difficult. MBMBR C was covered in a very thick bio-structure layer that was loosely compacted containing layers of dead cells.

Selected images of an unused fibre and fouled membrane fibres from the bioreactors are presented in Figure 3-13 through Figure 3-16. Inspection of the first slide shows the unused fibre in which the membrane support material is clearly shown with smooth membrane surface topology. Referring to the second slide, Figure 3-14, the biofilm of MBR A is clearly visualized with the support material still evident. Living cells, shown in teal on the left dominate the top layer where food is abundant. The topography is rough and clusters of proteins are identifiable on the surface above the membrane. Below the top layer, carbohydrates, lipids and proteins are visualized. Dead cells are found within the depths of the biofilm, where food sources are scarce.

The support structure is not evident in the side profile of MBMBR B (Figure 3-15). A dense bio-structure consisting of living cells, lipids, carbohydrates, proteins and dead
cells is clearly visualized. As with MBR A, the living cells are primarily found on the top layer.

Figure 3-13 – 375 µm × 375 µm CLSM images of an unused membrane sample taken tangential to the fibre. From left to right: Syto 63 (total cells in teal), Nile Red (lipids in red), ConA (carbohydrates in yellow), FITC (proteins in green) and Sytox Blue (dead cells in blue).

Figure 3-14 - CLSM imaging of a fouled membrane fibre from MBR A.

Figure 3-15 - CLSM imaging of a fouled membrane fibre from MBMBR B.
Figure 3-16 presents the side profile of MBMBR C. The total thickness of the biofilm is quite substantial when compared to MBR A and MBMBR B. Referring to the far right image, Sytox blue, the dead cells approach 85 μm thick in certain regions with an average thickness of 33.3 μm. Again, clusters of polymeric substances especially proteinaceous are found within the biofilm.

Examination of biofilm thickness in MBMBR C showed the biofilm thickness after NaOCl and citric acid recovery cleaning to be 3.63±0.24 μm and 3.87±0.33 μm respectively. However, citric acid cleaning further lowered the membrane filtration resistance significantly although biofilm remained unchanged. This serves to indicate citric acid cleaning may remove inorganic foulants (i.e., struvite) and open plugged pores on membrane surfaces improving porosity whilst not diminishing biofilm thickness. The variation of biofilm thickness with respect to filtration resistance can be found in Figure 3-18.

Figure 3-17 presents CLSM images after recovery cleaning. No observable difference can be seen between membrane surfaces after NaOCl and citric acid recovery cleaning. This further supports the hypothesis that inorganic substances contribute to fouling propensity and were not able to be imaged by the five-fluorescence-dye stains used in CLSM.
Figure 3-17 - CLSM imaging of membrane fibres to show cleaning efficacy of NaOCl and citric acid.
From top to bottom: fouled MBMBR C fibre, after NaOCl recovery cleaning and after citric acid recovery cleaning

Figure 3-18 - Biofilm thickness and filtration resistance for a dirty fibre, after NaOCl recovery cleaning and after citric acid recovery cleaning
Conclusions

- Long term fouling of parallel operated ultrafiltration membranes was not controlled through the use of a moving bed bioreactor and in fact the fouling rate was more than 4 times higher in two MBMBR systems as compared to a conventional MBR system;
- Colloidal TOC was statistically significant in the rate of fouling development and was observed to be the highest in MBMBR C followed by MBMBR B;
- Carbohydrates were poorly rejected by the membrane and did not produce significant fouling propensity whereas proteins and humic acids were well rejected by the membrane (~50%) and were found to be fouling influencing substances;
- A slight correlation between colloidal TOC and humic substances ($R^2 = 0.530$) was found in all three reactors but only weakly correlated between colloidal TOC and proteins or carbohydrates;
- Biopolymer foulants including polysaccharides, humic acids, proteins and carbohydrate as well as fluorinated organic halogens associated with the membrane module functional groups were observed on membrane fibre through FT-IR spectrometry that corroborated the degrees of fouling observed in permeability tests;
- A higher degree of cake layer resistance was observed in the MBR system as compared to the MBMBR systems however a higher degree of irreversible fouling due to pore blockage and biofilm gel layer formation was observed on the two MBMBR modules;
- CLSM identified average biofilm thicknesses of 4.6±1.0 μm, 10.8±4.4 μm and 33.3±8.0 μm in fouled MBR A, MBMBR B and MBMBR C fibres respectively;
Biofilm thicknesses were proportional to fouling resistance estimated from filtration resistance analysis and absorbance measurements from FT-IR spectrophotometry.
Chapter 4 Conclusions and Recommendations

Conclusions of Results

Results obtained after close to six months of operation of a pilot scale system treating real municipal wastewater indicated that moving bed bioreactors coupled with ultrafiltration membrane separation have potential applications in advanced wastewater treatment. Although the fouling propensity was found to be over four times higher than a conventional submerged membrane bioreactor, biological nutrient removal of nitrogenous substances was significantly improved. Total nitrogen and nitrate nitrogen were continuously monitored throughout the test protocol and MBMBR systems consistently produced statistically lower concentrations. It was found that biological nitrogen removal was enhanced by the presence of anoxic micro-zones that developed in the interior regions of biofilm that developed on the surface of the suspended carrier media. Ammonia nitrogen was found to be superiorly removed in the MBR system by the oxidizing environment of the suspended growth biomass that dominated the MBR system.

A newly designed carrier was proposed and preliminary research indicates that the highly porous packing material of the interior and the hydrodynamic shell of the exterior have several advantages. Primarily, the increased sheltered surface area per unit volume allowed for a higher carrying capacity when compared to the industry standard media. Among the three sizes tested, diameters of 21 mm, 27 mm and 33 mm, 47%, 28% and 28% of the volume was utilized for biomass colonization respectively. In comparing to
the industry standard finned media in which only 18% of volume was colonized by biofilm. Furthermore, the novel media handled the mixed liquor bio-flocs more smoothly and produced a significantly higher D10 and D50 particle size when compared to the industry standard finned media.

Fouling proliferation was found to be dominated by higher concentrations of colloidal TOC, protein substances and humic acids linked to soluble microbial products. Fibre analysis using Fourier transform infrared spectrometry confirmed the presence of humic acids, polysaccharides and proteins at higher degrees on the surface of MBMBR system fibres when compared to the MBR system fibre. Furthermore, the fluorinated functional groups of the membrane were more strongly expressed in the MBR system as compared to the MBMBR systems, indicating that a higher level of surface fouling was present on MBMBR fibres preventing the penetration of the infrared frequency. Confocal laser scanning microscopy confirmed the presence of proteins and carbohydrates on the fibre surfaces and the presence of living cells, dead cells and lipids. The biofilm thicknesses were estimated using CLSM and found to be 4.6±1.0 μm, 10.8±4.4 μm and 33.3±8.0 μm in fibres from the MBR system, the MBMBR operated using the industry standard finned media and MBMBR operated using the novel media, respectively.

Permeability studies of the membrane indicated that cake layer resistance was lower in the MBMBR systems as compared to the MBR system. Alternatively, the fouling layer produced by pore blockage and gel layer formation was found to be higher in the MBMBR systems. Filtration of the lower suspended solid mixed liquor consistent with the MBMBR systems yields the lower cake layer resistance values. However, a lack of cake layer formation exposed the membrane surface to pore blockage by colloidal TOC.
present in the supernatant of the mixed liquor. The accumulation of colloidal particles led to a steady decrease in membrane permeability and the accumulation of a fouling layer. The MBR system was capable of achieving close to six months of stable operation with an average fouling rate of \(-0.12\) kPa/day. The use of chemical recovery cleaning was not required to regain permeability in the MBR. The MBMBR systems however each required a single recovery cleaning during the first 48 days of operation. The industry standard finned media MBMBR and the novel media MBMBR had fouling rates of \(-0.50\) kPa/day and \(-0.56\) kPa/day respectively.

**Future Research Potential**

Based on the results obtained from this research, there exists significant research potential in the field of MBBR systems. To reduce the mixed liquor suspended solids concentration, the solids retention time (SRT) of the suspended growth portion was intentionally shortened in the MBMBR systems. However, it has been well reported that lower SRT can lead to increased fouling potential. In future research, the MBR and MBMBR reactors should be held at equivalent SRTs to reduce confounding variables. Moreover, suspended solids concentration could be reduced further by controlling the SRT of the suspended fraction equal to the hydraulic retention time in a single pass bioreactor with external membrane filtration.

Although some influence of filling fractions has been investigated in this research, future work should focus on varying filling fraction to obtain an ideal filling fraction to (1) control membrane fouling potential and (2) improve biological nutrient removal. The 21 mm diameter media was found to yield the highest biofilm growth per unit volume.
Therefore, a reactor filled exclusively with the 21 mm media may be capable of further enhancing nutrient removal and potential fouling propensity.

Although an effort was made to analyze the fouling layer on the surface of the membrane fibre, additional imaging could improve the understanding of fouling in attached growth systems. To date, very little research is available that employed CLSM imaging, FT-IR spectrometry or even scanning electron microscopes with energy-dispersive x-ray spectroscopy to observe foulants adsorbed to membrane fibres from attached growth systems.

*Engineering Significance*

Increasing pressure exerted on marine systems from over enrichment of anthropological nutrients, in particular phosphorous and nitrogen, is leading to eutrophication in fresh water lakes and hypoxia in coastal marine systems. Significant reduction of phosphorous and nitrogen is achievable in conventional activated sludge treatment, however more stringent government regulations will require advanced wastewater treatment to meet the new effluent limits for phosphorous and nitrogen. The moving bed bioreactor examined in this research does have the potential to lower the effluent concentrations of nitrogenous substances but at the cost of increased fouling propensity. To replace conventional activated sludge operations and in order for engineers to realize the full potential of the MBBR processes, a balance between nutrient removal and fouling proliferation must be achieved. Currently, the process contains deficiencies that limit long term stable operation.
Alternatively, a significant benefit of the moving bed bioreactor process is the simplicity of retrofitting existing membrane bioreactors to the MBMBR system. With the addition of freely moving carrier media into the bioreactor and sieving screens to restrain the media, significant reduction in nitrate levels is achievable. Further to this point, the novel media, newly developed in this research, may provide a more efficient biomass carrier with respect to the quantity of media required. The improved biofilm accumulation efficiency would allow engineers to specify lower total filling fractions or further improve performance without exceeding the operable filling fraction of approximately 70%.

The responsibility of protecting sources of water and the proper allocation of scarce resources will fall on environmental engineers as municipalities face more stringent effluent limits with tightening budgetary constraints. While denitrification is achievable with the MBMBR system, increased operation expense associated with the loss of membrane permeability will limit the widespread application of hybrid moving bed bioreactors coupled with membrane filtration. Further research and development into MBMBR systems, with particular importance placed on fouling mitigation, may allow engineers to meet these constraints jointly.
Chapter 5 References


macromolecular solutions in crossflow microfiltration. *Journal of Membrane
Science, 96*, 1-58.

biological reactors: modeling and experimental study of wastewater
denitrification. *Chemical Engineering Science, 43* (10), 2715-2728.

Nitrogen, and Fisheries: Integrating effects across local and global landscapes.
*Annual Review of Marine Science, 1*, 329-349.

Brookes, A., Judd, S., Reid, E., Germain, E., Smith, S., Alvarez, H., LeClech, P.,
membrane bioreactors. *Proceedings of International Membrane Science and
Technology Conference (IMSTEC)*, Sydney, Australia.

Canziani, R., Emondi, V., Garavaglia, M., Malpei, F., Pasinetti, E., & Buttiglieri, G.
(2006). Effect of oxygen concentration on biological nitrification and microbial
kinetics in a cross-flow membrane bioreactor (MBR) and moving-bed biofilm
reactor (MBBR) treating old landfill leachate. *Journal of Membrane Science, 286*,
202-212.

Chan, Y. J., Chong, M. F., Law, C. L., & Hassell, D. G. (2009). A review on anaerobic-
aerobic treatment of industrial and municipal wastewater. *Chemical Engineering

Chang, G. R., Liu, J. C., & Lee, D. J. (2001). Co-conditioning and dewatering of


