Characterization of Anaerobic Membrane Bioreactors (AnMBR) Treating Municipal Wastewater

by

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Author’s Declaration

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

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Abstract

The study investigated the impact of solids retention time (SRT), hydraulic retention time (HRT) and the addition of $FeCl_3$ on bioprocess and membrane performance of anaerobic membrane bioreactor (AnMBR) treating authentic municipal wastewater.

The impact of SRT (40~100 days) and HRT (8.5~12.5 hours) on bioprocess performance was assessed using one pilot and one bench scale AnMBRs. The results revealed superior permeate quality with respect to concentrations of chemical oxygen demand (COD) (<40mg/L) and 5-day biochemical oxygen demand (BOD_5) (<10mg/L) can be achieved in all tests. SRT and HRT did not significantly influence on the COD and BOD_5 removal efficiencies. Extended SRTs had reduced sludge production and enhanced methane production. Oversaturation of dissolved methane in permeate was assumed to be responsible for a consistent lack of mass balance closure in all tests. After calibration of biokinetic coefficients, PetWin 4 (EnviroSim Canada) was found to effectively simulate particulate COD, readily biodegradable COD and acetic acid concentrations over a range of SRTs and HRTs.

The long term membrane performance was evaluated when pilot AnMBR operated with varied SRT (100~40 days) and recovery cleaning. The results revealed reduced SRTs had reduced the fouling propensity of mixed liquor characteristic in terms of TSS concentration and dewaterability as indicated by colloidal COD (cCOD) concentration and capillary suction time (CST). The effect of these parameters corresponded to the short term fouling (i.e. cake accumulation) that was tested by critical flux tests. The recovery cleaning obtained efficient fouling resistance removal on both pilot plant operation and clean water flux tests. However, the long-term fouling rate was observed significantly higher on cleaned membrane than virgin membrane and appeared to be higher after each recovery cleaning regardless the varied mixed liquor characteristics. The mitigated membrane fouling with virgin membrane suggested initial membrane condition might contributed to the lack of consistency between mixed liquor and fouling as the membrane properties might be modified by residual foulants.

The study on long-term (90 days) impact of dosing $FeCl_3$ on the bioprocess performance and membrane performance was evaluated in the pilot AnMBR fed with non-Fe dosed sewage and fed with 26.0 mg$FeCl_3$/L to the sewage.The results showed the addition $FeCl_3$ enhanced the treatment performance of the pilot AnMBR regarding to the removal efficiencies of COD and BOD_5, but did not generate significant influence on the removal efficiencies of total Kjeldahl nitrogen(TKN) and total phosphorus(TP) and the methane yield. The membrane performance was significantly improved by dosing $FeCl_3$ which demonstrated by irreversible fouling lower than 5kPa and no reversible fouling for the first 75 days. The superior membrane performance can be correlated to the shift of particle size distribution to the particulate fraction and the reduced colloidal and soluble substances in the sludge, especially the soluble protein, carbohydrate, Ca and S. The confocal laser scanning microscopy (CLSM) tests showed with the addition of $FeCl_3$ a thicker foulant layer was developed and the deposition of protein and carbohydrate on the membrane surface was significantly prevented. Therefore a more porous foulant layer was formed and prevented the development of strongly-attached cake layer and pore blocking. The recovery cleaning study indicated $FeCl_3$ dosing enhanced the efficiency of current recovery cleaning protocol and the foulants formed in the Fe-dosed sludge was more of inorganic origin, as 75% of the foulant resistance was removed by citric acid. The superior membrane performance during the operation combined with enhanced cleaning efficiency by $FeCl_3$ dosing would significantly improve the sustainability of AnMBR in municipal wastewater treatment.

A transient study was conducted at pilot scale to assess the impact of Fe dosage on the dynamics of biological and membrane performance of the AnMBR. A transient model of the AnMBR system was employed to assist with interpretation of the measured responses in the mixed liquor under different $FeCl_3$ dosages. A high dosage (43mg/L) of $FeCl_3$ resulted in a significant accumulation of fixed suspended solids (FSS) and volatile suspended solids (VSS) and reduction of colloidal COD in the mixed liquor. The elevated dosages appeared to reduce the biodegradability of VSS that was present in the raw wastewater. Intermediate dosages of $FeCl_3$ (21-12 mg/L), had less effect on these responses and did not appear to affect VSS biodegradation. Membrane performance was significantly affected by $FeCl_3$ dosage as indicated by reversible and irreversible resistances. Reversible resistance was closely related to the colloidal COD in the mixed liquor, thus responded quickly to Fe dosage. Irreversible resistance had a delayed response to changes in the colloidal COD concentrations in the mixed liquor and this was attributed to the effect of slow mass transfer of colloidal matter between the mixed liquor and the membrane.

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I thought this part could be the easiest part to write, but it turned out to be the most difficult one because I am so grateful to have those people to make this thesis happen that I am so lost in my mind finding appropriate words to fully express my appreciation.

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Nomenclature

AD	Anaerobic digester
AnMBR	Anaerobic membrane bioreactor
ANOVA	Analysis of variance
BOD	Biological oxygen demand
BSA	Bovine serum albumin
C/P	Mass ratio of carbohydrate to protein
CA	Cleaning efficiency with citric acid
CE_{Total}	Total Cleaning Efficiency
CFV	Cross flow velocity
CLSM	Confocal laser scanning microscopy
COD	Chemical oxygen demand
pCOD	Particulate COD
cCOD	Colloidal COD
lcCOD	Large colloidal COD
fcCOD	Fine colloidal COD
sCOD	Soluble COD
rbCODc	Readily biodegradable COD (complex)
CST	Capillary suction time
CSTR	Completely Stirred Tank Reactor
CWF	Clean Water Flux
EDTA	Ethylenediaminetetraacetic acid
EPS	Extracellular polymeric substances
FSS	Fixed suspended solids
HRT	Hydraulic retention time
IR	Irreversible resistance
K_h	Hydrolysis rate coefficient (anaerobic reduction factor applied)
k_m	Aceticlastic Methanogenesis rate coefficient
K_X	Hydrolysis saturation coefficient
K_{fe}	Fermentation saturation coefficient
K_s	Aceticlastic Methanogenesis saturation coefficient

Nomenclature (continued)

LMH	Liter per square meter per hour
ML	Mixed Liquor
MT	Membrane tank
MWCO	Molecular weight cut off
OHO	Ordinary Heterotroph Organism
q_{fe}	Fermentation rate coefficient
Q	Influent flow
Q_w	Waste sludge flow
r_T	Rate coefficient at temperature of T
r_{20}	Rate coefficient at temperature of 20ºC
R_T	Total fouled membrane resistance
R_M	Virgin membrane resistance
R_{re}	Fouling resistances removed by recovery cleaning
R_{ir}	Fouling resistance not removed by the recovery cleaning
R_{ca}	Fouling resistances removed by citric acid and NaOCl
R_{NaOCl}	Fouling resistances removed by NaOCl
RR	Reversible resistance
PLC	Programmable logic controller
PVDF	Polyvinylidine fluoride
SD	Standard deviation
SEM	Scanning electron microscopy
SH	Cleaning efficiency with NaOCl
SMP	Soluble microbial products
SRT	Solid retention time
TKN	Total Kjeldahl nitrogen
TMP	Trans-membrane pressure
TMP(b)	TMP before Relaxation
TMP(a)	TMP after Relaxation
TMP(b-a))	Difference between TMP(b) and TMP(a)
TP	Total phosphor

Nomenclature (continued)

TS	Total soilds
TSS	Total suspended solids
TTF	Time to filter
UASB	Upflow anaerobic sludge blanket
V	Reactor volume
VFAs	Volatile fatty acids
VSS	Volatile suspended solids
X_{AD}	Concentration of particulate in reacto
X_0	Concentration of particulate in influent

Chapter 1

Introduction

1.1 Background

There is an increasing interest in developing wastewater treatment technologies that are sustainable. Anaerobic membrane bioreactors (AnMBRs) will likely play a significant role in the future as the anaerobic process has low energy and nutrients requirements, low sludge production and can generate biogas that can be directly employed as an energy source. The use of membranes for biomass separation can provide long solids retention times (SRTs) that are required to offset the low growth rates of anaerobic organisms while also producing a solids-free effluent (Beaubien et al., 1996; Liao et al., 2006; Huang et al., 2011). The low hydraulic retention times (HRTs) that can be achieved should help ensure the economical viability of the AnMBRs. Therefore AnMBR is a promising technology for municipal wastewater treatment.

Several previous studies have examined AnMBRs for municipal wastewater treatment with regard to treatment performance and membrane performance (Hu and Stuckey 2006; Ho and Sung, 2009; Lew et al., 2009; Gimenez et al., 2011; Huang et al., 2011; Salazar-Pelaez et al., 2011; Gao et al., 2014; Huang et al., 2013). The treatment performance responses have been reported include TSS concentration, effluent COD/BOD$_5$ and methane production. Membrane performance typically refers to membrane fouling and has been found to be impacted by mixed liquor characteristics such as TSS concentration, colloidal substances concentration, total and individual concentrations of EPS and SMP. Both treatment performance and membrane performance can be modified by operational conditions, such as SRT, HRT and addition of coagulants. Therefore, the effects of these parameters on the performance of AnMBR should further examined. Furthermore, an optimization of these parameters is needed to reach superior bioprocess and membrane performance simultaneously.

In the review of the literature on the performance of AnMBRs, the following issues were identified 1) the effect of SRT and HRT on anaerobic bioprocess and membrane performance is still unclear when treating authentic municipal wastewaters; 2) Most membrane cleaning tests have been conducted with bench scale AnMBRs and the results were obtained with clean water tests or with mixed liquor in short term. Long-term performance of cleaned membranes in pilot AnMBR has not been reported; 3) The addition of $FeCl_3$ has been demonstrated to mitigate membrane fouling in aerobic MBRs. Their effects on membrane fouling in AnMBR treating municipal wastewater had not been reported.

1.2 Purpose

To solve the stated problems, the proposed study aimed to: 1) investigate the effect of SRT and HRT on anaerobic bioprocess; 2) evaluate the effect of SRT and recovery cleaning on long-term membrane performance; 3) evaluate the addition of $FeCl_3$ on long-term bioprocess and membrane performance; 4) dynamically evaluate the effects of $FeCl_3$ dosage on anaerobic bioprocess and membrane performance.

1.3 Scope

The study was carried out using one pilot scale and one bench scale AnMBR located at the Wastewater Technology Centre (Science and Technology Branch of Environment Canada), in Burlington, Ontario. The municipal wastewater came from the Burlington Skyway Wastewater Treatment Plant. The research proposed is unique with respect to the use of AnMBR for authentic municipal wastewater treatment and developing protocols of AnMBR operation. The lessons learned from this research may assist municipalities operating full scale AnMBRs and considering upgrades to AnMBR with particular attention to enhancing the sustainability of the AnMBR with regard to the high quality effluent and fouling mitigation.

1.4 Thesis Structure

This thesis is divided into seven chapters, a glossary of relevant terms and references. Chapter 1 provides a brief introduction to the problem under investigation and the purpose of the research. Chapter 2 provides a review of the literature describing the impact of HRT and SRT on AnMBR treating municipal wastewaters and the impact of

$FeCl_3$ dosing on the membrane fouling management in aerobic MBR. In Chapter 3 the impact of SRT and HRT on bioprocess performance of AnMBR was investigated and a PetWin model was calibrated to simulate the anaerobic processes in AnMBR. Chapter 4 presents the impact of SRT and recovery cleaning on the long-term membrane performance. Chapter 5 assessed the addition of $FeCl_3$on the long-term bioprocess and membrane performance of pilot AnMBR. Chapter 6 dynamically characterized the responses of bioprocess and membrane performance to varied dosages of $FeCl_3$. The conclusions as well as recommendations for further research are stated in Chapter 7.

Chapter 2

Literature Review

The Anaerobic Membrane Bioreactor (AnMBR) process is a wastewater treatment technology that combines anaerobic suspended-growth biological treatment with membrane filtration. AnMBRs will likely play a significant role in wastewater treatment in the future as the anaerobic process has low energy and nutrients requirements, low sludge production and can generate biogas that can be directly employed as an energy source. The use of membranes for biomass separation can provide long solid retention times (SRTs) that are required to offset the low growth rates of anaerobic organisms while also producing a solids-free effluent (Liao et al., 2006; Adam et al, 2012). In addition low hydraulic retention times (HRTs) can be achieved to ensure the economical viability of the AnMBRs. Therefore AnMBR is a promising technology for municipal wastewater treatment. However, study on the bioprocess and membrane performance of AnMBRs for authentic municipal wastewater is relatively limited, as compared with aerobic MBRs.

2. 1 Anaerobic Bioprocess Performance of AnMBR

The literature with respected to bioprocess performance of AnMBRs was evaluated in terms of TSS concentration, effluent quality and methane production. Table 2-1 summarizes recent research on the bioprocess performance of AnMBRs for both synthetic and municipal wastewater treatment with varied SRT or HRT. From Table 2-1 it can been seen that extended SRTs (30-100 days or infinite)have been found to result in elevated TSS concentrations(6~13 g/L) due to growth of biomass and increased retention of suspended solids (Ho and Sung, 2009; Baek et al., 2010; Huang et al., 2011; Huang et al., 2013). In a study of the impact of SRT on AnMBR performance, the permeate COD concentrations were reduced from 16.5 to 5 mg/L and methane yields increased from 0.12~0.25 L CH_4/g COD (Huang et al., 2011) when the SRT was increased from 30 days to infinite. Therefore, extended SRT have been found to improve the bioprocess with regard to effluent quality and methane yield.

HRT significantly affects the AnMBR bioprocess performance. From Table 2-1 it can been seen that areduction in HRT from 12 to 3 hours resulted in an increase of TSS concentration from 6 to 22 g/L due to the high organic loading enhancing growth of biomass (Ho and Sung, 2009; Huang et al., 2011; Gimenez et al., 2011). The permeate COD concentration was observed to increase from 10 to 50 mg/L as HRT decreased (Hu and Stuckey 2006; Salazar-Peláez, et al., 2011). It has been suggested that lower HRTs decrease the contact time between microorganisms and substrate, allowing a part of the influent COD to leave the reactor without proper treatment (Liao et al., 2006). However, the methane production was enhanced by increased organic loading with reduced HRT. Therefore, HRT should be optimized on the basis of effluent quality and costs of construction and maintenance.

Based upon the literature reviewed in this section it is apparent that AnMBR is a promising technology for municipal wastewater treatment when operated with proper HRT and SRT. However, the impact of SRT and HRT was evaluated with regard to concentrations of components in mixed liquor and most studies employed synthetic wastewater. The effects of SRT and HRT on AnMBR treating authentic municipal wastewaters in terms of distribution of fed COD mass and anaerobic process biokinetics are still unclear. Hence there is a need to evaluate these impacts and further understand the role of SRT and HRT in AnMBR bioprocess to discover an optimal combination of HRT and SRT for a successful AnMBR operation.

Table 2-1 Anaerobic Bioprocess Performance in AnMBR Treating Municipal Wastewater

Type of Municipal WW	Scale/ Membrane module	Type of Reactor[a]	Volume (L)	Operation Time (day)	Temp (^oC)	SRT (d)	HRT (h)	Digester TSS (g/L)	Effluent COD (mg/L)	Biogas Production	Reference
Municipal WW COD:280~360mg/L	Bench/ Hollow Fiber	(IAFMBR)	5.8	160	35	-	8, 6, 4	-	13, 22,50	0.14~0.19L CH_4/g COD	Gao et al., 2014
Municipal WW COD:366~486mg/L	Bench/ Hollow Fiber	CSTR	6	40	25~30	30,60,90	10	8.0,12.6,12.7	47~73 (No impact by SRT)	0.04, 0.09, 0.10L CH_4/g COD	Huang et al., 2013
Synthetic (COD 513mg/L)	Bench/ Hollow Fiber	Upstream anaerobic bioreactor+AFMBR	10.64	120	35	-	4.2-5	11.6(TSS)	3~11	0.17LCH_4/g COD	Kim.et al., 2011
Synthetic (COD 550 mg/L)	Bench/ plate and frame	CSTR	6	150	25~30	30,60, infinite[b]	8,10,12	5.5-10.5	5.5~16.5	0.12~0.25 L CH_4/g COD	Huang et al., 2011
Pre-settled Sewage (sCOD 38~131)	Bench/ -	CSTR	10	440	-	19~217	12~48	1~7	sCOD 14~51	No gas production	Baek et al., 2010
Synthetic (OLR1~2kg/m3/d)	Bench/ Tubular	CSTR	4	270	25	90~360	6~12	6~11	10~40	0.22L CH_4/gCOD	Ho and Sung., 2009
Municipal WW (0.5mm screened COD: 350~540mg/L)	Full/Hollow Fiber	CSTR	2100	140	33	70	6~21	8~22	44~100	0.069L CH_4/gCOD	Gimenez et al., 2011
Pre-settled Sewage (COD 540mg/L)	Bench/Hollow fiber	CSTR	180	365	25	-	4.5, 6, 12	14~80 (TS)	65	-	Lew et., al 2009
Synthetic (COD 440~480 mg/L)	Bench/Hollow fiber and flat sheet	CSTR	3	100	35	-	48,24,12,6,3	Around 4 (TSS)	<50 (COD increasing with HRT decreasing)	0.22~0.33L CH_4/gCOD	Hu and Stuckey., 2006
Municipal WW (COD: 337~459mg/L)+ glucose=total COD (548~712)	Pilot/flat sheet	CSTR	350	100	35	-	~16.5	15	COD<80 BOD<25	0.2~0.25L CH_4/gCOD	Martinez-Sosa et al.,2011
Synthetic (COD340~260 mg/L)	Bench/tubular	UASB	12.5	-	-	-	4,8,12	-	40~65, (COD increasing with HRT decreasing)	-	Salazar-Peláez, et al., 2011

a: IAFMBR:Integrated anaerobic fluidized-bed membrane bioreactor AFMBR indicates anaerobic fluidized bed bioreactor; UASB: upflow anaerobic sludge blanket reactor; CSTR: completely stirred tank reactor

b: infinite indicates no sludge wasting

-: not indicated

2. 2 Membrane performance of AnMBR

Despite the obvious advantages of AnMBR processes, such as high effluent quality, their application has been limited due to membrane fouling, which reduces permeate flux, increases feed pressure, decreases product quality and ultimately shortens membrane life (Choo et al., 2000). Consequently, membrane fouling increases the costs by increasing (1) energy consumption, (2) system down time, (3) necessary membrane area, and (4) construction, labor, time, and material costs for backwashing and cleaning processes. Hence membranes in wastewater treatment are not only operated for maximum permeate production, but also to minimize the fouling. Therefore the analysis of AnMBR technology should also address membrane performance to establish a balance between permeate flux and membrane fouling for sustainable operation.

In the literature review membrane performance was evaluated in terms of trans-membrane pressure (TMP) and its increase with time (fouling rate). The components in the mixed liquor that have been indicated to cause fouling include TSS concentration, and total concentration and individual composition concentrations of EPS and SMP (Table 2-2). The TSS concentration has been identified as a key factor in membrane fouling. In general, high TSS concentrations have been reported to increase membrane fouling (Liao et al., 2006; Huang et al., 2011). It is believed that an increase in the suspended solids concentration increases the convective flow of solids towards the membrane surface and enhances cake formation and fouling. Therefore, TSS concentrations should be maintained low to mitigate membrane fouling.

EPS and SMP have also been determined to be significant foulants affecting membrane permeability (Huang et al., 2011). The presence of EPS has been found to increase membrane fouling in AnMBR treating municipal wastewater (Zhang et al., 2010) since EPS is associated with cake layer formation on the membrane surface. Furthermore, the presence of EPS has been reported to physically stabilize biofilms thereby protecting them from routine cleaning cycles (He et al., 2005). However, Huang et al. (2011) reported negative or zero effects of EPS on membrane fouling when cross flow velocity (CFV) and a discontinuous filtration mode were employed to mitigate the deposition of

EPS on a membrane surface. Therefore, it might be expected SMP will have more influence on membrane fouling than EPS when sufficient CFV is supplied.

Membrane fouling in AnMBR treating municipal wastewater has been reported to increase with SMP concentration (Zhang et al., 2010; Huang et al., 2011). SMP concentrations that have been reported in the literature are those that remain after filtering the mixed liquor through a filter (1.5 or 0.45µm) and can consist of organic matter that is either released into solution from substrate metabolism and biomass decay or may be present in the influent sewage. Based on the pore size of the filter, SMP may contain not only soluble matter but also some fine colloidal matter which are able to adsorb on either the membrane surface or inside the pores due to its small size (Herrera-Robledo et. al. 2011). Once attached on the membrane surface or in the membrane pores, SMP can generate significant fouling resistance (Liao et al., 2006) that would not be removed by CFV or discontinuous filtration modes but could be removed by chemical cleaning. SMP also reduces the cake porosity by filling the void spaces between the cell particles in the cake layer thereby increasing the fouling resistance (Ye et al., 2005; Shin et al., 2002; Nagaoka et al., 1998; Lee et al., 2003; Menget al., 2006; Jeong et al., 2010). Therefore, the concentrations of SMP and EPS should be maintained low to achieve sustainable membrane performance.

SRT and HRT had been reported to significantly affect membrane performnce. From Table 2-2 it can be observed that TMP has been reported to be related to HRT and SRT (Hu and Stuckey, 2006; Lew et al., 2009; Huang et al., 2011). Shorter HRT values (4-16 hours) were found to result in an increase in fouling rate from 0.22 to 0.83kPa/day (Lew et al., 2009). A longer SRT (30-140 or infinite days) also led to an increase in fouling rate from 0.05 to 0.66 kPa/day (Huang et al., 2011). The impact of SRT and HRT on fouling can be attributed to the fact that SRT and HRT control the extent of accumulation and/or production of foulants (i.e. TSS and individual and total concentrations of EPS and SMP) in the mixed liquor. Therefore, the impact of SRT and HRT on membrane fouling can be concluded as indirect and there is a need to optimize SRT and HRT to mitigate fouling and achieve superior bioprocess performance simultaneously.

Most reports of the impact of HRT and SRT on bioprocess and membrane performance upon HRT or SRT have been conducted at bench scale and have employed synthetic municipal wastewater (Ho et al., 2007; Hu and Stuckey, 2006; Gimenez et al., 2011; Martinez-Sosa et al., 2011). It is expected that the bioprocess performance and mixed liquor characteristics causing fouling in AnMBR fed with synthetic municipal wastewater would be different from that fed with authentic municipal wastewater as the synthetic municipal wastewaters typically did not contain non-biodegradable organic matter. Furthermore, fouling behavior in bench scale AnMBR has been reported to be different from pilot AnMBR due to the lower pressure drops in the membrane of bench AnMBR (Chang, 2011). Therefore there is a need to evaluate the effects of these operational conditions at pilot scale treating authentic municipal wastewater.

The operating temperatures of AnMBRs should be carefully selected as it will impact on the activity of microorganisms, solubility of methane (Smith et al., 2012) and the viscosity of mixed liquor (Cui et al., 2003; Martinez-Sosa et al., 2011). From Table 2-1 and Table 2-2, prior studies have typically been conducted at temperatures that ranged from 25ºC to 35ºC. This temperature range is higher than that observed in areas with significant seasonal variation in temperature. It is clear that from the perspective of practical application, the operating temperature in AnMBR studies needs to be lowered to emulate temperatures in many wastewater treatment plants.

Table 2-2 Membrane Performance in AnMBR Treating Municipal Wastewater

Type of WW	Operation Time (day)	Pore Size (μm)	Surface Area (m^2)	TMP (kPa)	Flux (LMH)	HRT (h)	SRT	Tem. (ºC)	TSS (g/L)	Mean Particle size in reactor (um)	SMP	EPS	Reference
Municipal WW COD:280~360mg/L	160	0.4	0.19	0.5, 1.2,2.0kPa/d with reduced HRT	11	4,6,8	-	35	-	-	Increased with reduced HRT	Same as SMP	Gao et al., 2014
Municipal WW COD:366~486mg/L	40	0.45	0.118	Highest at SRT=30d Lowest at SRT=60d	5	10	30,60,90	35	6.0~10 with increased SRT	Largest at SRT=30d Smallest at SRT=60d	Lowest at SRT=60d Highest at SRT=30d	Highest at SRT=30d Similar between SRT= 60 and 90d	Huang et al., 2013
Municipal WW (0.5mm screened COD: 350~540mg/L)	140	0.05	30	<10	10	6	70	33	22 (TS)	-	-	-	Gimenez et al., 2011
Synthetic (550 COD mg/L)	150	-	0.118	Varied with HRT and SRT	5.3-7.9	8,10,12	30, 60 infinite	25~30	5.5-10.5	Varied with HRT and SRT[a]	Varied with HRT and SRT[b]	Varied with HRT and SRT[c]	Huang et al., 2011
Synthetic (COD 513mg/L)	120	0.1	0.091	6~27	7-10	4.2-5	-	35	11.6(TSS)	-	-	-	Kim et al., 2011
Synthetic (COD340~260 mg/L)	-	MWCO 100k dalton	-	Constant TMP at 103.35kPa	~38	4,8,12	-	-	-	-	220, 170 and 150mg/L respectively at 4, 8, 12 hours HRT	~40mg/L in UASB effluent at all HRT conditions	Salazar-Peláez, et al., 2011
Sewage (COD159~500mg/L)	100	61	8	0-25 Slowly increased time	65	8	-	10~15	5.9~19.8 (VSS)	85.9-107.7	Varied with operation time[d]	Varied with operation time[e]	Zhang et al., 2010
Pre-settled Sewage (COD 540mg/L)	365	0.2	4	Varied with flux[f]	3.75, 7.5 and 11.25	4.5, 6 and 12	infinite	25	14~80 (TS)	-	-	-	Lew et al., 2009
Synthetic (COD 440~480 mg/L)	100	0.4	0.1	Varied with membrane module and flux[g]	1.25, 10, 15	48,24,12, 6,3	-	35	Around 4 (TSS)	60-65	-	-	Hu and Stuckey., 2006

a: The mean particle size increased from 34.8 to 76.2um (8-hour HRT) and from 43.7 to when SRT decreased from infinite to 30 days; when HRT decreased from 10 to 8 hours, the mean particle size decreased from 80.3 to 76.2 um (30-day SRT) and from 43.7 to 39.7 um (60-day SRT), while increased from 29.7 to 34.8 um (infinite SRT)

b: The carbohydrate concentrations of SMP were rather similar at HRT of 8, 10 and 12 h, the absolute protein concentration was decreasing and C/P was increasing with increasing in HRT; both carbohydrate and protein in SMP and C/P increased with increasing in SRT from 30 day to infinite.

c: The carbohydrate, protein and C/P in EPS decreased with increasing in HRT and SRT respectively

d: SMP increased from 0-1.2 g/m^2 on the membrane surface while decreased from 49-18 mg/g VSS in the sludge within 90-day operation

e: EPS increased from 0.7-5.4g/m^2 on the membrane surface while decreased from 270-65mg/g VSS in the sludge within 90-day operation

f: TMP was less than 15kPa within first 67 days, then jumped to 26kPa in 8 days when HRT was 12 hours (3.75 LMH); TMP was less than 15kPa within first 50 days, then jumped to 35kPa in 12 days when HRT was 6 hours (7.5LMH); TMP was less than 15kPa within first 18 days, then jumped to 26kPa in 7 days when HRT was 4.5 hours (11.25LMH);

g: 15 LMH with TMP of 49kPa for hollow fiber and 39kPa for flat sheet; 10 LMH with TMP of 38 kPa for hollow fiber and 28 kPa for flat sheet; 1.25 LMH with TMP of 8kPa for hollow fiber and 2kPa for flat sheet.

The addition of $FeCl_3$ to the mixed liquor of MBRs has been reported to effectively reduce the rate of membrane fouling. Table 2-3 summarizes studies that employed $FeCl_3$in aerobic MBRs for wastewater treatment. In most cases the tests were conducted in a jar-test apparatus for mixing the $FeCl_3$ with the mixed liquor and a bench scale filtration apparatus to test short-term membrane performance. These studies have shown that the optimal dosage of $FeCl_3$ have ranged from 8.5 to 121mg/g TSS. Compared with the original mixed liquor (no dosage), the fouling rate was reduced 53%-96% and the critical flux increased 14-46%. The improved membrane performance has been attributed to increased particle size and dewaterability and decreased viscosity and SMP. However, there is limited information in the literature on the impact of $FeCl_3$ on mixed liquor characteristics and long-term membrane performance in continuously operated pilot AnMBRs.

Table 2-3 Summary of Prior Studies of the Impact of $FeCl_3$ Addition on Aerobic Membrane Fouling

Optimal dosage ($mgFeCl_3/gTSS$)	Mixture protocol	SMP	Particle size	Fouling rate	Critical flux	dewaterability	Nutrient removal	Reference
Fe:P molar ratio at 4.8:1 in sewage	-	As TOC reduced from 12 to 5mg/L	-	Reduced from 1.0 to 0.7kPa/d	-	-	Effluent TP reduced from 6.4 to 0.3mg/L	Wang et al., 2014
121	-	10.5 (no dosage) - 8 mg/L(optimal dosage)	160 µm(no dosage) - 195 µm(optimal dosage)	Reduction rate 70.6%	-	-		Ji et al., 2010
8.5	Shaking for 1 hour at 20ºC and a frequency of 130 min-1	Removal efficiency 36%			Improvement 14%			Koseoglu et al., 2008
100	Stirring 5 min at a speed of 150 rpm and then stirring another 5 min at 30 rpm.	-	-		Permeate flux 50 (no dosage) - 100LMH (optimal dosage)		TP removal (no dosage) - 100LMH (optimal dosage)	Song et al., 2008
39.4	-	relatively similar	75 µm(no dosage) - 87 µm(optimal dosage)	Reduction rate 53%				Zhang et al., 2008
29.1-59.3	Stirring at 250 r/min for 1 minute, followed by a slow mixing at 70 r/min for 15 minutes	Colloidal TOC 19 (no dosage) - 7.5 mg/L(optimal dosage)	70 µm(no dosage) - 80 µm(optimal dosage)			TTF 160 (no dosage) - 70s (optimal dosage)		Fan et al., 2007
800mg/L influent	Stirring vigorously for 1 minute after adding the coagulant solution, and then were stirred gently for 15 minutes.	Supernatant COD reduced from 3300 to 2125 mg/l	TSS reduced from 260 to 45.6mg/L and 173 to 141 mg/Lin influent and anaerobic digester respectively					Song et al., 2001

As previously described, SRT and HRT conditions and the addition of $FeCl_3$have been found to influence membrane fouling by modifying the mixed liquor characteristics, but in all cases fouling will occur and will eventually increase to a level that is unsustainable for operation. At this time recovery cleaning has been found to be required to remove strongly-attached foulants from the membrane. Typically recovery cleaning removes foulants by soaking the membrane in a chemical solution. The cleaning agents (chemicals) may react chemically or physically with the foulant, to weaken the cohesion forces between the foulants themselves and the adhesion between the foulants and the membrane surface. Efficient recovery cleaning has been found to be critical for long term sustainable membrane performance in AnMBR.

Table 2-4 summarizes prior studies of the use of cleaning agents in AnMBRs and the cleaning agents that are recommended for use in MBRs by membrane suppliers. As can be seen in Table 2-4 the cleaning agents employed in AnMBR have included acids, bases, oxidants and chelants. Acidic and chelant cleaning has been extensively used to remove inorganic foulants, cleaning with bases, oxidants and caustic hypochlorite have been used to remove organic foulants (Le-Clech et al., 2006). Sequential cleaning with 2 agents has been commonly employed in both research studies and in practice and has been found to achieve higher permeability improvement than the use of individual agents. From Table 2-4 it can be seen that manufacturers recommend extended cleaning durations (2-24 hours) with typical reagent concentrations of 2–5g/L NaOCl coupled with 10–15mM/L citric acid or 50–100mM/L oxalic acid, and the cleaning is normally carried out once or twice a year. However, researchers have employed relatively lower cleaning concentrations, shorter cleaning duration, more types of cleaning agents, and have observed resistance removal of 70-86%. Research studies have typically conducted recovery cleaning once the TMP exceeded 25 or 40 kPa. However, the impact of cleaning has typically been assessed by filtering clean water or mixed liquor for short time periods in bench scale AnMBRs. The long-term performance of cleaned membranes in pilot AnMBR has not been reported.

Table 2-4 Summary of chemical cleaning in AnMBR

Agent (concentration)	Cleaning duration	Cleaning frequency	Cleaning effect	Performance of Cleaned membrane	Reference Or Membrane supplier
Sequentially NaOCl (1g/L) and NaOH(10mM/L)	1 hour for each step	Approximately every 40 days (Day 55 and 82 when TMP exceeded 25kPa)	TMP decreased from 25 to 8kPa (resistance removed by 70%	Increased from 8 to 25kPa in 5 days	Kim et al.,2011
NaOH(100mM/L)+HCl(270mM/L) +H_2O_2(10g/L)	-	-	Resistance removal: 75%	-	Lew et al., 2009
NaOCl (0.3g/L)	20min	20 min in every 6 hours filtration	-	-	Salazar-Peláez et al., 2011
Sequentially HNO_3 (10mM/L) and EDTA (0.5%)	1 h for each step at 50ºC	After operating for 135 days	Fouling Resistance removed by 86 %	-	Zhang et al. (2007)
Sequentially NaOCl (3g/L) and Citric acid (10mM/L)	2-24 hours	Once or twice per year	-	-	Mitsubishi
Sequentially NaOCl (5g/L) and Oxalic acid (100mM/L)	2-24 hours	Once or twice per year	-	-	Kubota

- not indicated

2.3 Summary of literature review

On the basis of the literature reviewed it has been found that the use of AnMBR is feasible for low-strength wastewater treatment and may be as capable as aerobic MBR for the removal of COD/BOD, if the system is operated under appropriate HRT (4-48 hours) and SRT (30-140 days or infinite) conditions. In addition, anaerobic processes have several inherent merits, including low sludge production, potential for bioenergy generation, and savings in the aeration energy cost. Hence in municipal wastewater treatment plants employing separate stage nitrification/denitrification, an AnMBR may be both feasible and economical. However, the literature reported limited information on the effect of HRT and SRT on bioprocess performance and membrane performance.

Membrane fouling, the main operational issue, has been found to be significantly governed by mixed liquor characteristics, which include the TSS concentration, formation of EPS and SMP and particle size. As the mixed liquor characteristics are mainly controlled by HRT, SRT and can be modified by dosing $FeCl_3$, these three factors can influence fouling.

Recovery cleaning has been conducted to remove foulants and recover membrane permeability. Sequentially soaking in citric acid and NaOCl has been commonly employed in recovery cleaning due to demonstrated ability to remove fouling resistance in short term filtration tests in bench scale systems. However, the long term performance of cleaned membranes in pilot AnMBR has not been reported. Hence it identified that further investigation of long-term membrane performance in pilot AnMBR treating authentic municipal wastewater is needed.

Therefore, the current study sought to systematically investigate 1) the impact of HRT and SRT on anaerobic digestion and membrane fouling; 2) reveal the impact of recovery cleaning on long-term membrane performance in AnMBR treating municipal wastewater; 3) investigate the impact of addition of $FeCl_3$ on mixed liquor characteristics and reveal its effect on membrane fouling in pilot AnMBR.

Chapter 3

Influence of SRT and HRT on Bioprocess Performance in Anaerobic Membrane Bioreactors Treating Municipal Wastewater

Key Words: HRT, SRT, Municipal Wastewater, Biokinetics

3.1 Introduction

Anaerobic membrane bioreactors (AnMBRs) may be a sustainable wastewater treatment technology because of low energy and nutrient requirements, low sludge production and the potential to generate biogas. The integration of membrane modules into the anaerobic bioreactor (Pierkiel and Lanting, 2005; Liao et al., 2006) enables the slow-growth biomass to be retained in the bioreactor, thus enhancing the anaerobic process. Therefore, AnMBRs are becoming increasingly popular for wastewater treatment.

SRT has been reported to be an important operational parameter in AnMBR. In AnMBRs that were fed with synthetic wastewaterand operated with extended SRTs (30-100 days or infinite) elevated TSS concentrations(5-15 g/L)have been reported and this was attributed to enhanced growth of biomass and increased retention of suspended solids (Hu and Stuckey, 2006; Lew et al., 2009; Zhang et al., 2010; Huang et al., 2011). In one study permeate COD concentration were reported to be reduced from 16.5 to 5 mg/L and methane yield was reported to increase from 0.12~0.25 L CH_4/g COD (Huang et al., 2011) when the SRT was increased from 30 days to infinite. Therefore, extended SRTs have been found to result in improved effluent quality and methane yield.

HRT has also been reported to affect AnMBR bioprocess performance. It has been reported that in AnMBR fed with synthetic wastewater the reduction of HRTfrom12 to 3 hours resulted in an increase in TSS concentration from 6 to 12 g/L due to the increase in organic loading that enhanced growth of biomass (Hu and Stuckey, 2006; Ho and Sung, 2009). However, the permeate COD concentration was observed to increase from 10 to

50 mg/L) as HRT decreased (Hu and Stuckey 2006; Salazar-Peláez, et al., 2011). It has been suggested that lower HRTs decrease the contact time between microorganisms and substrate, allowing a part of the influent COD to leave the reactor without proper treatment (Liao et al., 2006). Therefore, the HRT selected for use in AnMBRs should be optimized on the basis of effluent quality and costs of construction and maintenance.

Based upon the literature reviewed it is apparent that the bioprocess performance of AnMBR is significantly affected by SRT and HRT. However, their impact on AnMBR treating authentic municipal wastewaters has not been reported. Authentic wastewaters contain a complex mixture of biodegradable and non-biodegradable components that are present in both soluble and insoluble forms. Hence the objective of this study was to characterize the impact of HRT and SRT on the bioprocess performance of AnMBRs treating authentic municipal wastewaters.

3.2 Materials and Methods

A pilot scale AnMBR and a bench scale AnMBR with similar configurations (Figure 3-1) were fed with 3 mm screened sewage from the Burlington Skyway Wastewater Treatment Plant (Ontario, Canada). A detailed description of the design and operating parameters of the AnMBRs is presented in Table 3-1. The pilot and bench scale AnMBRs had common operating and control equipment. The AnMBRs consisted of completely mixed anaerobic digesters (AD) and separate membrane tanks (MT). The MT held a polyvinylidine fluoride (PVDF) hollow fibre membrane module. The fibres had length of 1.2m (pilot) and 0.4m (bench) and a diameter of 1.9mm (outer) and 0.8mm (inner). The AD contents were mixed by recirculation of the contents with positive displacement pumps. In addition the AD contents were circulated through the MT using a centrifugal pump that withdrew mixed liquor from the bottom of the AD and pumped it to the bottom of the MT after which it flowed to the top of the AD by overflow. This circulation mixed the MT contents and generated a cross flow velocity (CFV) that would enhance surface shear for membrane fouling control. Biogas produced in the AD was released from the head space of the AD and its production was measured by a gas flow meter (Aalborg

GFM17). Biogas was recirculated through the MT with a blower to reduce membrane fouling.

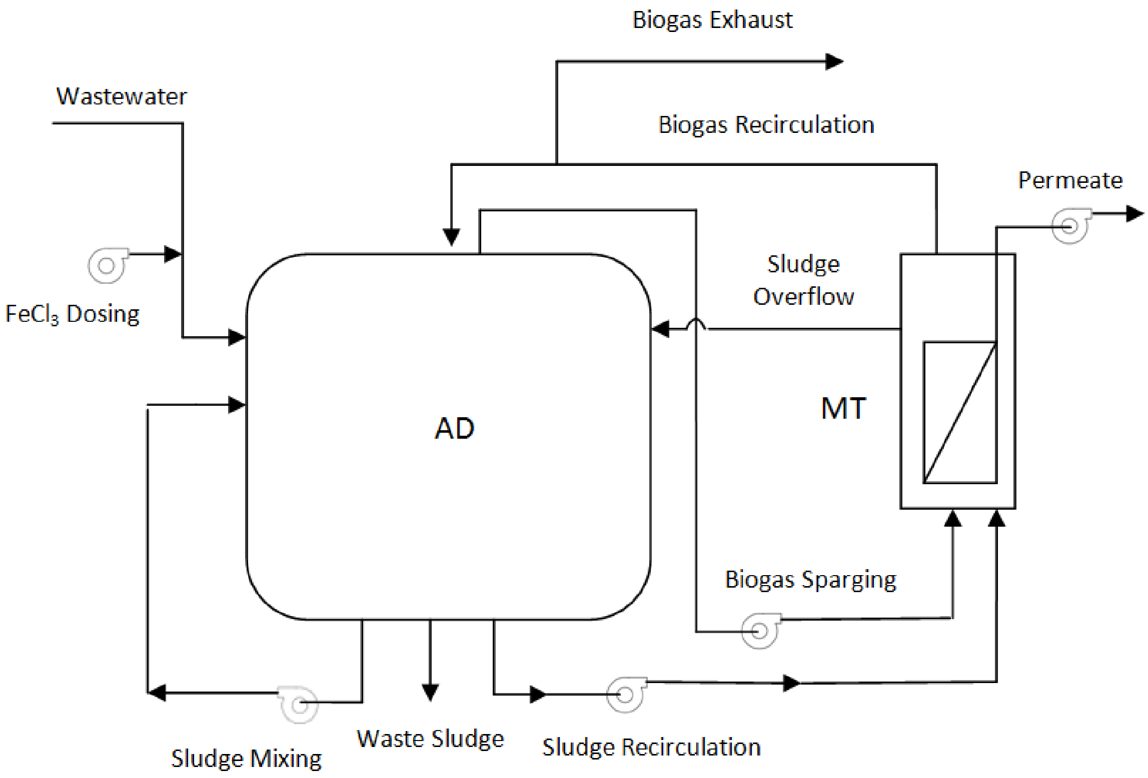


Figure 3-1 Schematic of AnMBR System

The pilot and bench scale AnMBRs were operated at identical condition as described below. Throughout the study a concentrated $FeCl_3$ solution (7.4% w/w) was dosed into the influent to achieve 26mg $FeCl_3$/L in both pilot and bench scale AnMBRs. The temperature of the AD was maintained using heat tape that was controlled by temperature controllers which were informed by temperature sensors in the digesters. To buffer the decrease in pH associated with the dosed $FeCl_3$, the pH of the ADs was controlled through $NaHCO_3$ addition that was informed by pH sensors in the digesters. The operation and data acquisition were controlled using a programmable logic controller (PLC). The feeding of raw sewage and the wasting of anaerobic digester contents for SRT control were controlled on the basis of the weight of the digester that was monitored by load cells installed at the base of the pilot digester and liquid level sensor installed in the bench digester.

Table 3-1 AnMBR Operational Parameters

Parameter	Pilot AnMBR	Bench AnMBR
AD Volume (L)	550	8
MT Volume (L)	80	5
Membrane Surface Area (m^2)	5.4	0.07
Membrane Pore Size (μm)	0.04	0.04
Temperature (°C)	23±1	23±1
pH	6.7~6.8	6.7~6.8
Mixing Rate (L/h)	3600	50
Recirculation Rate (L/h)	918	12

Wastewater, permeate and mixed liquor samples were collected twice a week from the outlets of the feed pump (upstream of the $FeCl_3$ dosing), permeate pump and anaerobic reactor, respectively. The samples were analyzed for total suspended solids (TSS), volatile suspended solids (VSS) and total COD, particulate COD (pCOD), total $BOD_5$and sulfate according to standard methods (APHA, 2005).VFAs (acetic acid, propionic acid, butyric acid and valeric acid) were measured by using Dionex ICS-2000 Ion Chromatograph with an AS40 Automated Sampler. The methane concentration in the biogas was measured using a gas chromatograph (Agilent Technologies G2802A).

The research was conducted with 3 operating conditions in the pilot AnMBR at an HRT of 8.5 hours and 2 operating conditions in the bench AnMBR at an HRT of 12.5 hours. The detailed testplan is presented in Table 3-2. The pilot AnMBR was initially operated at an extended SRT (100 days in Test P1) and subsequent tests evaluated intermediate (70 days in Test P2) and short (40 days in Test P3) SRTs. The bench AnMBR was initially operated at a short SRT (40 days in Test B1) and this is followed by a test with increased SRT (70 days in Test B2). Steady state conditions were considered to be established in a test when the VSS concentrations in the digester were essentially constant (SD/Mean<10%). Test B2 did not reach steady state due to insufficient operation time. The membrane performance and related mixed liquor characteristics of bench-scale AnMBR is presented in Appendice A-2.

Table 3-2 Testplan

Pilot AnMBR (HRT=8.5 hours)			Bench AnMBR (HRT=12.5 hours)		
Test	State	Duration	Test	State	Duration
P1 (SRT=100d)	Transient	Day 1-45	B1 (SRT=40d)	Steady	Day 1-69
	Steady	Day 46-84			
P2 (SRT=70d)	Transient	Day 85-130	B2 (SRT=70d)	Transient	Day 70-120
	Steady	Day 131-165			
	High Sewage COD	Day 166-219			
P3 (SRT=40d)	Transient	Day 220-319	-	-	-
	Steady	Day 320-400			

The influence of SRT and HRT on the bioprocess performance was assessed statistically using ANOVA tests. In the subsequent discussion of results the significance of the statistical analysis is presented in brackets (i.e. p< xxx) whenever a statistical assessment was conducted to determine if a comparison was statistically significant.

3.3 Results and Discussion

3.3.1 Bioprocess Performance

The bioprocess performance was evaluated at steady state in the pilot and bench AnMBRs on the basis of the concentrations of COD and BOD_5 in the permeates and the production of sludge and methane (Table 3-3). From Table 3-3 it can be seen that there was no significant difference in the concentrations of COD ($p<0.82$) and BOD_5 ($p<0.89$) in the sewages between Tests P2 and P3. However, the concentrations of COD and BOD_5in the sewage in these tests were 27.6% ($p<0.001$) and 17.5% ($p<0.02$) higher than in Test P1. The COD concentration in the sewage in Test B1 was 6.2% ($p<0.03$) higher than Test B2, however no significant difference was observed in BOD_5 concentration ($p<0.90$). Therefore, considering the variation in sewage quality, the removal efficiency was employed to characterize the influence of SRT and HRT on the treatment performance.

The average (±SD) concentrations of these responses in the sewage and permeate and the removal efficiencies are presented in Table 3-3. From Table 3-3 it can be seen that the average COD concentrations in the permeates were less than 40mg/L (the VFA concentration ranged 1.7~5.9 mg/L) and the average BOD_5 concentrations were less than 10 mg/L in all tests. The superior permeate quality may be attributed to complete interception of solids and colloids by the membrane (pore size: 0.04 µm). The membrane also enhances the accumulation of biomass which can result in enhanced hydrolysis and subsequent methanogenesis. These results indicate that all the investigated HRT and SRT combinations were able to produce good effluent quality in terms of COD and BOD_5.

To normalize for the variability in raw sewage quality, removal efficiencies were calculated to further investigate the effect of SRT and HRT on the removal of COD and BOD_5. From Table 3-3 it can be observed that the average removal efficiencies of COD and BOD_5 were higher than 88% and 93% respectively in all tests. Statistic analyses showed there was no significant effect of SRT ($p<0.42$) or HRT ($p<0.14$) on removal of COD. Similarly the removal efficiencies for BOD_5 were not significantly affected by either SRT ($p<0.36$) or HRT ($p<0.67$). Therefore, it was concluded that SRT and HRT had no influence on the removal of COD and BOD_5. It was however hypothesized that SRT or HRT might shift the distribution of organic mass between sludge production and methane production while not affecting the overall removal of COD and BOD_5. Therefore the productions of sludge and methane were calculated on the basis of fed COD mass to further characterize the influence of HRT and SRT on the bioprocess performance.

Sludge production is an important factor to consider when assessing the sustainability of AnMBRs (Liao et al., 2006; Smith et al., 2012). In this study sludge production was assessed on the basis of the VSS mass flow in the wasted sludge and the daily COD loading at steady state. The effect of SRT on VSS yield was evaluated by comparing the VSS yields in the 3 pilot AnMBR tests (Table 3-3). The results showed the average VSS yield in Test P3 was 17.6% ($p<2.7*10^{-5}$) and 33.3% ($p<6.9*10^{-7}$) higher than in Test P2 and P1 respectively. The results indicated a significant reduction in the VSS yield as the

SRT was increased from 40 to 100 days. The results suggested that the increased SRT in the range of 40 to 100 days resulted in increased hydrolysis of VSS and hence a reduction of VSS production. In addition, the biosolids characteristics in terms of disposal were summarized in Appendice A-1.

The production of methane can contribute to the sustainability of AnMBRs as it can be employed as an alternative energy source. Previous studies (Yeo and Lee, 2013; Smith et al., 2015) have reported substantial dissolved methane in the permeate and hence there is a need to consider this in the estimation of the methane yield. Therefore, the methane measured in the biogas and the estimated methane dissolved in the permeate (Henry's Law: 0.0016 $\text{mol}_{\text{Methane}}$/L/atm at 25ºC) were employed to calculate the methane yield based on the fed COD. The impact of SRT on methane yield was investigated by comparing the steady-state data in the 3 pilot AnMBR tests (Table 3-3). From Table 3-3 it can be seen average methane yield in Test P1 was 26.4% ($p<0.003$) and 51.3% ($p<1.3*10^{-7}$) higher than in Test P2 and P3. The improved methane yields at the extended SRTs were attributed to enhanced hydrolysis and subsequent methanogenesis at longer retention times. The increased methane yields were consistent with the reduced VSS yields at the longer SRTs.

Table 3-3 Steady State Treatment Performance

Responses	Pilot AnMBR			Bench AnMBR
	P1	P2	P3	B1
SRT (Day)	100	70	40	40
HRT (Hour)	8.5	8.5	8.5	12.5
Influent COD mg/L	304±45	388±65	383±48	412±79
Permeate COD (mg/L)	31.6±8.5	36.2±5.9	31.5±8.5	33±4.7
COD Removal Efficiency (%)	88.0±3.9	90.6±3.0	91.8±1.9	92.3±1.5
Influent BOD_5 (mg/L)	120±40	141±28	143±46	140±28
Permeate BOD_5 (mg/L)	6.9±3.3	7.1±3.0	7.2±3.0	7.1±3.0
BOD_5 Removal Efficiency (%)	94.0±2.1	94.6±2.2	93.8±1.5	94.6±2.2
VSS Yield ($g/gCOD_{Fed}$)	0.15±0.04	0.17±0.03	0.20±0.01	0.18±0.02
CH_4 Yield ($ml/gCOD_{Fed}$)	115±21	91±19	76±14	72±13

As SRT is decoupled from HRT in AnMBRs, it was hypothesized that HRT would have no significant impact on the yields of VSS and methane. To evaluate this hypothesis, the steady-state data collected in Test P3 and B1 were employed to assess the effect of HRT on the yields of VSS and methane. From Table 3-3 it can be seen that HRT had no significant influence on the VSS yield ($p<0.08$) or methane yield ($p<0.1$). Hence, over the range of HRTs tested this parameter did not affect the fate of COD entering the AnMBR.

As previously discussed, SRT was found to influence the distribution of fed COD between sludge production and methane production. Therefore, a COD mass flow model was developed to evaluate the effect of SRT and HRT on the distribution of influent COD to either the permeate, wasted sludge and methane (Table 3-4). The fraction of COD in the permeate was expected to correspond to COD removal efficiency. From Table 3-4 it can be seen that the fraction of COD in the permeate was less than 10% of the influent, which was consistent with the COD removal efficiency. Therefore, it was concluded that SRT and HRT have no impact on the fraction of COD entering the permeate.

The fractions of COD in the wasted sludge and methane were investigated and expected to correspond to the VSS and methane yields respectively. The average fraction of COD in the wasted sludge in Test P3 was 14.8% ($p<6.7*10^{-4}$) and 41.9% ($p<4.3*10^{-7}$) higher than in Test P2 and P1 respectively, while the average fraction of COD as methane in Test P3 was 20.2% ($p<0.001$) and 51.4% ($p<1.7*10^{-4}$) lower than Test P2 and P1 respectively. There was no significant difference between Test P3 and B1 in fractions of COD in the wasted sludge ($p<0.1$) and COD as methane ($p<0.5$). These results were consistent with the impact of SRT and HRT on VSS yield and methane yield. Therefore, it was concluded that as SRT increased the distribution of the fed COD mass flow shifted from the wasted sludge (VSS production) to methane production, while HRT had no impact on the distribution of COD mass. It should be noted that a consistent fraction (~29%) of the fed COD mass was not accounted for in all tests (Table 3-4). This response will be discussed subsequently.

Table 3-4 Steady State COD Mass Distribution

COD Mass Flow	Pilot AnMBR						Bench AnMBR	
	P1 (Mean±SD)		P2 (Mean±SD)		P3 (Mean±SD)		B1 (Mean±SD)	
	gCOD/d	%	gCOD/d	%	gCOD/d	%	gCOD/d	%
Influent	539±79	100	673±98	100	668±75	100	9.4±1.0	100
Permeate	55.9±15.0	10.4±2.8	63.8±10.3	9.5±1.5	56.4±15.2	8.4±2.3	0.8±0.1	8.0±1.2
Wasted Sludge	153±8.7	28.4±1.6	236±23	35.1±3.4	269±16.4	40.3±2.5	4.0±0.2	42.2±2.4
Methane	179±32.5	33.0±6.0	176±26.9	26.2±8.0	146±26.8	21.8±4.0	1.8±0.3	19.1±3.6
Missing	152±22.8	28.1±4.2	197±10.8	29.8±1.6	197±16.6	29.4±2.5	2.9±0.4	30.7±4.0

3.3.2 Calibration of Bioprocess Kinetics

The previous observation of HRT and SRT impacts were based upon performance of the pilot and bench scale AnMBR at pseudo-steady state. However the testing plan provided evidence of bioreactor performance over a number of steady state and transient operations as the SRT was transitioned between tests. To thoroughly analyze the biological behavior, the PetWin 4 process simulator (EnviroSim, Canada) was employed to obtain insight into the anaerobic processes. The anaerobic processes in the PetWin model include hydrolysis of particulate COD to complex readily biodegradable COD (rbCODc) by heterotrophs. These same organisms subsequently ferment the rbCODc to VFAs. The long chain VFAs are converted to acetic acid and hydrogen by acetogens. The acetic acid and hydrogen are utilized by acetoclastic and hydrogenotrophic methanogens to produce methane respectively. Hydrogen, acetic and propionic acid are also utilized by sulfate reducing bacteria. As long chain VFAs and hydrogen were consistently undetected throughout the study in both the pilot and bench scale AnMBRs, hydrolysis, fermentation and aceticlastic methanogenesis were selected for calibration.

The simulations conducted with PetWin employed the average values of measured wastewater characteristics (Table3-5) as inputs in each test. The calibration of the biokinetics coefficients for each anaerobic process was conducted sequentially by employing the mean value of reported rate coefficients (K_h, q_{fe} and k_m for hydrolysis (anaerobic reduction factor applied), fermentation and aceticlastic methanogenesis respectively) in literature and adjusting the associated saturation coefficients (K_X, K_{fe} and

K_s) such that the simulated responses matched observed response. The rate coefficients in literature were reported at 20ºC. The mean of reported rate coefficients employed in simulations were adjusted to 23ºC using Equation 3-1 that is a default in PetWin and has an effective range between 10ºC to 40ºC.

$r_T = r_{20} * 1.029^{(T-20)}$(Equation 3-1)

Where r= rate constant, d^{-1}

T = Operating temperature, ºC

Table 3-5 Sewage Characteristics

Responses	Pilot AnMBR			Bench AnMBR	
	P1	P2	P3	B1	B2
SRT (Day)	100	70	40	40	70
HRT (Hour)	8.5	8.5	8.5	12.5	12.5
COD (mg/L)	304±45	388±65	383±48	412±79	376±67
pCOD (mg/L)	269±30	328±45	327±57	360±63	326±55
BOD_5 (mg/L)	120±40	141±28	143±46	140±28	116±20
TSS (mg/L)	163±77	208±63	189±29	215±48	189±28
VSS (mg/L)	154±68	172±61	166±26	191±42	165±26
Sulfate (mg/L)	50.1~55.7				

The accumulation of pCOD in the AnMBR was employed to characterize the hydrolysis process. Figure 3-2 presents the pCOD concentrations that were observed in the pilot AnMBR over the duration of the study. From Figure 3-2 it can be observed that during Test P1 the pCOD concentrations gradually increased from 18000 to 26000 mg/L in the transient phase and then stabilized. Upon the reduction of the SRT from 100 to 70 days in Test P2, the pCOD concentration decreased with time and stabilized at approximately 23400 mg/L. However, after Day 158 the pCOD increased significantly to 29000 mg/L at the end of Test P2 and this was attributed to an increase in the sewage COD concentration of 24% in this period. When the SRT was reduced to 40 days in Test P3, the pCOD concentration declined due to the reduced SRT and a decline in the sewage COD concentrations. The responses provided considerable evidence of dynamic performance for model calibration.

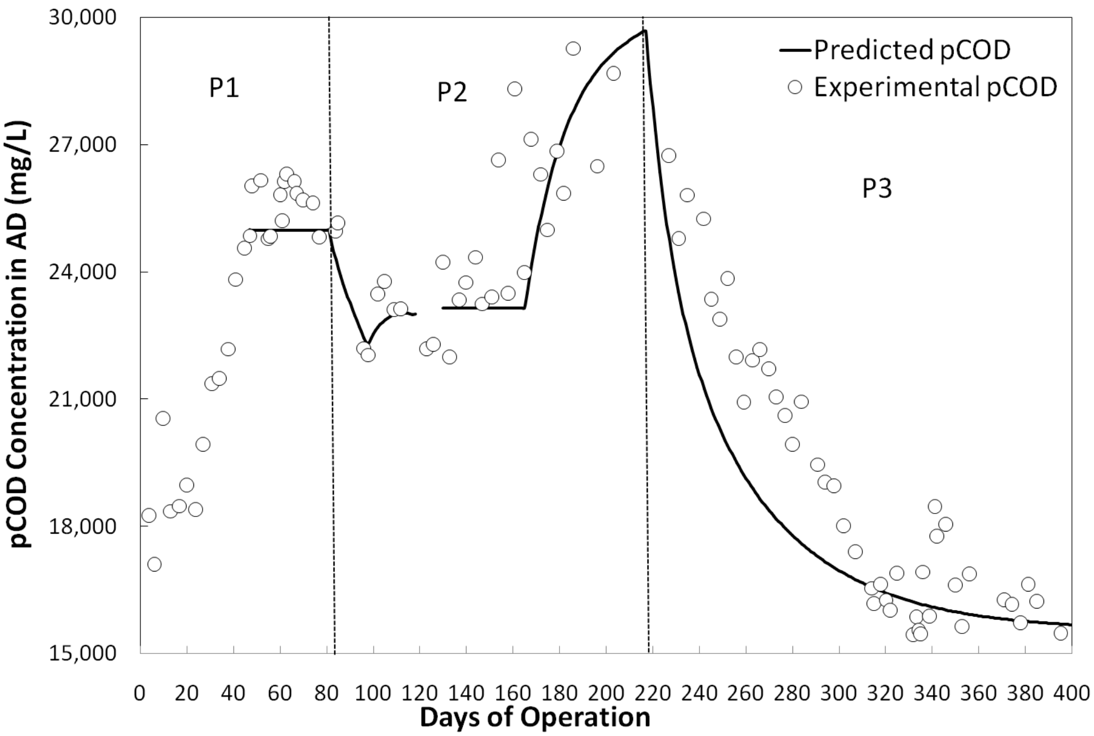


Figure 3-2 pCOD Concentration in AD Contents

The simulation of pCOD concentration was conducted with the mean value of the maximum specific rate of hydrolysis (K_h) (anaerobic reduction factor applied) that was reported in the literature while the hydrolysis saturation coefficient (K_X) was estimated to produce the best fit of the data (Table 3-6). Figure 3-2 presents the results of these simulations in comparison to the observed results. From Figure 3-2 it can be seen that generally the model was able to effectively simulate the accumulation of pCOD in the AnMBR as SRT and sewage COD loading varied. The slightly faster decrease in simulated values as compared to the observed values during the transient phase in Test P3 was attributed to a decline with time of the sewage COD concentration whereas the model employed the mean value of the sewage concentration for Test P3. When the entire times series was examined it was deemed that the values of K_h and K_X presented in Table 3-6 reasonably characterized hydrolysis of pCOD in AnMBR treating municipal wastewater.

To further investigate the hydrolysis process, the calibrated $K_X$value was compared with reported K_X values and the predictedratio of pCOD to Ordinary Heterotroph Organism

(OHO) concentrations. From Table 3-6 it can be seen that the calibrated K_X was within the range reported in literature, thus the rate of hydrolysis in this study could be concluded to be comparable to those reported in literature. Further, the predicted ratio of pCOD to OHO concentrations that ranged between 40~50 was more than 10 times higher than the calibrated K_X. Thus the K_X in Monod relationship could be approximated by zero-order kinetics. Therefore, the rate of hydrolysis in this study was likely controlled by K_h.

Table 3-6 Calibrated Biokinetic Coefficients

	Hydrolysis		Fermentation		Aceticlastic Methanogenesis	
	K_h (20ºC) (d^{-1})	K_X (g pCOD/g OHO)	q_{fe}(20ºC) (d^{-1})	K_{fe} (mgCOD/L)	k_m(20ºC) (d^{-1})	K_s (mgCOD/L)
Literature (Mean)	1.2~3.6 (2.4)	0.1~1.0	3~5 (4)	10~4	2.7~2.9 (2.8)	11~28
Calibrated	-	3.3±2.8	-	178±37	-	29±9
Reference	Henze et al., 1999; Furumai et al., 1999; Soejima et al., 2008; Drewnowski and Makinia, 2013				Gujer and Zehnder, 1983; Pavlostathis and Giraldo-Gomez, 1991	

The accumulation of readily biodegradable COD (complex) (rbCODc) in the AnMBR was employed to characterize the process of fermentation. The rbCODc was estimated as the difference between the BOD_5 and COD equivalence of the VFAs in the permeate. Figure 3-3 presents the rbCODc concentrations that were observed in the pilot AnMBR over the duration of the study. From Figure 3-3 it can be seen that observed concentration of rbCODc was essentially constant and in the range of 6.5±1.5 mg/L over the entire experiment. This response was well described by the simulation after calibration of K_{fe} (Table 3-6). It was concluded that the calibrated q_{fe} and K_{fe} values can be employed to characterize fermentation of rbCODc in AnMBR treating municipal wastewater.

To further investigate the fermentation process, the calibrated K_{fe} value was compared with reported K_{fe} values and the observed concentrations of rbCODc. From Table 3-6 it can be seen that calibrated value of K_{fe} was more than 10 times higher than the values reported in literature, thus the rate of fermentation in this study could be concluded to be lower than those reported in literature. In addition, the concentration of rbCODc in this study (6.5±1.5 mg/L) was less than 5% of the calibrated K_{fe} value. Thus the Monod form effectively simplified to first-order kinetics in the simulation. Therefore, the rate of fermentation was likely to have a linear relation to the concentration of rbCODc.

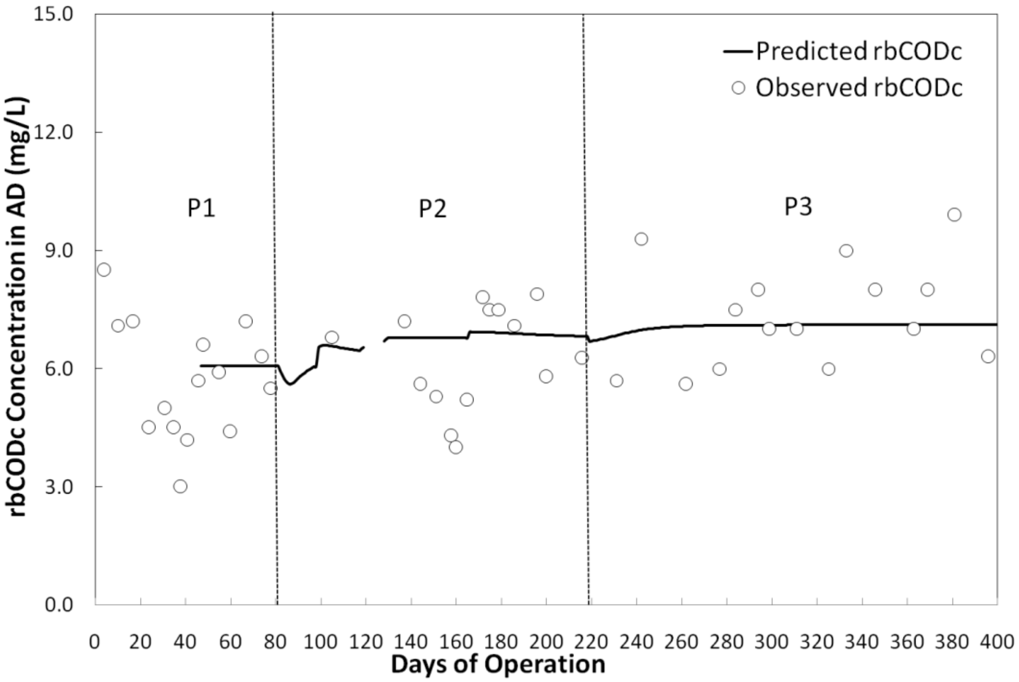


Figure 3-3 rbCODc Concentration in AD Contents

The accumulation of acetic acid in the pilot AnMBR was employed to characterize the aceticlastic methanogenesis process. Figure 3-4 presents the acetic acid concentrations that were observed in the pilot AnMBR over the duration of the study. From Figure 3-4 it can be seen the concentrations of acetic acid were in the range of 1.5~4.0 mg/L over the entire experiment. The values of k_m and the calibrated value of K_s are reported in Table 3-6. From Figure 3-4 it can be seen that the simulation results essentially matched the observed results in Test P1 and P3 (Figure 3-4). The values in Test P2 were somewhat overestimated but observed values were very small and for practical purposes there was little difference. Therefore it can be concluded that the values of k_m and K_s that were developed can characterize the aceticlastic methanogenesis in AnMBR treating municipal wastewater.

To further investigate the aceticlastic methanogenesis process, the calibrated value of K_s was compared with reported values of $K_s$and observed concentration of acetic acid. From Table 3-6 it can be seen that the calibrated K_s value overlapped the values reported in literature, thus the rate of aceticlastic methanogenesis in this study could be concluded to be comparable to those reported in the literature. The concentrations of acetic acid in this study ranged 2.4±1.3 mg/L were less than 10% of the calibrated K_s value, thus the Monod form effectively simplified to first-order kinetics. Therefore, the rate of aceticlastic methanogenesis in this study was likely to have a linear relation to concentration of acetic acid.

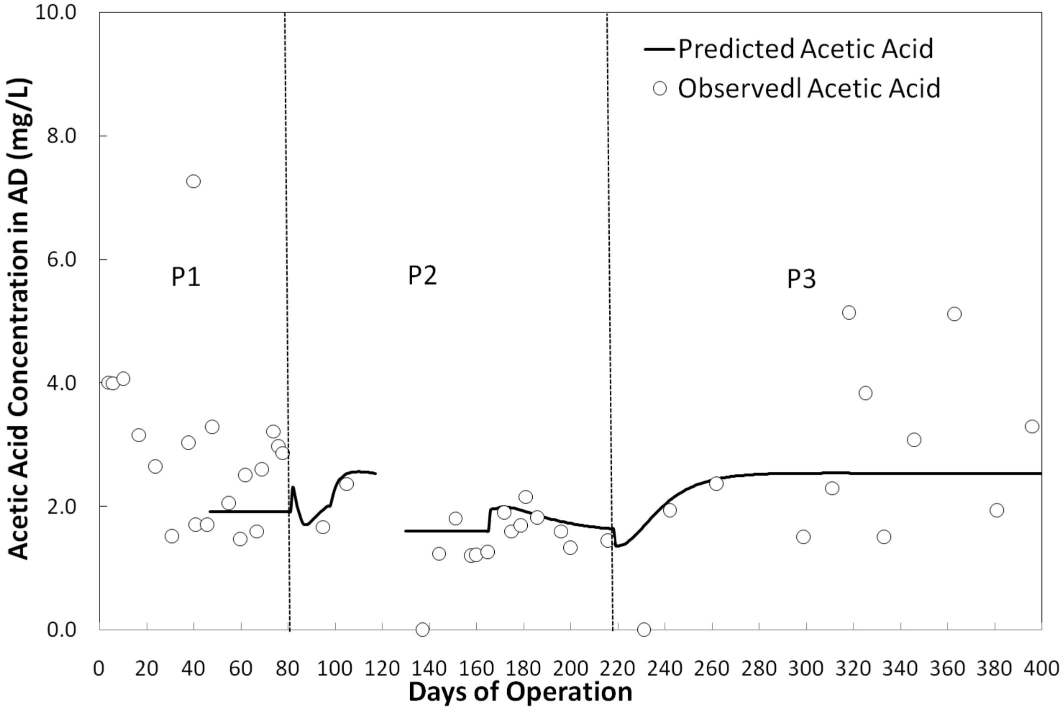


Figure 3-4 Acetic Acid Concentration in AD Contents

As discussed the calibrated biokinetic coefficients presented in Table 3-6 were found to effectively simulate the processes in anaerobic digestion when the AnMBR was operated over a range of SRT from 100 to 40 days and an HRT of 8.5 hours. The validity of the model which was calibrated with the pilot AnMBR data was assessed with the bench AnMBR data that was collected at an HRT of 12.5 hours. The model simulations employed the mean values of the reported values for rate coefficients, the calibrated values of saturation coefficients (Table 3-6) and the measured wastewater characteristics (Table 3-5). The model simulations were compared with measured responses in the bench scale digester. Figure 3-5 presents the concentrations of pCOD, rbCODc and acetic acid in the bench scale test. From Figure 3-5 it can be seen that calibrated model was able to effectively simulate the AnMBR operation at the longer HRT. Hence it was concluded that the calibrated model could be applied over a range of HRTs and SRTs.

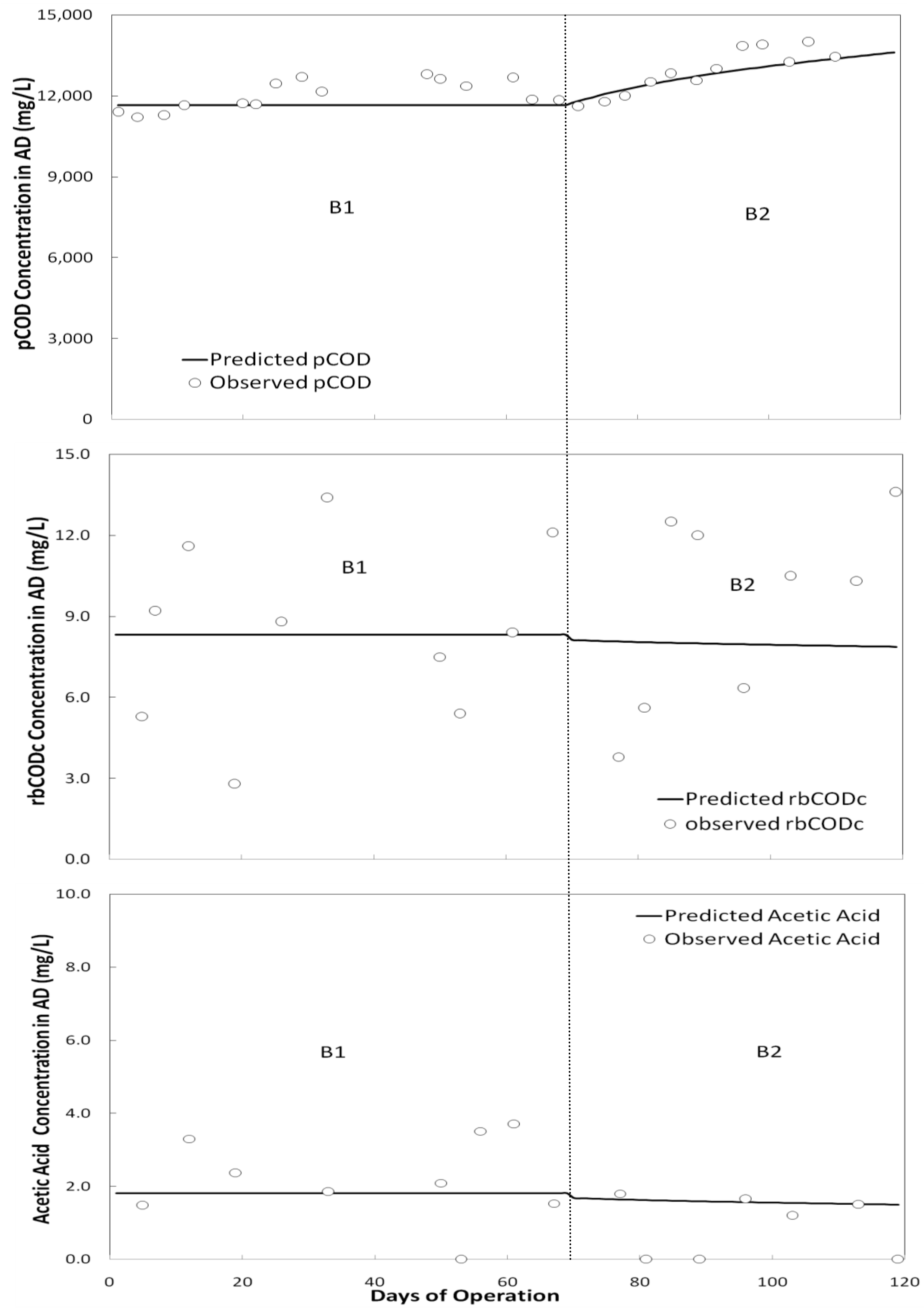
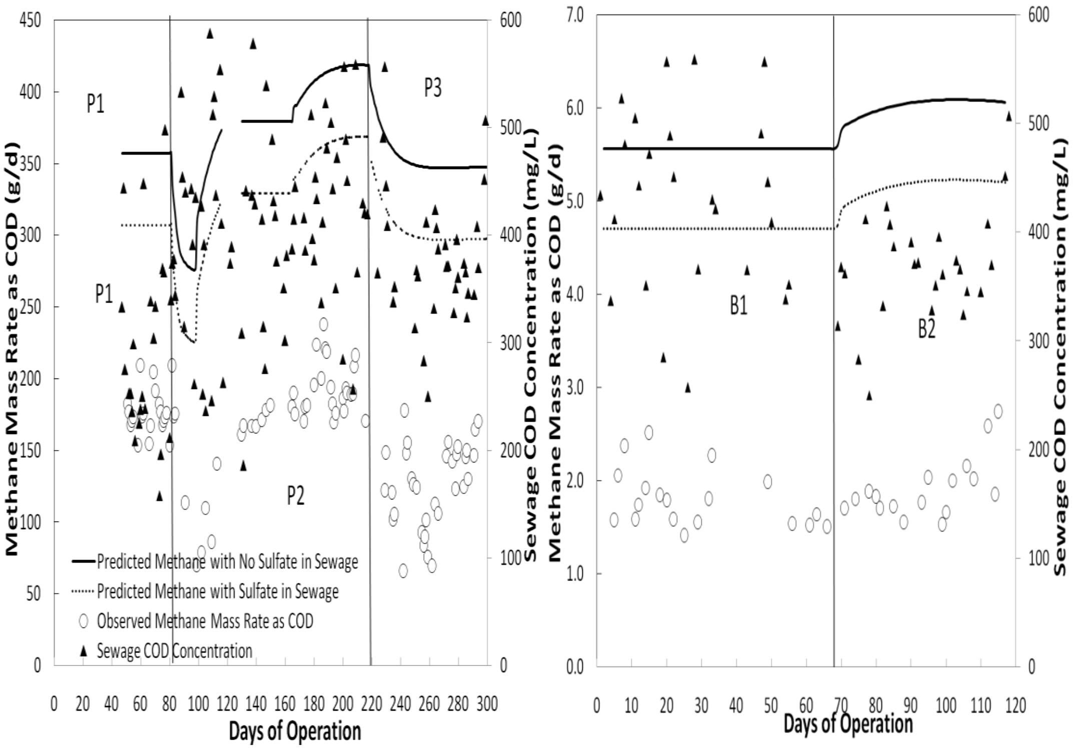


Figure 3-5 PetWin Simulation on Bench AnMBR

As previously discussed, the calibrated model was found to effectively simulate hydrolysis, fermentation and aceticlastic methanogenesis processes on the basis of responses in liquid phase. Therefore, it was hypothesized that the methane production could be effectively simulated as well. Figure 3-6 presents the observed and simulated COD equivalents of the methane production. The observed methane mass flow consisted of the measured methane in the gas phase and the dissolved methane in the permeate based on saturation with respect to a Henry's Law coefficient of 0.0016 $mol_{Methane}$/L/atm at 25ºC. From Figure 3-6 it can be observed that the simulated results consistently followed the trends in the observed results except in the middle of Test P3 and at the end of Test B2. The failure of the simulated results to match the observed results might be attributed to significant variations in the sewage COD concentration. The correspondence between daily methane production and sewage COD concentration demonstrates that methane production is a function of both methane yield that is controlled by SRT and COD loading. When the entire times series was examined it was deemed that the calibrated model could predict results that were consistent with observed results.

The consistency in trends was interpreted to indicate that the calibrated model could effectively simulate methanogenesis. However, the simulated values were consistently higher than the observed results. This was consistent with the previously described lack of COD mass balance closure that might be attributed to either the reduction of dosed ferric iron and sulfate in sewage or the oversaturation of methane in permeate.



(a) Pilot AnMBR **(b) Bench AnMBR**

Figure 3-6 Methane Mass Flows as COD

Under anaerobic conditions the reduction of sulfate and ferric iron will compete with aceticlastic methanogenesis and consume organic matter that could be utilized by methanogens for methane production (Gimenez et al., 2011) and likely contributed to the non-closure in the COD mass balance. To further quantify the COD consumed by sulfate reduction, methane production was simulated by the calibrated PetWin model with the assumption of no sulfate in the sewage. Minimal differences in pCOD, rbCOD and acetic acid simulations were observed when sulfate was removed from the sewage, but lower methane production was observed with sulfate in the sewage. The results of this analysis revealed that the reduction of sulfate represented approximately 53gCOD/d and 0.8gCOD/d in pilot and bench AnMBR respectively indicating approximately 83.3% of the sulfate in sewage (50.1~55.7mg/L sewage) was reduced. Hence, this electron acceptor represented approximately 8~11% of the total influent COD. However, the presence of sulfate as an electron acceptor did not account for the entire lack of COD mass balance closure (~29%).

The reduction of ferric iron to ferrous iron would also contribute to the lack of COD mass balance. If it were assumed that all the dosed ferric iron was reduced to ferrous iron, the dosed ferric iron (26 mg$FeCl_3$/L sewage) was estimated to represent 1.3 mgCOD/L. This accounted for less than 1% of the total COD mass flow entering the AnMBRs and hence could not close the COD mass balance. Therefore, the oversaturation of methane in the permeate was characterized to obtain further insight into the non-closure of COD mass balance.

It was hypothesized that the oversaturation of dissolved methane in the liquid phase relative to Henry's Law was responsible for the non-closure of the COD balance. Assuming that dissolved methane was responsible for all the difference between observed and simulated methane mass flows, it was estimated that the liquid methane (sulfate reduction included) was 180~290% higher than that predicted by Henry's Law. Oversaturation has been reported in other studies (Yeo and Lee, 2013; Smith et al., 2015). The ratio in the current study was generally comparable to that reported previously (150%~260%). The oversaturation of methane might be attributed to the production of methane in the fouling layer (Smith et al., 2015) as consistently higher VFA concentrations in were observed in the mixed liquor (2.6±1.4 in mg/L as COD) as compared to the permeate (consistently not detected) was observed. However, this difference represented only 0.7~1.0% of the COD mass flow entering the systems and could not match the gap (~20%) in the COD balance. Hence, it was hypothesized that the oversaturation may result from other mechanisms such as the limitation of liquid-gas mass transfer processes. Further study is required to understand the mechanisms leading to oversaturation.

3.4 Significance

The results obtained in this study provided insight into the bioprocess performance of AnMBRs when operated over a range of SRTs and HRTs on municipal wastewater. An increase of SRT from 40 to 100 days resulted in reduced sludge production and increased methane production due to an enhancement of hydrolysis and subsequent methanogenesis at longer retention times. There was no significant influence of HRT (8.5 and 12.5 hours) on these responses when SRT was held constant. A COD mass balance revealed that the COD mass flow shifted from wasted sludge to produced methane at longer SRTs and was unaffected by HRT. A consistent fraction (~29%) of fed COD mass was not accounted for in all tests and this was attributed to reduction of sulfate and ferric iron and oversaturation of dissolved methane in the permeate.

The hydrolysis, fermentation and aceticlastic methanogenesis models in PetWin were calibrated with the pilot test data. The calibrated saturation coefficients revealed hydrolysis could be simplified to zero-order kinetics while the fermentation and aceticlastic methanogenesis processes could be simplified to first-order kinetics. The calibrated model was able to describe steady-state and transient responses over a range of HRTs and SRTs.

As bioprocess performance was concluded to be benefit from extended SRT, the effect of SRT on membrane performance was not clear. Therefore, the subsequent chapter investigated the long-term membrane performance of pilot AnMBR with varied SRT from 100 to 40 days.

Chapter 4

Long-term Membrane Performance of an Anaerobic Membrane Bioreactor Treating Municipal Wastewater

Key Words: SRT, Recovery Cleaning, Residual Foulants

4.1 Introduction

The development of sustainable technologies for wastewater treatment has focused on anaerobic membrane bioreactors (AnMBRs) because the anaerobic process has low requirements for energy and nutrients, low sludge production and can generate methane that can be employed as an alternative energy source (Metcalf and Eddy, 2003). The integration of membrane modules into the anaerobic bioreactor (Liao et al., 2006; Perkiel and Lanting, 2005) enables biomass to be completed retained in the bioreactor. Hence, the hydraulic retention time (HRT) is decoupled from solids retention time (SRT). Therefore, AnMBRs are becoming increasingly popular for wastewater treatment.

Despite the advantages of AnMBR processes, their application has been limited due to membrane fouling. It has been reported thatmembrane fouling in AnMBRs will be affected by the mixed liquor characteristics that include a complex mixture of materials which are present in suspended and colloidal forms (Liaoet al., 2006). The suspended materials, as measured by TSS, have been identified as a key factor in membrane fouling. Membrane fouling has been reported to be related to its concentration in the mixed liquor (Liao et al., 2006; Huang et al., 2011). It is believed that an increase in the suspended solids concentration increases the convective flow of solids towards the membrane surface and enhances cake formation and fouling. Hence, it could be expected that cake-layer fouling might be mitigated by reducing the concentrations of TSS.

The materials in colloidal form, as represented by colloidal COD, have been reported to besignificant contributors to fouling in MBRs and AnMBRs (Liao et al., 2006; Fan et al., 2006Choo and Lee, 1998; Dagnew et al., 2012). These materials are reported to contribute to the formation of a strongly-attached fouling layer on/into membrane that resists physical cleaning. Therefore, strategies that enable sustainable operation of AnMBR are designed to reduce the exposure of the membrane to these substances and to efficiently remove these substances from membrane.

Optimization of the SRT is a possible strategy for reducing the sludge fouling propensity. Optimization of the SRT has been reported to mitigate the production/accumulation of foulants in bench scale AnMBR that were fed with synthetic wastewater. It has been reported that extending the SRT (30-100 days or infinite) has been found to result in elevated TSS concentrations (5-15 g/L) due to enhanced growth of biomass and increased retention of suspended solids (Hu and Stuckey, 2006; Lew et al., 2009; Zhang et al., 2010; Huang et al., 2011) that led to an increasing in fouling rate from 0.05 to 0.66 kPa/day (Huang et al., 2011). However, the effect of SRT on colloidal COD has not been reported and there is limited information in the literature describing the impact of SRT on the membrane performance in a pilot AnMBR treating authentic municipal wastewater.

Recovery cleaning that involved soaking the membrane in chemical cleaning solutions is a strategy that has been employed to remove fouling substances from the membranes.. The cleaning agents employed in AnMBRs have included acids (10mM/L HNO_3, 270mM/L HCl, 10-15mM/L citric acid and 100mM/L oxalic acid), bases (10mM/L NaOH), oxidants (0.3-5g/L NaOCl and 10g/L H_2O_2) and chelants (EDTA) and have been reported to achieve permeability improvements of 75%-200% (Kim et al.,2011; Lew et al., 2009; Salazar-Peláez et al., 2011; Zhang et al., 2007).Among these citric acid and NaOCl have been reported to achieve higher foulant removal efficiencies and sequential cleaning with citric acid and NaOCl has been found to achieve higher permeability improvement than use of the individual agents. However, these cleaning results were characterized with tests that filtered either clean water or mixed liquor for a short term in bench scale AnMBRs. The long-term performance of cleaned membranes in pilot AnMBR has not been reported.

The hypothesis tested in this study was that the mixed liquor characteristics will depend upon SRT and thus the membrane performance in an AnMBR treating authentic municipal wastewater will also be affected by SRT. A pilot AnMBR was employed to investigate the influence of SRT and recovery cleaning on membrane performance of the AnMBR when treating authentic municipal wastewater. A comprehensive characterization of mixed liquor properties and membrane fouling was conducted at each SRT. Cleaning efficiency was measured after each recovery cleaning.

4.2 Materials and Methods

A pilot scale AnMBR that was fed with 3 mm screened sewage from the Burlington Skyway Wastewater Treatment Plant (Ontario, Canada) was employed in this study (Figure 3-1). The pilot AnMBR consisted of a550L completely mixed anaerobic digester (AD) and an 80L membrane tank (MT) that held a polyvinylidine fluoride (PVDF) hollow fibre membrane module with a surface area of 5.4 $m^2$and a pore size of 0.04µm (GE: ZeeWeed 500). The hollow fibres had a length of 1.2m and outer and inner diameters of 1.9mm and 0.8mm respectively. The AD contents were mixed by recirculation of the contents at a flow of 3600 L/h with a positive displacement pump. The AD contents were circulated through the MT using a centrifugal pump that withdrew mixed liquor from the bottom of the AD and pumped it to the bottom of the MT after which it was flowed to the top of the AD by overflow. This circulation mixed the MT contents and generated a cross flow velocity (CFV) that would enhance surface shear for membrane fouling control. Biogas produced in the AD was released from the head space of the AD andits production was measured by an electrical gas flow meter. Biogas was recirculated through the MT at a flow of 2.5 cubic feet per minute (equal to 0.786 m^3/h (20ºC and 1 atm)) with a blower (KNF NEUBERGER, PM23820-150.1.2) to reduce membrane fouling.The impact of sparging rate and temperature on membrane fouling was evaluated with a nested short-term test on pilot AnMBR and the results are presented in Appendice A-3.

Throughout the study a concentrated $FeCl_3$ solution (7.4% w/w) was dosed into the influent to achieve 26.0mg $FeCl_3$/L in both systems. The temperature of the digester was maintained at 23±1°C by a heat tape that was controlled by a temperature controller which was informed by a temperature sensor in the digester. The pH of the digester was controlled through $NaHCO_3$ addition to maintain a value in the range of 6.7-6.8. Pilot operation and data acquisition were controlled using a programmable logic controller (PLC). The feeding of raw sewage and the wasting of anaerobic digester contents for SRT control were controlled on the basis of the weight of the digester that was monitored by load cells installed at the base of the digester.

The pressures of the headspace in the MT and permeate line were recorded using digital pressure guages. The trans-membrane pressure (TMP) was calculated as the difference between the pressure in the MT and that of the permeate line. To reduce membrane fouling, a discontinuous filtration mode was incorporated into the pilot operation. The discontinuous filtration mode consisted of a repeating cycle that had filtration for 8 minutes and relaxation for 2 minutes. Membrane performance was characterized by monitoring the TMP after relaxation. These TMP values were considered to be indicative of fouling that could not be removed by mixed liquor recirculation and biogas sparging.

Recovery cleaning of the membranes was conducted and the performance of cleaned membrane was evaluated by comparing with virgin membrane. In the recovery cleaning the membrane module was sequentially soaked in solutions of 2000mg/L of citric acid and 2000mg/L of NaOCl for 16 hours respectively. This cleaning protocol was based on a systematical investigation of cleaning chemical and soaking duration that was conducted offline by a loop apparatus and the results are presented in Appendice A-4. Clean water flux (CWF) tests were carried out on the virgin, fouled and cleaned membranes. The CWF tests involved permeating tap water through the membrane with a series of flux values that each had a fixed duration and monitoring the TMP at each flux value. The flux values were set at 5, 10, 15, 20, 25, 30 and 35LMH, and each step was conducted for 8 minutes, and between each flux there was a 2-minute relaxation. Linear regression of the TMP and flux values from each CWF test was employed to estimate the resistance of the membrane.

Fouled fibres were collected before each recovery cleaning for foulants analysis and the results are presented in Appendice A-5.

The critical flux tests were conducted based on the flux step method (Le-Clech et al., 2003) to further assess the membrane performance with mixed liquor characteristics. This method involved increasing the permeate flux in steps for a fixed duration and monitoring the TMP at each flux value. Linear relationship between TMP and flux was expected to be observed within the sub-critical flux region and TMP would increase exponentially at fluxes beyond the critical flux value. In this study, the flux was increased from 17 to 29LMH with an increment of 2LMH and decreased to 17LMH directly. The duration of each flux was 8 min and this was followed by a 2 min relaxation time to eliminate built up of foulants before the next flux value was implemented.

Wastewater, permeate and mixed liquorsamples were collected twice a week from the outlets of the feed pump (upstream of the $FeCl_3$ dosing), permeate pump and anaerobic reactor, respectively. The samples were analyzed twice per week for total suspended solids (TSS), volatile suspended solids (VSS), COD and BOD_5. All analyses were conducted according to standard methods (APHA, 2005). The dewaterability of the mixed liquor was characterized using the capillary suction time (CST) test (Vesilind, 1988).

Colloidal matter in the mixed liquor that has been reported as a key foulant in AnMBRs treating municipal wastewater (fully discussed in Chapter 5) and waste activated sludge (Dagnew et al., 2012) was measured as colloidal COD (cCOD). The mixed liquor and permeate were analyzed for cCOD once per week to provide insight into the presence of potential foulants. Whole samples that were obtained after filtration through 1.5µm filters were analyzed for COD. The 1.5µm-filtered COD was analyzed after centrifuging the mixed liquor sample at 4000 rpm for 12minutes then filtering the supernatant through a 1.5-µm glassfiber filter. The cCOD was calculated as the difference between 1.5µm-filtered COD and the permeate COD.

The research was conducted in 3 phases in the pilot AnMBR that was operated at a constant HRT of 8.5 hours. The pilot AnMBR initially was operated with a cleaned membrane at an extended SRT (100 days in Phase 1) and this was followed by sequential phases of intermediate (70 days in Phase 2) and short (40 days in Phase 3) SRTs. Recovery cleaning was conducted once in each of Phase 1 and 2 and twice in Phase 3. Virgin membranes were employed to replace fouled membranes in Phase 2 and 3 respectively. The detailed testplan is presented in Table 4-1.

Table 4-1 Testplan

Phase	1		2		3			
SRT/HRT	100 days/8.5 hours		70 days/8.5 hours		40 days/8.5 hours			
Initial Membrane Condition	Cleaned	Cleaned	Cleaned	Virgin	Uncleaned	Cleaned	Cleaned	Virgin
Duration	Day 1-50	Day 55-84	Day 90-119	Day 125-222	Day 228-304	Day 309-356	Day 360-395	Day 403-455

4.3 Results and Discussion

4.3.1 Long-term TMP Profile

The membrane performance was assessed by examining the TMP profiles after relaxation and its changes with time (fouling rate). These TMP values were assumed to be indicative of the accumulation of foulants on the membrane surface due to the formation of either a strongly-attached cake layer or pore blocking.Figure 4-1 presents the TMP values that were observed over the testing period. From Figure 4-1 it can be observed that there were a number of periods of increasing TMP values that were interpreted as being indicative of membrane fouling. Throughout the study a number of interventions including recovery cleaning and installation of virgin membranes were made to reduce TMP values.

TMP values declined substantially after the recovery cleaning in each of the 3 phases and this was interpreted to indicate an effective removal of foulants from the membrane surface. However, the low TMP values observed after recovery cleaning were not sustained. The fouling rates that were observed after recovery cleaning ranged from 0.15

to 0.61kPa per day (kPa/d). Further, when multiple recovery cleanings were conducted sequentially with replacement of the membrane, the fouling rate increased with each cleaning.

The installation of virgin membranes resulted in lower initial TMP values than those of the cleaned membranes. In addition the fouling rate was significantly reduced with values of 0.025 kPa/d and 0.028 kPa/d that were observed in the first 60 days of operation in Phases 2 and 3 respectively. In Phase 2 the fouling rate increased to 0.15kP/d when the AnMBR was operated for another 37 days (Day 185-222), however this value was lower than those observed after the fouled membranes were cleaned. The superior performance of the virgin membranes as compared to that of the cleaned membranes suggested the accumulation of foulants that were not removed during cleaning. The subsequent discussion examines the relationship between fouling trends and mixed liquor properties to obtain insight into the nature of the fouling.

Prior to this study, the pilot AnMBR had been operated without addition of $FeCl_3$. The long-term membrane performance of pilot AnMBR without addition of $FeCl_3$was summarized in Appendice A-6.

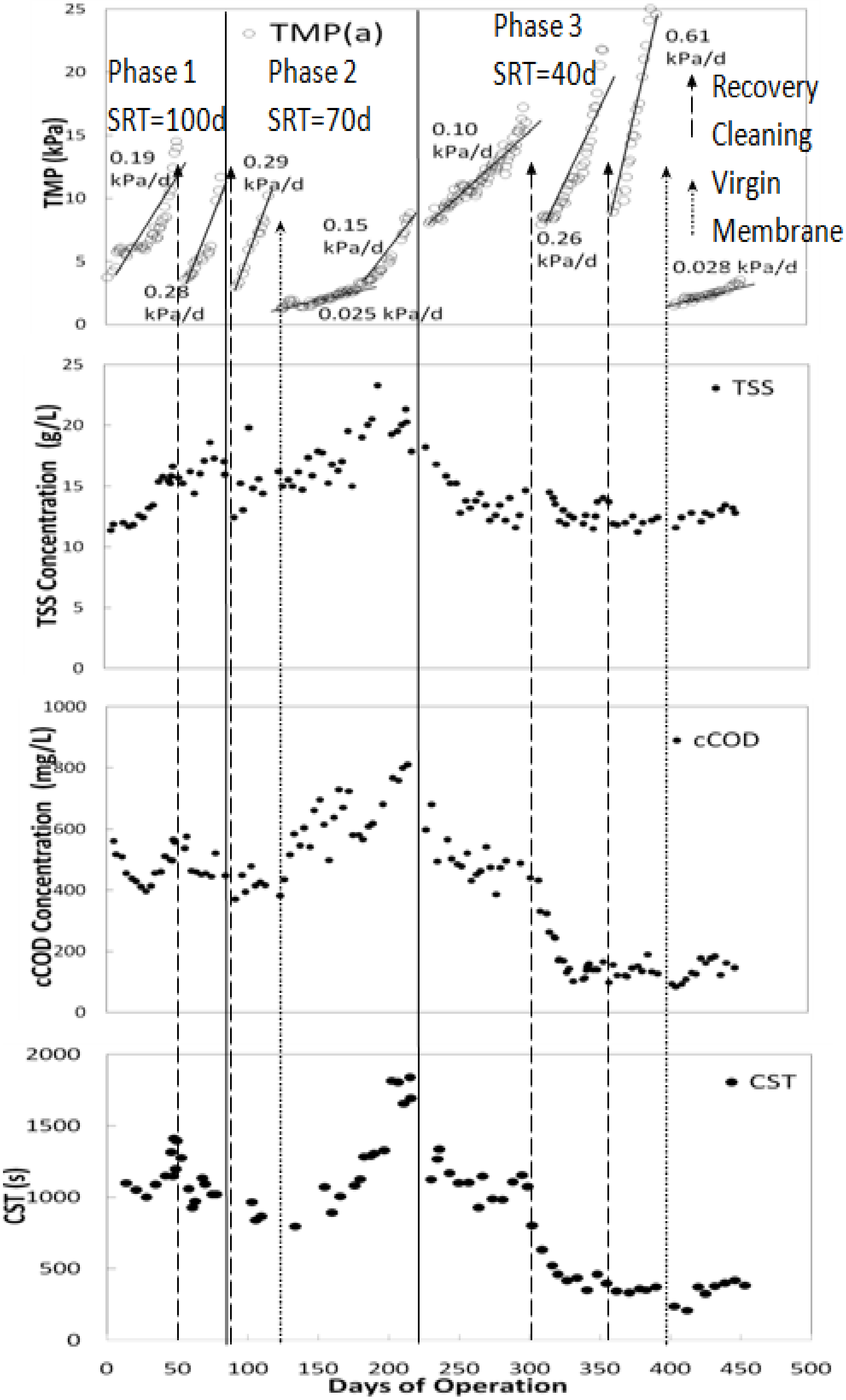


Figure 4-1 TMP Profile and Mixed Liquor Characteristics

4.3.2 Effect of Mixed Liquor Characteristics on Membrane Fouling

SRT has been reported as a controllable parameter that can be employed to modify the mixed liquor characteristics (Huang et al., 2011; Chapter 3). In the current study, the SRT was reduced from 100 to 40 days from Phases 1 to 3. Therefore, it was hypothesized that the mixed liquor characteristics would vary from phase to phase and that this would impact upon membrane performance. Hence, mixed liquor characteristics including the concentration of TSS and the dewaterability of the mixed liquor as indicated by the cCOD concentration and CST were investigated to evaluate this hypothesis. Other foulants in mixed liquor such as protein and carbohydrate in SMP and EPS was found to be consistent with cCOD and not discussed specifically. The results are presented in Appendice A-7.

The TSS concentration of the mixed liquor has been reported as a key factor affecting fouling (Liao et al., 2006; Huang et al., 2011; Gimenez et al., 2011). It is believed that an increase in particulate concentrations results in an increase in the convective flow of solids towards the membrane surface and enhances cake formation and fouling. From Figure 4-1 it can be observed that during Phase 1 the TSS concentrations increased from 11.3 to 16.2 g/L in the transient phase and then stabilized. Upon reduction of the SRT from 100 to 70 days in Phase 2, the TSS concentration initially decreased with time. However, after Day 158 the TSS increased to 21.3 g/L at the end of Phase 2.This was attributed to a 24% increase in the sewage COD concentration in this period. When the SRT was subsequently reduced to 40 days in Phase 3, the TSS concentration declined with time and stabilized at approximately 11.5 g/L due to the reduced SRT and a decline in the sewage COD concentrations. Hence, it was anticipated that membrane performance might have been influenced by the range of TSS concentrations in the mixed liquor.

To further investigate the potential effects of TSS on membrane fouling, the trends in TMP were compared with that of TSS concentrations. From Figure 4-1 it can be observed that elevated fouling rates (0.28-0.61 kPa/d) were under conditions of both high (Day 60-119) and low (Day 315-392) TSS concentrations. Further, lower fouling rates (0.025-0.028 kPa/d) were observed with virgin membranes at both extremes of the TSS conditions. Therefore, it was concluded that TSS concentration over the range of values developed in this study was not a good predictor of membrane fouling.

The presence of cCOD in the mixed liquor had been reported to cause fouling as it can contribute to the formation of a strongly attached cake layer and pore blocking (Fan et al.,2007; Meng et al., 2007). Therefore, the cCOD concentration was employed to evaluate the impact of this mixed liquor property on fouling. From Figure 4-1 it can be seen that the concentration of cCOD was relatively stable (467±54 mg/L) in Phase 1 and for the first 30 days of Phase 2. After Day 158 the cCOD increased to 800 mg/L at the end of Phase 2. When the SRT was reduced to 40 days in Phase 3, the cCOD concentration declined with time and stabilized at approximately 140 mg/L due to the reduced SRT and a decline in the sewage COD concentrations. The trend in cCOD concentrations was generally consistent with the trend in TSS concentrations suggesting an interaction between the mixed liquor properties.

The relationship between cCOD concentrations and membrane fouling was assessed by comparing the trend in TMP values with that of cCOD. As previously described, the cCOD concentrations generally corresponded to the TSS concentrations that failed to explain the rapid increase in TMP on cleaned membranes and the reduced TMPs on virgin membranes. Therefore, it was concluded that cCOD was not a significant factor impacting the long term membrane performance.

Membrane fouling has been reported to be correlated to the dewaterability of the mixed liquor (Huang et al., 2013). Dewaterability is typically easier to measure than direct measurement of potential foulants such as cCOD. In the current study the dewaterability of the mixed liquor was measured by the CST test and the results are presented in Figure 4-1. From Figure 4-1 it can be seen that the trend of CST values closely followed cCOD concentrations. Linear regression of the CST values against the cCOD concentrations demonstrated a strong linear relationship ($r^2=0.81$) between these parameters. As previously discussed the trend in cCOD concentrations were not consistent with the trends in fouling after installation of new membranes and after recovery cleaning. Hence there was a similar lack of consistency between the CST values as a measure of the dewaterability of the mixed liquor and the fouling responses.

Although the long term TMP responses suggested little relationship between mixed liquor properties and membrane fouling it was anticipated that short term fouling (i.e. cake accumulation) would be affected by mixed liquor properties. To evaluate this hypothesis, critical fluxes were estimated using the flux-step method (Le-Clech et al., 2003) on uncleaned membranes in Phase 2 and 3. To ensure similar membrane conditions, the critical flux tests were conducted after virgin membranes had been employed for 55 days in both Phases and the TMP was approximately 3.0 kPa. Figure 4-2presents the results of the critical flux tests. From Figure 4-2 it can be seen that an exponential increase in TMP was observed at fluxes of 23 and 29 LMH in Phase 2 and 3 respectively. This indicated the critical fluxes ranged 21~23 LMH and 27~29 LMH in Phase 2 and 3 respectively. The higher critical flux in Phase 3 than Phase 2 was consistent with the lower TSS and cCOD concentrations and CST values in Phase 3 than in Phase 2. Hence, it was concluded that these parameters did impact upon short term fouling responses however the longer term TMP accumulation was due to other fouling mechanisms.

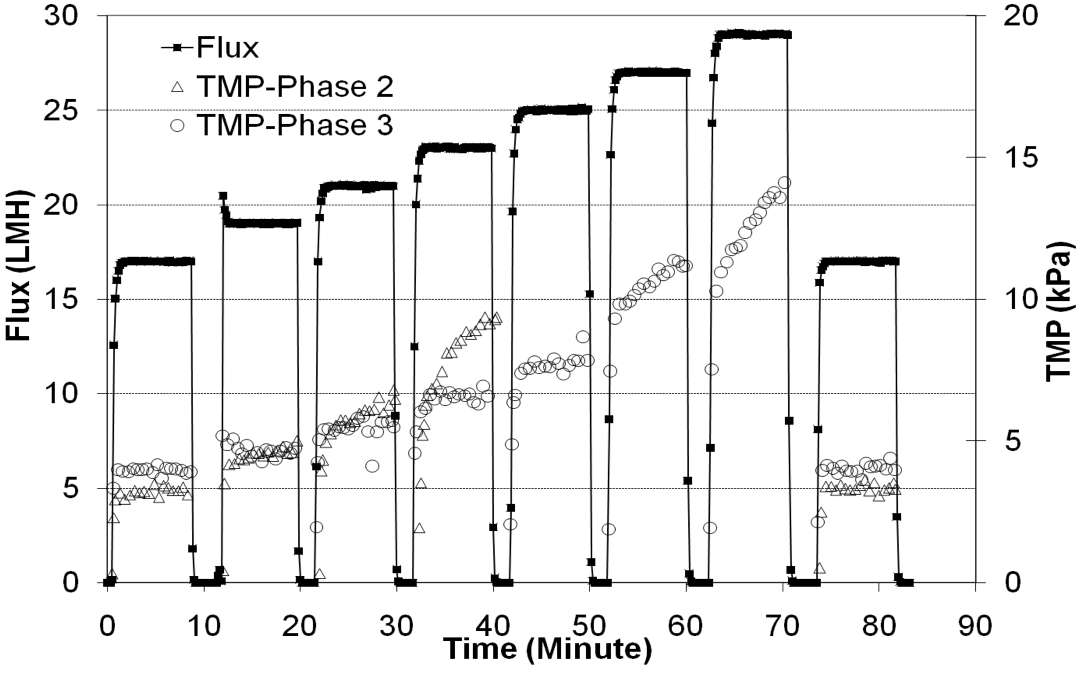


Figure 4-2 Critical Flux Test

4.3.3 Effect of Recovery Cleaning on Membrane Fouling

As previously described, the rate of TMP increase with virgin membranes was lower than that observed with cleaned membranes. It was therefore hypothesized that the membrane fouling that was observed after recovery cleaning was caused by the residual foulants that resisted recovery cleaning. The presence of these residual foulants appeared to have modified the membrane properties such that the accumulation of foulants occurred at an elevated rate as compared to the virgin membranes. Hence, clean water flux (CWF) tests were conducted before and after each recovery cleaning to characterize the impact of the residual foulants on membrane resistance. The flux values and the corresponding TMPs were analyzed by linear regression to estimate the resistances of fouled and cleaned membrane according to Darcy's Law (Equation 4-1).

$$R = \frac{\Delta \mathrm{P}}{J * \mu} \qquad \text{(Equation 4-1)}$$

where R is the resistance, ΔP is TMP, μ is the dynamic viscosity and J is the membrane flux.

The resistances estimated from clean water tests of the fouled and cleaned membranes are presented in Figure 4-3. From Figure 4-3 it can be seen that in all cases recovery cleaning resulted in a substantial reduction in membrane resistances in all cleanings which was consistent with the TMPs that were initially observed after recovery cleaning with the pilot plant. Furthermore, the resistance of cleaned membranes as determined by the CWF test appeared to be higher after each cleaning indicating more residual foulants were left on the membrane. This was consistent with the higher fouling rates that were observed in the pilot plant after each cleaning. To further quantify the effectiveness of the cleaning a resistance model was employed and is discussed subsequently.

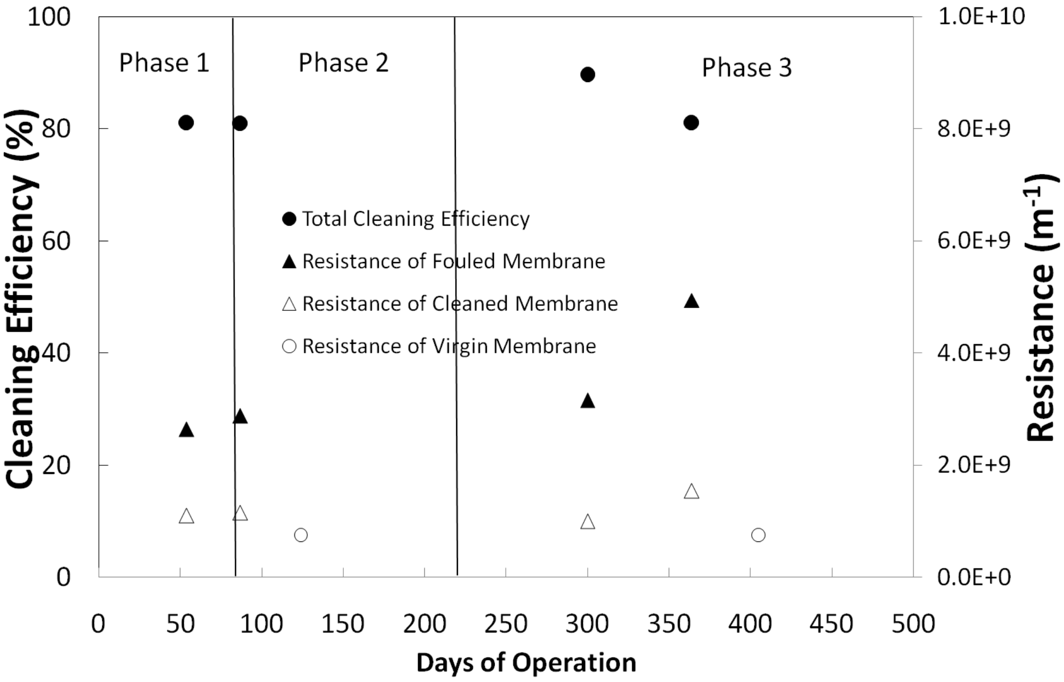


Figure 4-3 Cleaning Efficiency and Membrane Resistance by CWF

To characterize the cleaning efficiency, the total resistance of the fouled membrane (R_T) was fractionated into the virgin membrane resistance (R_M), the fouling resistance removed by recovery cleaning (R_{re}) and the fouling resistance not removed by the recovery cleaning (R_{ir}) (Equation 4-2). R_M and R_T values were estimated from the CWF tests on the virgin and fouled membrane respectively. R_{re} was calculated as the difference in resistance between the fouled membrane and the cleaned membrane. R_{ir} was calculated as the difference in resistances between the cleaned membrane and the virgin membrane.

$$R_T = R_M + R_{re} + R_{ir} \qquad \text{(Equation 4-2)}$$

Where R_T= Total fouled membrane resistance (m^{-1}),

R_M= Virgin membrane resistance (m^{-1}),

R_{re} = Fouling resistances removed by recovery cleaning (m^{-1}),

R_{ir} = Fouling resistance not removed by the recovery cleaning(m^{-1}).

The total cleaning efficiency (CE_{Total}) provides evidence of the extent of residual fouling resistance after recovery cleaning that could have modified the membrane properties. Hence, the CE_{Total} was calculated according to Equation 4-3 and the resulting values

(Figure 4-4) indicated over 80% of the fouling resistance was removed by the recovery cleaning. The cleaning efficiencies were relatively constant across all cleaning events despite having considerably different initial resistances. The high cleaning efficiencies suggested most of the foulants were removed from the membrane, but there was still approximately 20% of the fouling resistance caused by residual foulants. These residual foulants caused low resistance as indicated by the low initial TMPs when either mixed liquor or clean water was filtered suggesting that a majority of the membrane pore spaces were recovered in cleaning. However, the residual foulants appear to have modified membrane properties such as surface charge. The modified properties resulted in more rapid fouling on cleaned membrane than virgin membrane when filtering mixed liquor.

$$CE_{Total} = R_{re}/(R_{re}+R_{ir}) * 100\% \qquad \text{(Equation 4-3)}$$

Similar cleaning efficiency and rapid fouling has been observed by Kim et al., 2011 after recovery cleaning that involved sequentially soaking the membrane in NaOCl and NaOH when a bench scale AnMBR was operated at infinite SRT. In the study of Kim et al, the rapid fouling was significantly mitigated by reducing the SRT from infinite to 25 days to reduce the foulant concentration in mixed liquor. The failure to mitigate fouling after recovery cleaning in the current study may have been due to the use of SRTs in the range of 100 to 40 days that might have retained higher foulant concentrations..

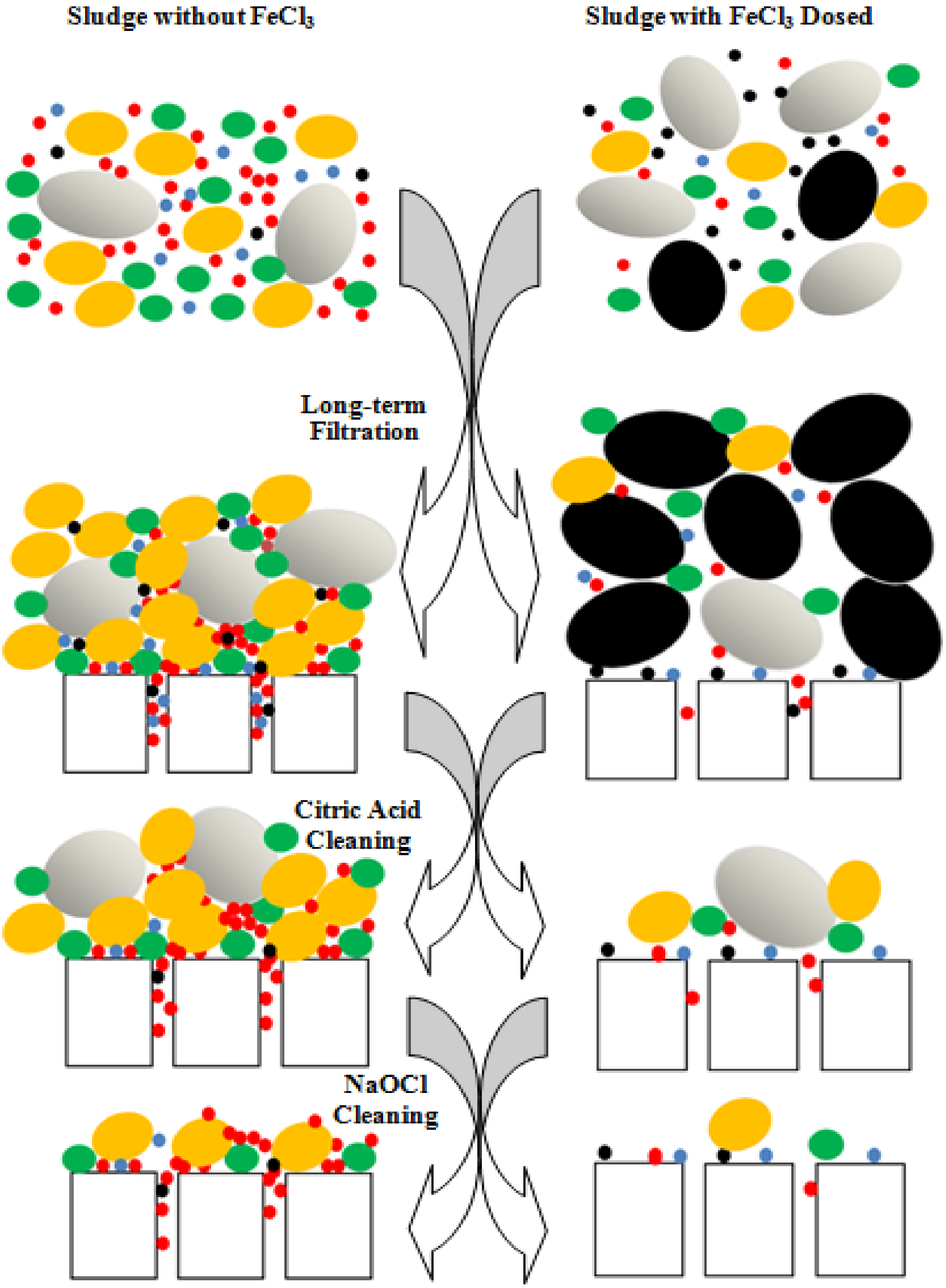
4.4 Significance

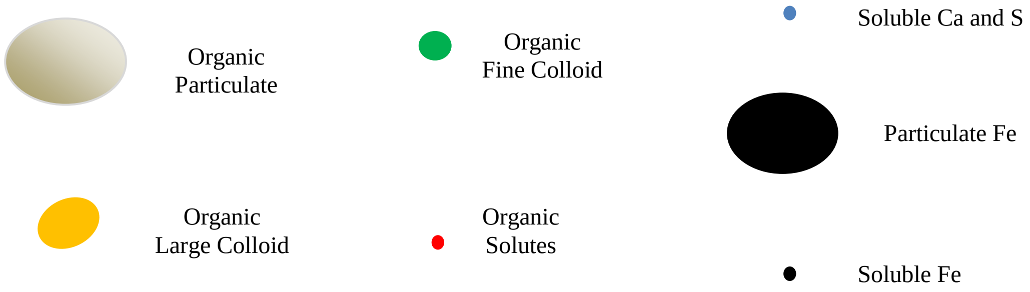
The results obtained in this study provided insight into the membrane performance of AnMBRs when operated over a range of SRTs and recovery cleaning on municipal wastewater. A decrease of SRT from 100 to 40 days resulted in reduced concentrations of TSS concentration and improved dewaterability as indicated by reduction in cCOD concentration and CST. Short term membrane fouling was found to correspond to the varied mixed liquor characteristics as indicated by the results of critical flux tests. Hence it was concluded that these parameters did impact upon short term fouling responses. The longer term fouling behaviour was not consistent with these parameters, but was consistent with the replacement of fouled membranes that was initially cleaned by virgin membranes. Therefore, it appears that the residual foulants that resisted recovery cleaning appear to have modified membrane properties such as surface charge. The modified properties resulted in more rapid fouling on cleaned membrane than virgin membrane when filtering mixed liquor.

Chapter 5

Impact of $FeCl_3$ Dosing on AnMBR Treatment of Municipal Wastewater

Pictorial Abstract:





Key Words: Pilot Anaerobic Membrane Bioreactor, Municipal Wastewater, $FeCl_3$ as Flux Enhancer, Porous Cake Layer

5.1 Introduction

Anaerobic membrane bioreactors (AnMBRs) will likely play a significant role in wastewater treatment in the future as the anaerobic process has low energy and nutrients requirements, low sludge production and can generate biogas that can be directly employed as an energy source. The use of membranes for biomass separation can provide long solid retention times (SRTs) that are required to offset the low growth rates of anaerobic organisms while also producing a solids-free effluent (Liao et al., 2006; Huang et al., 2011). In addition low hydraulic retention times (HRTs) can be achieved to ensure the economical viability of the AnMBRs. Therefore AnMBR is a promising technology for municipal wastewater treatment.

Despite the advantages of AnMBR processes, such as high effluent quality, their application has been limited due to membrane fouling, that reduces permeate flux, increases feed pressure, decreases product quality and ultimately shortens membrane life (Choo et al., 1998). Fouling increases costs by increasing (1) energy consumption, (2) necessary membrane surface area, and (3) construction, labor, shut-downtime, and material costs for cleaning processes. Hence membranes in wastewater treatment are not only operated for a maximum permeate production, but also to minimize fouling.

Membrane fouling in AnMBRs will be affected by the mixed liquor (ML) characteristics that include a complex mixture of organic and inorganic materials which are present in suspended, colloidal and dissolved forms (Liao et al., 2006). Organic fouling results from the accumulation of organic substances on the membrane surfaces and in the membrane pores and can originate from the sewage itself or can be produced by microorganisms in the bioreactor (Le-Clech et al., 2006). The organic substances in soluble phase such as soluble microbial products (SMP) and attached to suspended solids such as Extracellular polymeric substances (EPS) have been reported as significant organic contributors to fouling in MBRs and AnMBRs (Liao et al., 2006). These substances consist of a heterogeneous mixture of polymeric materials including carbohydrates, proteins, lipids, and nucleic acids. However, carbohydrates and proteins are generally considered to be the dominant components in both soluble phase and solid phase (Le-Clech et al., 2006). Proteins are considered to be more hydrophobic than carbohydrates and hence have a greater affinity to membranes than carbohydrates (Masse et al., 2006). Therefore, mixed liquor with a low ratio of carbohydrate to protein (C/P) content in soluble phase and attached to suspended solids would favour accumulation of these materials on the membrane (Liao et al., 2006; Meng et al., 2006; Zhou et al. 2008).

Organic materials in AnMBRs are present in suspended, colloidal and dissolved forms (Liao et al., 2006). Among these forms, the soluble and colloidal organic materials have been reported to be primarily responsible for fouling of MBRs for municipal wastewater treatment (Fan et al., 2006) and AnMBRs for high-strength wastewater treatment (Choo and Lee, 1998) and sludge treatment (Dagnew et al., 2012). Therefore, strategies that could reduce the exposure of the membrane to these substances might mitigate membrane fouling. The addition of $FeCl_3$ has been proven to be effective in mitigating membrane fouling in bench-scale aerobic MBR systems (Koseoglu et al., 2008; Ji et al., 2010; Fan et al., 2007; Song et al., 2008; Zhang et al., 2008). The reduction in fouling was attributed to increased particle sizes and lower concentrations of SMP and colloidal materials. However, there is limited information in the literature on the impact of $FeCl_3$ on membrane performance in continuously operated AnMBRs.

Inorganic substances have also been reported to contribute to fouling (Choo and Lee, 1996; Kang et al., 2002; An et al., 2009; Lin et al., 2009; Calderón et al., 2011; Stuckey, 2012).Inorganic fouling results from precipitation that can occur when inorganic species are present at concentrations exceeding their solubility limits. Choo and Lee (1996) and Kang et al. (2002) showed that inorganic materials such as Al, Ca, Fe, Mg and S can be responsible for irremovable and irreversible membrane fouling by precipitating within the membrane pores and/or on the membrane surface. Hence, it could be expected that inorganic fouling might be mitigated by reducing the concentrations of problematic inorganic species before they have an opportunity to precipitation the membrane.

The hypothesis tested in this study was that dosing of $FeCl_3$ into the influent of AnMBRs treating municipal wastewater would change mixed liquor characteristics and thus lead to improved membrane performance. A pilot AnMBR was employed to investigate the influence of $FeCl_3$ dosing on bioprocess performance and membrane performance of the AnMBR when treating municipal wastewater. A comprehensive characterization of mixed liquor properties, membrane fouling and cleaning responses was conducted with and without $FeCl_3$ dosing.

5.2 Materials and Methods

A pilot scale AnMBR that was fed with 3 mm screened sewage from the Burlington Skyway Wastewater Treatment Plant (Ontario, Canada) was employed in this study (Figure 3-1). The pilot AnMBR consisted of a550L completely mixed anaerobic digester (AD) and an 80L membrane tank (MT) that held a polyvinylidine fluoride (PVDF) hollow fibre membrane module with a surface area of 5.4 m^2 and a pore size of 0.04μm (GE: ZeeWeed 500). The AD contents were mixed by recirculation of the contents at a flow of 3600 L/h with a positive displacement pump. The AD contents were circulated through the MT using a centrifugal pump that withdrew mixed liquor from the bottom of the AD and pumped it to the bottom of the MT after which it was flowed to the top of the AD by overflow. This circulation mixed the MT contents and generated a cross flow velocity (CFV) that would enhance surface shear for membrane fouling control. Biogas produced in the AD was released from the head space of the AD andits production was measured by an electrical gas flow meter. Biogas was recirculated through the MT at a flow of 2.5 cubic feet per minute (0.786 m^3/h (20ºC and 1 atm)) with a blower (KNF NEUBERGER, PM23820-150.1.2) to reduce membrane fouling.

The research was conducted in 2 phases and at the beginning of each phase a virgin membrane was installed in the pilot. Each phase had a duration of 90 days and in Phase 1 the pilot was fed with non-dosed sewage while in Phase 2 a concentrated $FeCl_3$ solution (7.4% w/w) was dosed into the influent to achieve 26.0mg $FeCl_3$/L. Throughout the study the digester HRT and SRT were maintained at 8.5 hours and 70 days respectively while the membrane flux was maintained at 17 LMH with a progressive cavity pump. The temperature of the digester was maintained at 23±1°C by a heat tape that was controlled by a temperature controller which was informed by a temperature sensor in the digester. The pH of the digester was controlled through $NaHCO_3$ addition to maintain a value in the range of 6.7-6.8. Pilot operation and data acquisition were controlled using a programmable logic controller (PLC). The feeding of raw sewage and the wasting of anaerobic digester contents for SRT control were controlled on the basis of the weight of the digester that was monitored by load cells installed at the base of the digester.

The pressures of the headspace in the MT and permeate line were recorded using digital pressure gages. The trans-membrane pressure (TMP) was calculated as the difference between the pressure in the MT and that of the permeate line. To minimize membrane fouling, a discontinuous filtration mode and weekly membrane chemical cleaning were incorporated into the pilot operation. The discontinuous filtration mode consisted of a repeating cycle that had filtration for 8 minutes and relaxation for 2 minutes. The weekly membrane cleaning consisted of backpulsing with 2000mg/L citric acid at 2.9L/min for 4 minutes through the membrane.

Membrane performance was characterized by monitoring the TMP before (TMP(b)) and after (TMP(a)) relaxation. TMP(a) values were considered to be indicative of irreversible fouling that could not be removed by mixed liquor recirculation and biogas sparging. The difference between TMP(b) and TMP(a) values (TMP(b-a)), was considered to result from the presence of reversible foulants that built up on the membrane surface during one filtration cycle but could be removed during relaxation.

At the end of each phase a recovery cleaning of the membranes was conducted to provide information on the nature of the fouling by characterizing the response to cleaning with different chemicals. In the recovery cleaning the membrane module was sequentially soaked in solutions of 2000mg/L of citric acid and 2000mg/L of NaOCl for 16 hours respectively. Clean water flux (CWF) tests were carried out on the virgin and fouled membranes after each chemical exposure. The CWF tests involved permeating tap water through the membrane with a series of flux values that each had a fixed duration and monitoring the TMP at each flux value. The flux values were set at 5, 10, 15, 20, 25, 30 and 35LMH, and each step was conducted for 8 minutes, and between each flux there was a 2-minute relaxation. Linear regression of the TMP and flux values from each CWF test was employed to estimate the resistance of the membrane.

Wastewater, permeate and mixed liquor samples were collected twice a week from the outlets of the feed pump (before the $FeCl_3$ dosing), permeate pump and anaerobic reactor, respectively. The samples were analyzed twice per week for total suspended solids (TSS) volatile suspended solids (VSS), fixed suspended solids (FSS), COD and BOD_5 and once per week for total Kjeldhal nitrogen (TKN), total phosphorus (TP), volatile fatty acids (VFAs) and total and soluble inorganic species (Al, Ca, Fe, Mg and S). All analyses were conducted according to standard methods (APHA, 2005). The methane concentration in the biogas was measured using a gas chromatograph (Agilent Technologies G2802A). The dewaterability of the mixed liquor was measured using the capillary suction time (CST) test (Vesilind, 1988).

The mixed liquor and permeate were analyzed for selected COD fractions once per week to provide insight into the presence of potential foulants. Whole samples and samples that were obtained after sequential filtration through 1.5µm and 0.45µm filters were analyzed for COD. The 1.5µm-filtered COD was analyzed after centrifuging the mixed liquor sample at 4000 rpm for 12 minutes then filtering the supernatant through a 1.5-µm glassfiber filter. The 0.45μm-filtered COD was analyzed after filtering the 1.5μm-filtered COD sample through a 0.45-μm glassfiber filter. The total COD in the mixed liquorwas then fractionated into particulate COD (pCOD), large colloidal COD (lcCOD), fine colloidal COD (fcCOD) and soluble COD (sCOD) according to the modified method reported by Fan et al.,(2006).

The presence of proteins and carbohydrates in the soluble phase and attached to suspended solid in the mixed liquor has been reported to contribute to membrane fouling (Liao et al., 2006; Huang et al., 2011). Both soluble and extracted substances may either be produced by biomass in digester or come from the influent sewage. In the current study samples of the mixed liquor were collected weekly and centrifuged at 8000rpm for 17 min to separate the solids. The supernatant was then filtered through a 0.45-μm glassfiber filter for analysis of soluble substances (Huang et al., 2011) and the solids were extracted with EDTA to obtain the substances associated with particulates (Comte et al., 2006). In light of the pore size of the filter, the filtered samples may have contained fine colloidal matter in addition to soluble matter.

The EDTA extractable materials are typically considered to consist of the products attached to suspended solids (Comte et al., 2006). However, in Phase 2 of this study it was expected that these extracts would also include colloidal substances that would be incorporated into the suspended solids through coagulation by $FeCl_3$. The modified Lowry method (Frølund et al., 1995) and Dubois phenolesulphuric acid method (Dubois et al., 1956) were employed to quantify protein and carbohydrate concentrations in the samples. Bovine serum albumin (BSA) and glucose were employed as the standard references, respectively.

The presence of foulants on the membranes was examined through extraction of fouled membrane fibres that were cut from the modules at the end of the tests. Selected fibres were extracted with ultrasound under basic conditions (0.1M/L NaOH) for 1 hour. The basic extracts were filtered through 0.45 μm glassfiber filters, neutralized with H_2SO_4, then analyzed for TOC (Hall and Berube, 2006). Separate fibres were extracted with ultrasound under acidic conditions (2000 mg/L citric acid) for 1 hour. The acid extracts were filtered through a 0.45-µm glassfiber filter, neutralized with NaOH, then analyzed for inorganic elements (Mg, Ca, Fe, Al and S). Further, the thickness of the foulant layer and the distributions of proteins and carbohydrates on the fouled membrane samples was examined microscopically with an upright confocal laser scanning microscope (CLSM) (Leica DM RE microscope connected to a Leica TCS SP2) according to the methods described by Lin et al, 2009.

The influence of the addition of $FeCl_3$ on the treatment performance and sludge characteristics was assessed statistically (ANOVA). In the subsequent discussion of results the significance of the statistical analysis is presented in brackets (i.e. p< xxx) whenever a statistical assessment was conducted to determine if a comparison between the Fe-dosed response and non-Fe-dosed response was statistically significant.

5.3 Results and Discussion

5.3.1 Start-up Phase

Prior to Phase 1 the pilot AnMBR was operated at an HRT of 8.5 hours and SRT of 70 days for 5 months without $FeCl_3$ addition. At this time a virgin membrane was installed and all of Phase 1 was assumed to be at steady state as indicated by constant VSS concentrations (Mean±SD: 5.6±0.6g/L). Prior to Phase 2, the AnMBR system was operated with $FeCl_3$addition to the influent at 26mg/L for 5 months. The membrane was then replaced with a virgin membrane and Phase 2 was initiated. The VSS in the first 75 days in Phase 2 stabilized at 12.8±2.0g/L, indicating the steady-state operation was achieved. However, from Day 76 to 90, the VSS increased because the sewage COD increased by approximately 24% ($p<0.009$). Therefore, the data collected in the first 75 days was deemed to represent steady state and was employed in the subsequent analysis.

5.3.2 Effect of $FeCl_3$ Dosing on Bioprocess Performance

The bioprocess performance was evaluated with respect to COD, BOD_5, TP and TKN. The average (±SD) concentrations of COD, BOD_5, TKN and TP in the sewage and permeate and the removal efficiencies are presented in Table 5-1. Due to the seasonal variation, the average concentrations of COD, BOD_5 and TP in the sewage in Phase 2 were 53.4% ($p<1.0*10^{-10}$), 46.9% ($p<2.2*10^{-6}$) and 41.7% ($p<0.001$) higher than in Phase 1. However, no significant difference was found in sewage TKN concentration ($p<0.32$). Therefore the removal efficiency was employed to characterize the influence of $FeCl_3$ addition on the treatment performance.

From Table 5-1 it can be seen that the average COD removal efficiencies were 79.9% and 93.7% in Phases 1 and 2 respectively while the average BOD_5 removal efficiencies were 84.2% and 95.0% respectively. Hence, the removal efficiencies of COD and BOD_5in Phase 2 were 17.3% ($p<2.86*10^{-11}$) and 12.8% ($p<5.88*10^{-7}$) higher than in Phase 1. The results suggest that the addition of $FeCl_3$ had significant influence on the removal efficiencies of COD and BOD_5. It would appear that some of the organic matter that was soluble could be coagulated to form floc that was retained in the reactor by the membrane.

Table 5-1 Treatment Performance Characteristics

	Without $FeCl_3$ Dosing (Mean±SD)			$FeCl_3$ Dosed (Mean±SD)		
Response	Sewage (mg/L)	Permeate (mg/L)	Removal Efficiency (%)	Sewage (mg/L)	Permeate (mg/L)	Removal Efficiency (%)
COD	251±59	45.8±11	79.9±7.7	385±112	36.2±5.9	93.7±2.0
BOD_5	96±19	14.7±4	84.2±5.0	141±28	7.7±3.7	95.0±1.5
TP	3.6±0.9	2.0±0.7	39.8±7.2	5.1±1.1	2.7±0.6	49.6±12.9
TKN	41.1±8.9	24.7±3.9	41.3±14.7	44.8±6.0	30.2±5.5	30.3±10.6

In contrast to the high removal efficiencies of COD and BOD_5, the removals of TKN and TP were modest in both phases. $FeCl_3$ dosing showed no significant influence on the removal of TKN ($p<0.09$) and TP ($p<0.11$). By comparison Gomez et al.(2013) observed an increase in TP removal efficiency from 54.7% to 85.6% and a decrease in TKN removal efficiency from 92.5% to 84.7% when a similar concentration of Fe^{3+} was dosed into an aerobic MBR treating municipal wastewater. The absence of an effect on TP and TKN removals observed in the current study was attributed to the reduction of ferric iron to ferrous iron in the anaerobic environment that would modify the nature of the complexes and precipitates that were formed. Hence, the permeate of AnMBRs treating municipal sewage will have elevated concentration of P and N regardless of whether iron is dosed into the sewage.

The production of methane can contribute to the sustainability of AnMBRs as it might be employed to compensate for the energy consumed in AnMBR operation. However, the addition of Fe^{3+} might reduce the methane production due to sequestration of organic matters or by acting as an external electron acceptor. Therefore, the methane measured in the biogas and the estimated methane dissolved in the permeate (Henry's Law) were employed to calculate the methane yield based on the fed COD. The methane yields were 102±29.4 $mlCH_4/gCOD_{fed}$ in Phase 1 and 91±37.8 $mlCH_4/gCOD_{fed}$ in Phase 2 (0ºC and 101.3kPa) and were not statistically different ($p<0.31$). Hence it was concluded that $FeCl_3$ dosing did not inhibit the activity of methanogens or reduce the availability of the organic matter in the sewage.

Sludge production is an important factor to consider when assessing the sustainability of AnMBRs (Liao et al., 2006; Smith et al., 2012). Hence, the sludge production was assessed in both phases on the basis of VSS, FSS and TSS in the wasted sludge and daily COD loading (Figure 5-1). The average yields of VSS and FSS were significantly higher in Phase 2 than in Phase 1 (54.0% ($p<6.13*10^{-8}$) and 630.0% ($p<6.99*10^{-7}$) respectively). This resulted in a significant reduction in the VSS/TSS ratio from 0.92 in Phase 1 to 0.73 in Phase 2 ($p<7.6*10^{-8}$). The results indicate that the addition of $FeCl_3$ captured organics into the sludge stream as VSS that were not captured in its absence. As the membrane was expected to capture all colloidal COD in both phases it would appear that organics that are normally considered to be soluble were captured by $FeCl_3$ addition.

The addition of $FeCl_3$ had a greater impact upon the production of FSS and this was likely due to the formation of precipitates of Fe^{2+} that would be formed in the digester (Hansen et al., 1999). The substantial production of these precipitates would add to the mass of sludge requiring disposal. However, it is worth noting that even with $FeCl_3$

addition, the overall sludge yields were less than those associated with aerobic wastewater treatment (Metcalf and Eddy, 2003). It was anticipated that the substantial production of fixed suspended solids would modified the properties of the mixed liquor and hence impact the membrane performance. This response is subsequently described.

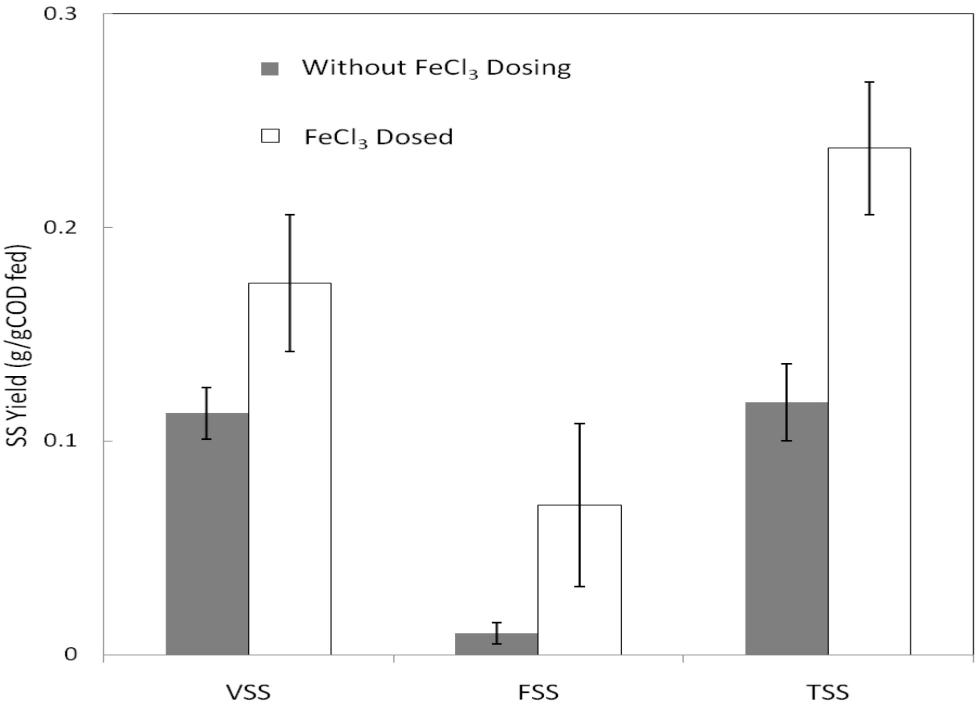


Figure 5-1 Suspended Solids Yields

5.3.3 Membrane Performance

The impact of $FeCl_3$ dosing on membrane performance was assessed by examining the TMP profiles after relaxation (TMP(a)) and the TMP recovery during relaxation (TMP(b-a)) (Figure 5-2). Changes in TMP(a) were assumed to be indicative of the accumulation of irreversible foulants on the membrane surface which was caused by the formation of strongly-attached cake layer and pore blocking. From Figure 5-2 it can be seen that without $FeCl_3$ addition TMP(a) values were in the range of 5.7~6.3 kPa for the first 45 days but then increased to 21.5kPa by day 91. By contrast, with $FeCl_3$ addition TMP(a) values were in the range of 1.5~5.1 kPa for the first 75 days and then increased to 8.8kPa by day 90. The results indicate that the addition of $FeCl_3$ can mitigate the development of irreversible fouling and maintain low fouling rates over an extended period. The mitigated irreversible fouling with $FeCl_3$ addition may have been due to the coagulation of colloidal and soluble substances in the mixed liquor as they have been reported to directly contribute to irreversible fouling (Lee et al., 2001; Wu et al., 2008; Meng et al., 2009). The results of the investigation of these foulants will be discussed subsequently.

The reduction in TMP during membrane relaxation (TMP(b-a)) was assumed to represent the presence of reversible foulants that accumulated during filtration were removed by biogas sparging and mixed liquor recirculation during relaxation which was caused by the loosely-attached cake layer. From Figure 5-2 it can be seen that without $FeCl_3$ addition the TMP(b-a) values were in the range of 2.0~3.1kPa for the first 33 days and then increased to 18.8kPa by day 91. By contrast with $FeCl_3$ addition the TMP(b-a) values were in the range of 0~0.2 kPa for the first 75 days and then increased to 2.5kPa by day 90. The results indicate that operation with $FeCl_3$ addition achieved superior membrane performance through mitigation of the formation of reversible foulants in addition to the irreversible fouling previously discussed.

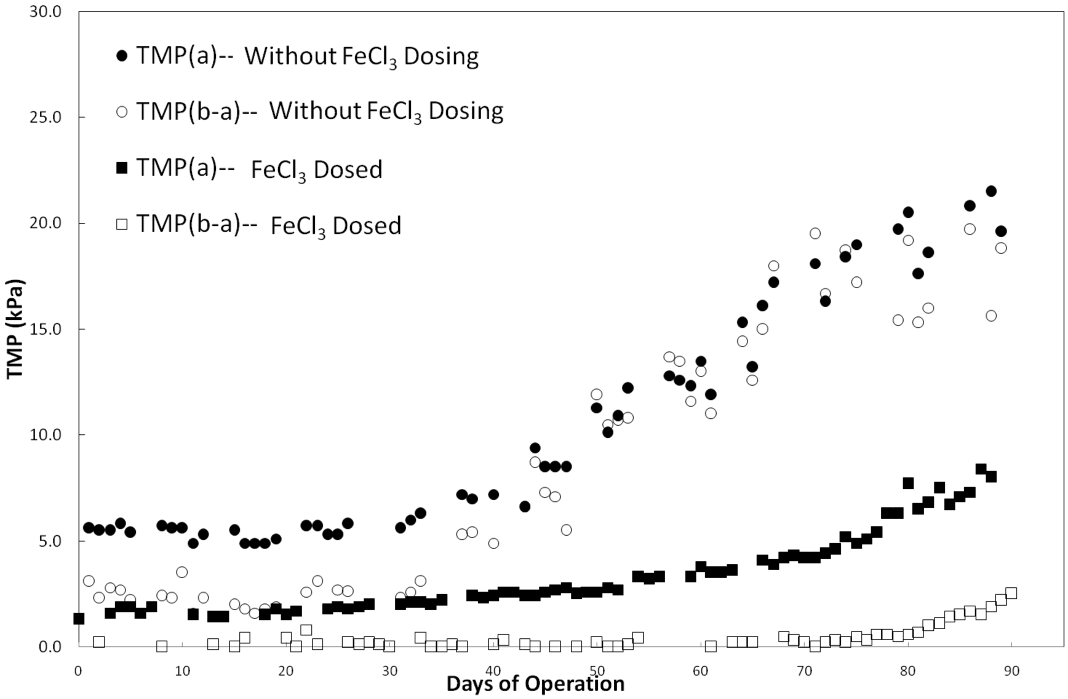


Figure 5-2 TMP Profile

It is interesting to note that the membrane performance was assessed at a flux of 17 LMH. This flux was higher than that of other reported AnMBRs for municipal wastewater treatment, which ranged from 5 to 12LMH (Kim et al., 2011; Huang et al., 2011; Gimenez et al., 2011; Salazar-Peláez et al., 2011; Martinez-Sosa et al., 2011). The flux of 17LMH is close to the operational flux range reported for aerobic MBRs for municipal wastewater treatment (20-27 LMH) (Judd, 2002; Patsios et al., 2011; Hwang B.K. et al., 2012; Van den Broeck et al., 2012). Hence, $FeCl_3$ dosing is believed to be an effective strategy for membrane fouling mitigation that would enable AnMBRs to be competitive with aerobic MBRs when flux is considered.

5.3.4 Investigation of Potential Foulants and Role of $FeCl_3$ as a Flux Enhancer

As previously described, the addition of $FeCl_3$ to the raw wastewater resulted in a substantial reduction in the fouling of the membranes in the AnMBR. The following analysis was conducted to obtain insight into the membrane fouling with and without dosing $FeCl_3$. In AnMBRs the anaerobic mixed liquor is in direct contact with the membrane and hence it can be expected that its composition will play a key role in membrane fouling. Therefore the mixed liquor TSS, COD fractions, SMP and EPS were evaluated with and without $FeCl_3$ dosing and correlated to the membrane performance.

The TSS concentration has been identified as a key factor for membrane fouling (Liao et al., 2006; Huang et al., 2011; Gimenez et al., 2011). It is believed that an increase in the suspended solids concentration results in an increase in the convective flow of solids towards the membrane surface and enhances cake formation and fouling. However, in this study both reversible and irreversible fouling were reduced with $FeCl_3$ addition despite the fact that TSS increased by 205% from approximately 5.8g/L in Phase 1 to 17.7g/L in Phase 2. Hence, it was hypothesized that the superior membrane performance observed with $FeCl_3$ dosing resulted from the modifications of mixed liquor characteristics, such as particle size distribution and availability of protein and carbohydrate in soluble phase and attached to suspended solid.

In this study, the particle size distribution was investigated by measuring the concentration of each COD fraction in the mixed liquor using a series of filter sizes (Figure 5-3). From Figure 5-3 it can be seen that $FeCl_3$ dosing resulted in an increase in the pCOD concentration by 170.3%. By comparison the average lcCOD, fcCOD and sCOD concentrations decreased by 33.4%, 27.1% and 26.2% respectively. ANOVA tests showed that all of the changes in COD fractions were statistically significant (pCOD ($p<5.7*10^{-26}$), lcCOD ($p<1.7*10^{-11}$), fcCOD ($p<9.6*10^{-7}$) and sCOD ($p<0.002$)). The shift in particle sizes from the colloidal to particulate fractions likely reduced the fouling of the membrane. The larger particles are less likely to clog pores to cause irreversible fouling and can be more readily removed by shear stresses during relaxation (Fan et al., 2006; Lin et al., 2009).

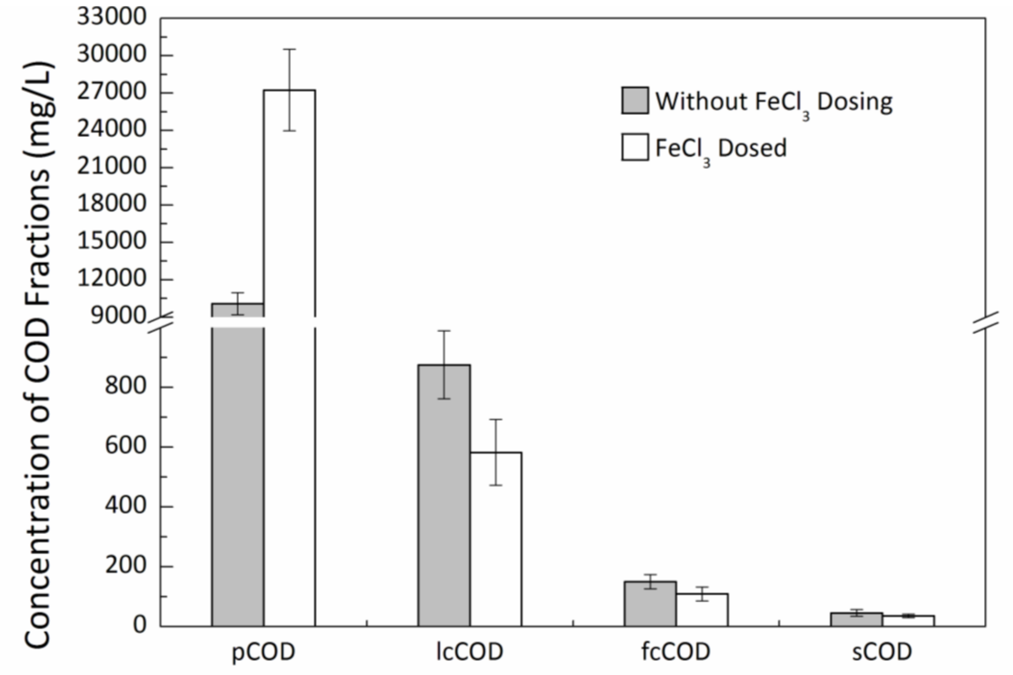


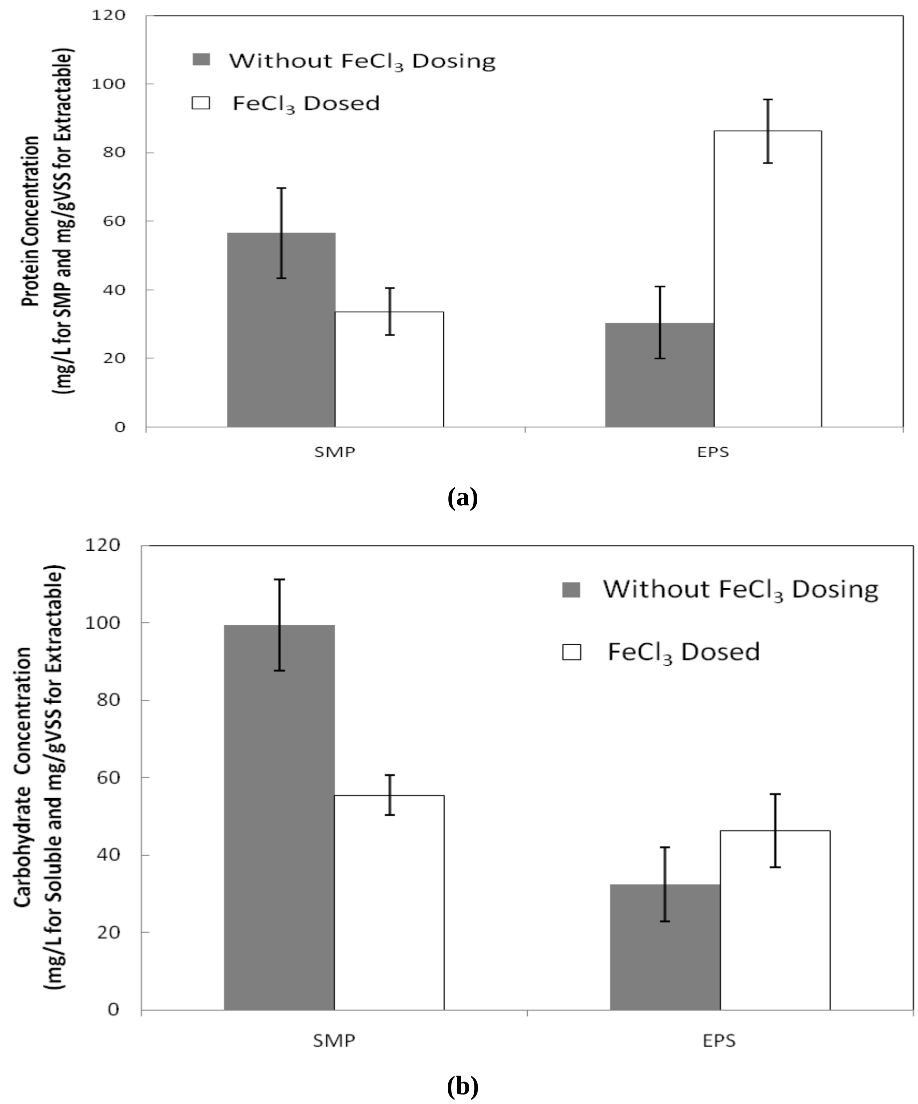
Figure 5-3 Concentrations of COD Fractions in Mixed Liquor

An increase in the particulate species and a reduction in the colloidal and soluble substances have been found to improve the dewaterability of the sludge as measured by the CST test. Hence, the CST test was conducted to characterize the change in the dewaterability of the mixed liquor upon $FeCl_3$ addition. The results showed the average CST was reduced by 48.0% from approximately 2700±106s in Phase 1 to 1316±288s in Phase 2 ($p<3.1*10^{-21}$). The reduced CST values were consistent with the reduced fouling of the membrane and the observed shift in the particle sizes to larger particles. Hence, the CST test may be a viable method for assessing the impact of coagulant dosing on fouling reduction in AnMBRs.

Carbohydrates and proteins in the soluble phase and extracts of the solids were characterized to obtain better understanding of these potential foulants in the mixed liquor. Figure 5-4 shows that the addition of $FeCl_3$ reduced the average concentration of protein in the SMP by 40.5% from 56.6 mg/L to 33.7 mg/L ($p<0.0002$) and the average concentration of soluble carbohydrates by 44.2% from 99.4 mg/L to 55.5mg/L ($p<5.8*10^{-8}$). These significant reductions in soluble proteins and carbohydrates were likely due to the bridging of anionic groups such as OH^-, COO^-, SO_4^{2-} and PO_4^{3-} on these compounds (Razska et al., 2006; Meng et al., 2007) by Fe^{2+} that would bridge them to form flocs or attach them to the surface of the flocs. The reduction in these soluble species was consistent with the previously described reductions in soluble COD fractions with $FeCl_3$ addition.

It is hypothesized that the changes in soluble species composition contributed to the reduction in membrane fouling that was observed with $FeCl_3$ addition. The reduced concentrations of soluble proteins and carbohydrates in the mixed liquor would favor fouling mitigation by reducing pore blockage and the formation of a strongly-attached cake layer that have been reported to be stimulated by these substances (Liao et al., 2006; Herrera-Robledo et. al. 2011). Therefore, the reversible and irreversible fouling in Phase 2 were dramatically lower than Phase 1.

The presence of extractable protein and carbohydrate (often referred to as EPS) has been reported to contribute to membrane fouling (He et al., 2005 and Zhang et al., 2010) since EPS was associated with loosely-attached cake layer formation on the membrane surface and further physically stabilized the cake layer to be strongly attached to the membrane thereby protecting them from routine cleaning cycles. Figure 5-4 demonstrates that $FeCl_3$ addition increased the average concentration of extracted protein by 183%, from 30.5 mg/gVSS to 86.3 mg/gVSS ($p<1.09*10^{-11}$) and the average concentration of extracted carbohydrates by 42.5% from 32.5 mg/gVSS to 46.3 mg/gVSS ($p<0.004$). The increased concentrations of extracted species were attributed to the capture of soluble proteins and carbohydrates to the solid phase by coagulation that was induced by $FeCl_3$ addition. The reduced fouling in the presence of increased extractable protein and carbohydrate concentrations when $FeCl_3$ addition was employed contradicts the trends that have been reported in the literature. It appears that when these components were captured in the suspended solids they were bound in a manner that reduced their propensity to foul the membrane. This may have been due to modifications in charge as well as increased particle sizes.



(a)

(b)

Figure 5-4 Soluble and Extractable Protein (a) and Carbohydrate (b) Concentrations

In both phases of the study the fouled membranes were harvested before recovery cleaning to investigate the composition of the foulants on the membrane. Basic (0.1M/L NaOH) and acidic extracts (2000mg/L citric acid) were analyzed for TOC and inorganic elements (Al, Ca, Fe, Mg and S) respectively. Figure 5-5 presents the mass of each extracted component per unit of membrane surface area. From Figure 5-5 it can be seen that $FeCl_3$ dosing reduced the average accumulation of TOC on the membrane by 41.5% ($p<0.001$). The reduced TOC on the membrane with $FeCl_3$ addition indicates a reduced accumulation of potential foulants and was consistent with the previously described reduced presence of colloidal and soluble organic substances in the mixed liquor.

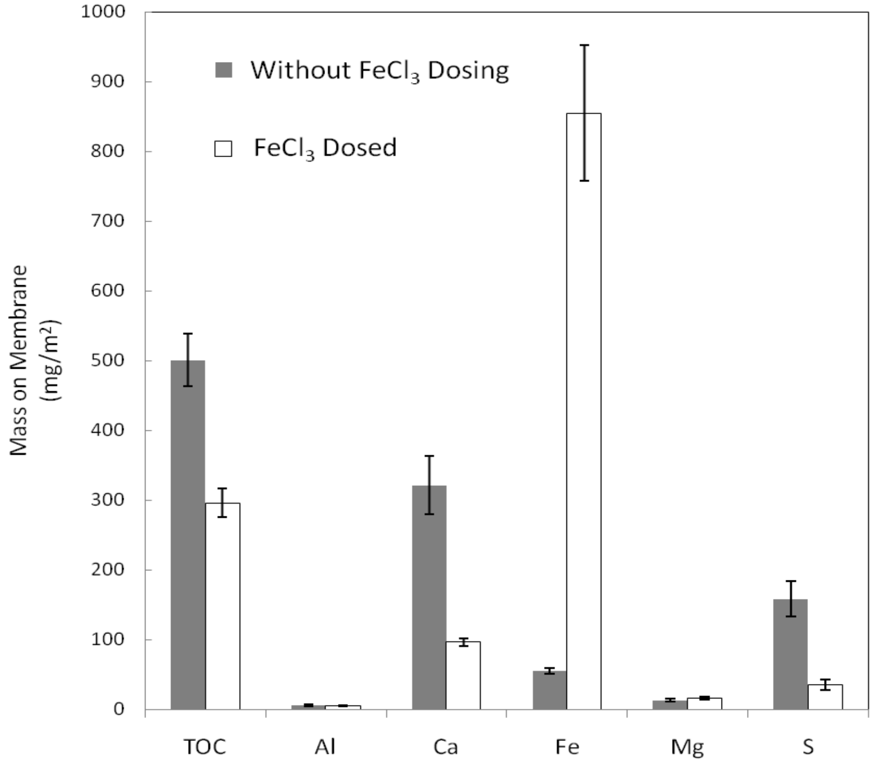


Figure 5-5 Extracted Components from Fouled Membranes

The addition of $FeCl_3$was expected to modify the deposition of inorganic elements on the membrane due to the increased iron concentrations which would form inorganic precipitates and also potentially compete with other cations in substitution reactions. Figure 5-5 shows that $FeCl_3$ dosing resulted in a 15.8 fold increase in Fe ($p<0.0001$) on the membrane surface, whereas the average accumulations of Ca and S were reduced by 70% ($p<0.0008$) and 78% ($p<0.001$) respectively. The masses of Al ($p<0.70$) and Mg

($p<0.13$) on the membrane were considerably smaller than the other measured elements and were not changed with Fe addition.

The presence of the extracted Ca, Fe and S on the membrane upon the $FeCl_3$ addition was related to their concentrations in the mixed liquor (Table 5-2). The particulate concentrations of these inorganic species represent the difference between the total concentration and soluble concentration. From Table 5-2 it can be seen that the Fe concentration in sewage has no statistical difference ($p<0.79$) while in Phase 2 the average concentrations of soluble Fe and particulate Fe in mixed liquor increased by 56% ($p<0.03$) and 11.5 fold ($p<1.6*10^{-24}$) respectively, which could be attributed to the dosed $FeCl_3$ and the precipitates formed by Fe. Therefore, the increased extracted Fe on the membrane could be explained by the increased soluble and particulate Fe in mixed liquor.

To characterize the influence of $FeCl_3$ addition on the concentrations of S and Ca in mixed liquor, their total concentrations in sewage and soluble and particulate concentrations in mixed liquor are investigated. Table 5-2 shows with $FeCl_3$ addition the average soluble concentrations of S in mixed liquor was reduced by 15% ($p<0.005$), while the average particulate concentration of S in mixed liquor increased by a fold of 4.8 ($p<2.7*10^{-9}$) which resulted in the average total concentration of S in mixed liquor increased by a fold of 4.7 ($p<4.3*10^{-12}$). Considering the total concentration of S in sewage was reduced by 18% ($p<0.005$) in Phase 2, the reduced soluble S and increased particulate S were likely due to the precipitation of FeS in the mixed liquor.

The fate of Ca upon the addition of $FeCl_3$ was consistent with that of S. The average total concentration of Ca in sewage and the average soluble concentration of Ca in mixed liquor were reduced by 17.7% ($p<1.5*10^{-5}$) and 16.3% ($p<2.08*10^{-6}$) respectively, while the average total and particulate concentration of Ca in mixed liquor increased by 83% ($p<1.5*10^{-7}$) and 168% ($p<2.6*10^{-11}$). Therefore the reduced soluble Ca and increased particulate Ca could be attributed to the addition of $FeCl_3$. However, the underlying mechanism is still not known.

The forms S and Ca presented in mixed liquor may play a key role when they contact with membrane. With less soluble and more particulate S and Ca in mixed liquor when $FeCl_3$ was dosed into the influent, less these inorganic elements were extracted from the fouled membrane. It can be concluded that the fate of accumulated S and Ca depend on their soluble concentrations.

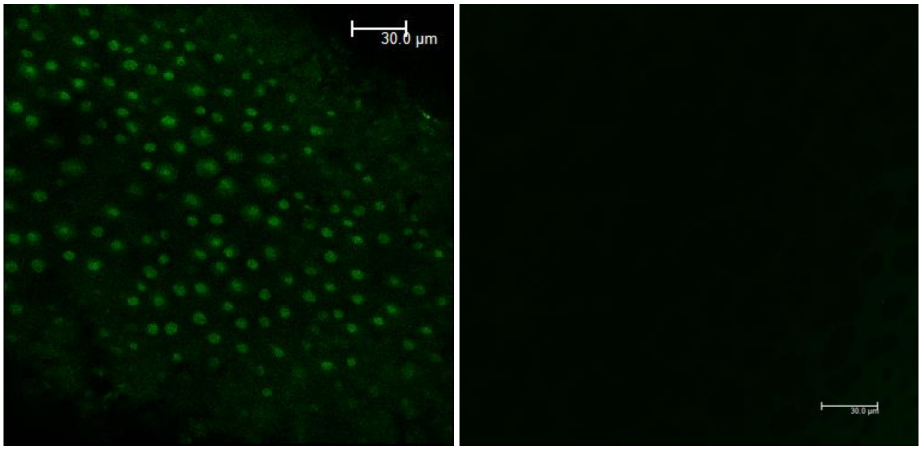
Table 5-2 Inorganic Elements in Sewage and AD

	Sewage		Soluble in AD		Particulate in AD	
	Without $FeCl_3$ Dosing (Mean±SD)	$FeCl_3$ Dosed (Mean±SD)	Without $FeCl_3$ Dosing (Mean±SD)	$FeCl_3$ Dosed (Mean±SD)	Without $FeCl_3$ Dosing (Mean±SD)	$FeCl_3$ Dosed (Mean±SD)
Ca (mg/L)	90.9±8.8	74.7±8.0	86.1±7.4	73.0±4.1	166.0±53.1	445.7±27.6
Fe (mg/L)	2.5±1.7	2.9±1.0	0.11±0.09	0.18±0.06	193.2±31.4	2425.6±213.6
S (mg/L)	28.3±4.2	23.1±4.6	6.8±1.9	4.9±1.3	216.3±42.8	1254.9±381.4

Reduced membrane fouling was observed in spite of the substantial increase in Fe accumulation on the membrane when $FeCl_3$ was dosed. The improved performance may have been at least partially due to the reduction in Ca and S accumulation on the membrane. The observed Fe likely did not contribute to fouling as it was effectively bound in the particulate matter.

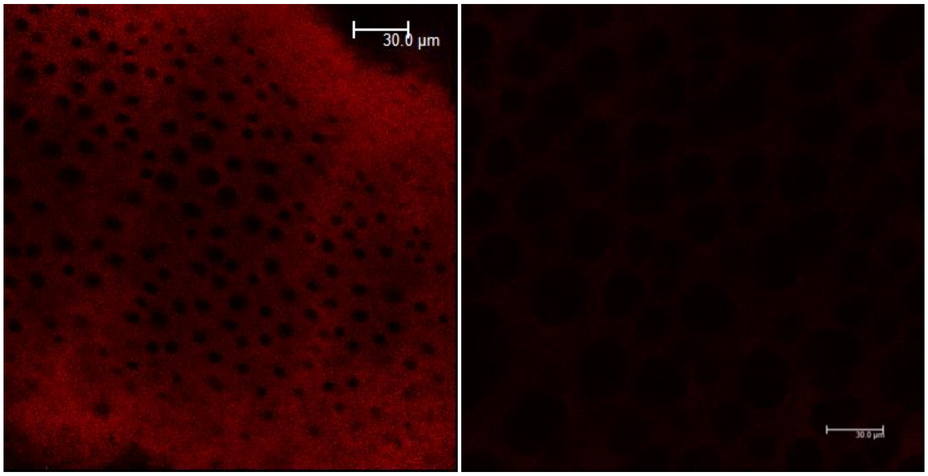
The previous discussion illustrated that there were substantial differences in the quantities of substances extracted from the membrane when $FeCl_3$ was dosed into the wastewater. Hence, it was hypothesized that the thickness and composition of the foulant layer would be impacted. Fouled membranes were harvested and examined by CLSM to estimate the thickness of the foulant layer. The average measured thickness of the foulant layer in Phase 1 was 21±1.7 µm and this increased to 31±3.6 µm (Mean±SD, n=4) in Phase 2 ($p<0.01$). The previously described chemical extraction results indicated reduced TOC, Ca and S accumulation and increased Fe accumulation in Phase 2. When considered with the CLSM data it would appear that the additional mass of material contributing to the fouling later was inorganic in nature and associated with the Fe content. Further, considering the reduced membrane fouling observed in Phase 2, with a thicker foulant layer, it appears that the fouling layer had a more porous structure when $FeCl_3$ was dosed.

The profile of proteins and carbohydrates deposited on the membrane surface can provide insight into the mechanisms leading to foulant accumulation on the membrane (Lin et al., 2009). Hence, the CLSM images were also employed to investigate the deposition of proteins and carbohydrates on the membrane surface. Figures 5-6 and 5-7 present the typical images of the protein and carbohydrate responses on the membrane surface for samples that were obtained from both phases of testing. From these images it can be seen that without $FeCl_3$ dosing, most of the membrane surface was covered by protein (green) and carbohydrate (red), while with $FeCl_3$ dosing the blank color (black) dominated the images indicating protein and carbohydrate were present at significantly lower levels on the membrane surface. These results are consistent with the results of soluble protein and carbohydrate in mixed liquor. In addition, the affinity of particulate substances to the membrane could be enhanced because the addition of $FeCl_3$transferred the soluble protein and carbohydrate to the particulate phase by coagulation which has been proved by the results of extractable protein and carbohydrate. Therefore, the particulate substances deposited on the membrane surface developing a porous foulant layer, which prevented the direct contact between the soluble protein and carbohydrate and the membrane. Therefore, there was less protein and carbohydrate observed on the membrane surface with the addition of $FeCl_3$.



Without $FeCl_3$ Dosing **$FeCl_3$ Dosed**

Figure 5-6 CLSM Images on Protein (Green) Distributions in Fouling Layers



Without $FeCl_3$ Dosing **$FeCl_3$ Dosed**

Figure 5-7 CLSM Images on Carbohydrate (Red) Distributions in Fouling Layers

5.3.5 Responses to Recovery Cleaning

At the end of each phase the fouled membranes were subjected to chemical recovery cleaning and then clean water flux (CWF) tests were conducted. These results were examined to obtain further insight into membrane fouling mechanisms and the role of $FeCl_3$ addition as a flux enhancer. Figure 5-8 shows the results of the CWF tests of fouled and cleaned membranes from both phases. As was expected from the results of the pilot operation, the fouled membrane without $FeCl_3$ addition had higher TMP responses than that from the $FeCl_3$ dosed phase. Recovery cleaning resulted in a substantial reduction in TMPs in both cases although the $FeCl_3$ dosed membrane values approached closer to those of the virgin membranes than the non-dosed membrane. To further quantify the effectiveness of the cleaning a resistance model was employed and is discussed subsequently.

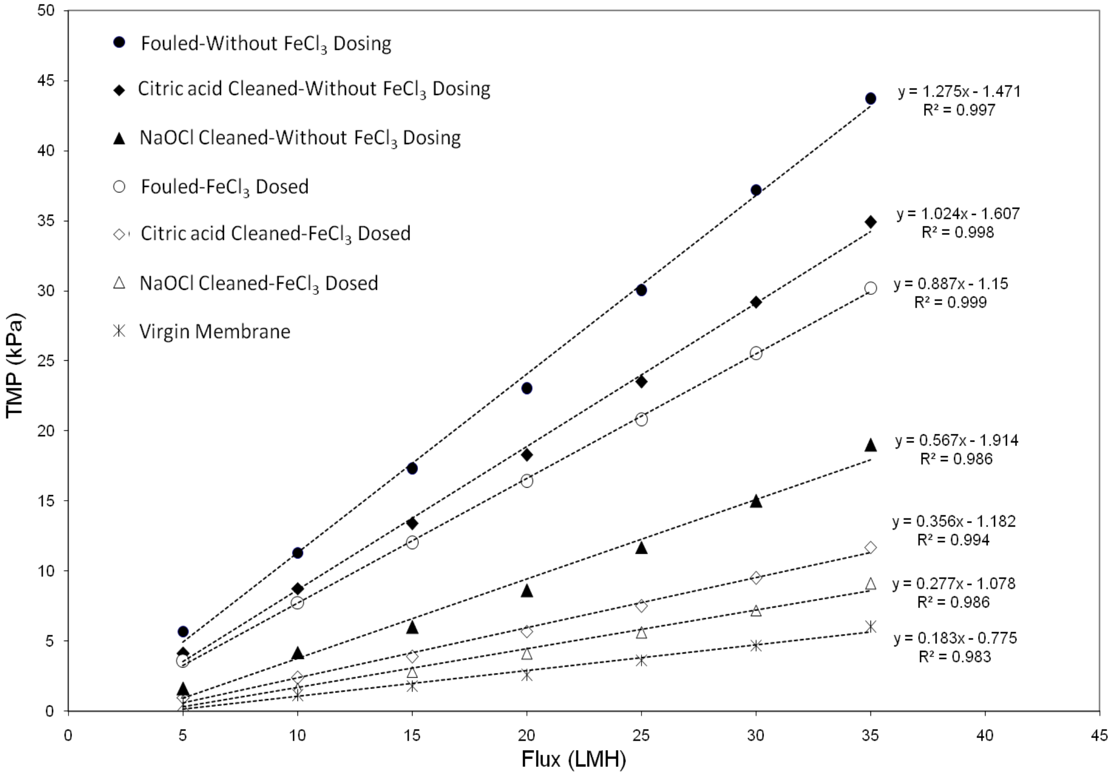


Figure 5-8 Clean Water Flux Tests on Fouled and Cleaned Membranes

Linear regression of the CWF flux values and the corresponding TMPs was employed to calculate the resistance according to Darcy's Law (Equation 4-1). To characterize the cleaning efficiency of each step, the total resistance of fouled membrane (R_T) can be fractioned into virgin membrane resistance (R_M), the fouling resistance removed by citric acid (R_{ca}), the fouling resistance removed by NaOCl (R_{NaOCl}) and the fouling resistance not removed by the cleaning protocol (R_{ir}) (Equation 5-1).

$$R_T = R_M + R_{ca} + R_{NaOCl} + R_{ir} \qquad \text{(Equation 5-1)}$$

Where R_T is the total fouled membrane resistance, R_M is the virgin membrane resistance, R_{ca} and R_{NaOCl} are the fouling resistances removed by citric acid and NaOCl respectively, and R_{ir} is the fouling resistance not removed by the cleaning protocol. R_M and R_T values were estimated from the CWF tests on the virgin and fouled membrane respectively. R_{ac} values were calculated as the difference in resistances between the fouled membrane and the membrane cleaned by citric acid. R_{NaOCl} values were calculated as the difference in resistances between the membrane cleaned by citric acid and the membrane cleaned by NaOCl. R_{ir} values were calculated as the difference in resistances between the membrane cleaned by NaOCl and the virgin membrane.

To investigate the effect of the cleaning protocol on flux recovery, the total cleaning efficiency (CE_{Total}) was calculated according to Equation 5-2. The results indicated 87% of the total resistance was removed by the cleaning protocol in Phase 2 and in Phase 1 this value decreased to 65%. The higher value of CE_{Total} in Phase 2 indicated that a higher fraction of the irreversible foulants was removed from the membrane when Fe dosing was employed. Hence, not only did Fe addition reduce the rate of fouling during permeation, the recovery of this flux during cleaning was higher. Both of these responses suggested that Fe addition could enhance the viability of AnMBR operation.

$$CE_{Total}=(R_{ca}+R_{NaOCl})/(R_{ca}+R_{NaOCl}+R_{ir})*100\% \qquad \text{(Equation 5-2)}$$

To investigate the effect of each cleaning step on flux recovery, the cleaning efficiencies with citric acid (CA) and the NaOCl (SH) were calculated with Equations 5-3 and 5-4 respectively and these values are presented in Figure 5-9. From Figure 5-9, it can be seen that 75% and 11% of the total resistance were removed by citric acid and NaOCl respectively in Phase 2. Conversely, in Phase 1 the recoveries with citric acid and NaOCl were 23% and 42% respectively. NaOCl has been reported to remove organic foulants while citric acid dissolves inorganic foulants (Le-Clech et al., 2006). Hence the higher value of CA in Phase 2 suggests that the foulants formed with Fe-dosed mixed liquor associated with inorganics. Correspondingly the higher value of SH in Phase 1 suggests that the foulants formed with non-Fe-dosed mixed liquor are organic. These results are consistent with the extracted foulant results as the TOC in Phase 1 and the inorganic elements in Phase 2 accounted for 42% and 77% of the total extracted mass respectively.

$CA = R_{ca}/(R_{ca}+R_{NaOCl}+R_{ir})*100\%$ (Equation 5-3)

$SH = R_{NaOCl}/ (R_{ca}+R_{NaOCl}+R_{ir})*100\%$ (Equation 5-4)

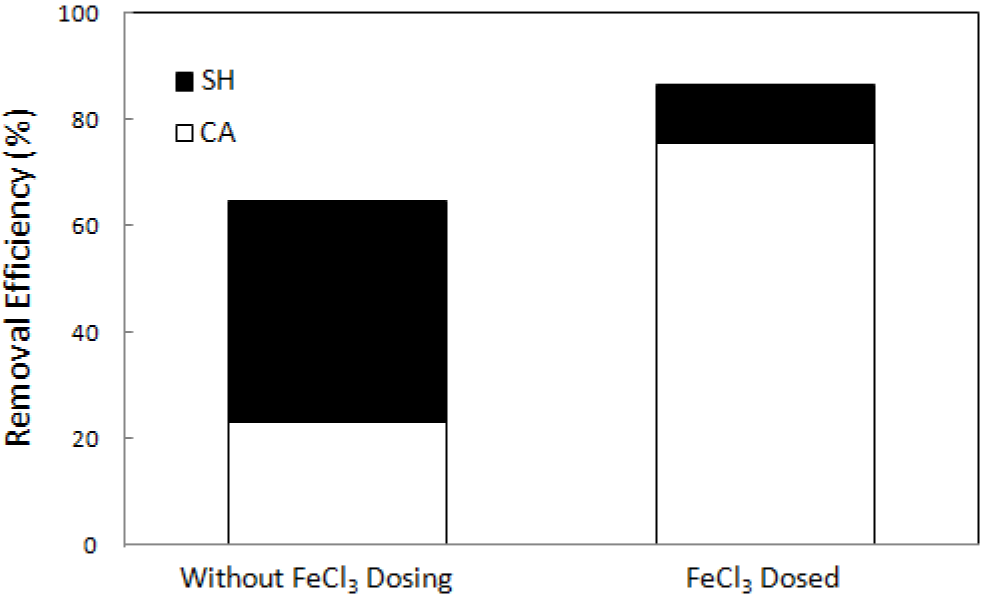


Figure 5-9 Individual Cleaning Effect of Citric Acid and NaOCl

5.3.6 Fouling Mechanism Summary

To obtain a comprehensive understanding on the membrane fouling, a conceptual model (Figure 5-10) was established to demonstrate the general fouling mechanisms. As the conceptual model implied, the general fouling mechanism includes organic fouling and inorganic fouling (Liao et al, 2006). The organic fouling was resulted from the particulate, colloidal and soluble substances which primarily contributed to the formation of the loosely-attached cake layer, strongly-attached cake layer (gel layer) and pore blocking respectively and can be removed by NaOCl (Le-Clech et al., 2006). The inorganic species affect the membrane fouling by precipitation and the effect of bridging (Stuckey, 2012). The inorganic precipitation may be formed into the membrane pore as pore blocking and on the membrane surface as strongly-attached cake layer. The positively charged inorganic species would also bridge the negatively charged organic substances. The bridging of particulate substances contributed to the formation of loosely-attached cake layer on the membrane. The bridging of colloidal and soluble enhanced the development of the strongly-attached cake layer and pore blocking. Those precipitated and bridged inorganic species can be removed by citric acid. Therefore, the levels of these organic and inorganic substances in the mixed liquor will play a key role in the membrane fouling and the efficiency of membrane cleaning.

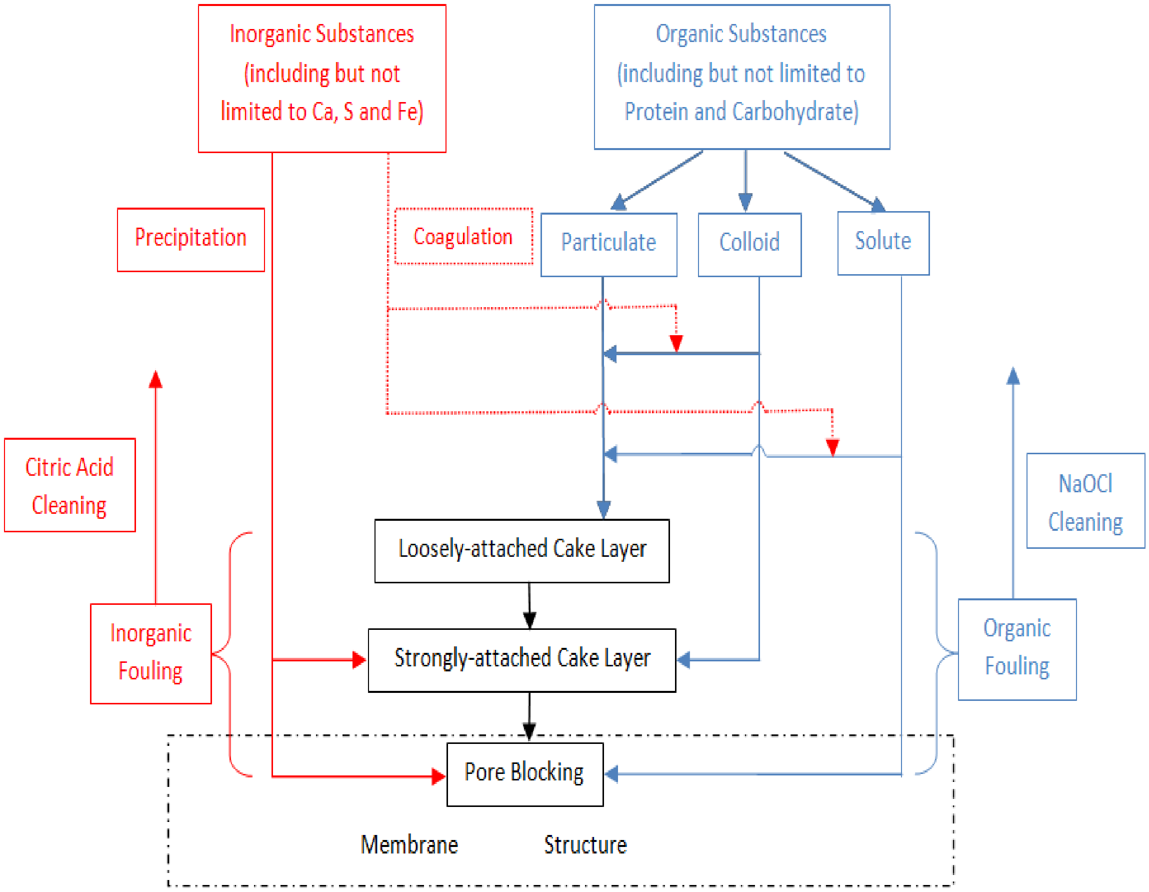


Figure 5-10 Conceptual Model of Membrane Fouling

The addition of $FeCl_3$ would modify the level of organic and inorganic components in the mixed liquor and affect the membrane fouling and the cleaning responses. Table 5-3 summarized the key parameters correlated to fouling in the mixed liquor without and with the addition of $FeCl_3$. By comparison of the SS fractions and COD fractions without and with $FeCl_3$ addition in Table 5-3, it demonstrates that by the addition of $FeCl_3$ the colloidal and soluble substances such as protein, carbohydrate, Ca and S were coagulated into particulate substances and contributed to the VSS and FSS. Hence, the development of strongly-attached cake layer and pore blocking can be mitigated, while the loosely-attached cake layer formation can be enhanced.

The further analysis on the extracted TOC, Ca and S and CLSM images demonstrated that the influence of adding $FeCl_3$ on deposition of these foulants was consistent with the influence on the soluble and colloidal concentrations of these foulants in mixed liquor. Even significantly more Fe was extracted from the membrane, it may present in the particulate form which is consistent with the concentration of particulate Fe in AD. The particulate substances can develop a thicker foulant layer as indicated by the CLSM analysis. This foulant layer may have a more porous structure, which did not contribute to fouling and further prevented the contact between the membrane and the colloidal and soluble substances. Hence, the formation of strongly-attached cake layer and pore blocking can be mitigated and the membrane performance can be enhanced as indicated by the TMPs.

The modification of foulants on the membrane affects the cleaning efficiency. From Table 5-3 it can be seen that the addition of $FeCl_3$ enhanced the deposition of Fe on the membrane, therefore the cleaning efficiency of citric acid was increased. While the cleaning efficiency of NaOCl was reduced as the TOC deposition on the membrane was mitigated. Therefore the addition of $FeCl_3$ transformed the fouling from organic origin to inorganic origin.

Table 5-3 Summary of Fouling and Potential Foulants in Mixed Liqour

Response	Without $FeCl_3$ Dosing	$FeCl_3$ Dosed
TMP(a) (kPa)	5.7~21.5	1.5~8.8
TMP(b-a) (kPa)	2.0~18.8	0~2.5
VSS (g/L)	5.5±0.6	13.0±2.4
FSS (g/L)	0.52±0.25	5.0±1.7
pCOD (mg/L)	10076±881	27239±3275
lcCOD (mg/L)	875±113	583±109
fcCOD (mg/L)	150±24	109±23
sCOD (mg/L)	45.8±11	36.3±5.9
Soluble Protein (mg/L)	56.6±13.1	33.7±6.9
Soluble Carbohydrate (mg/L)	99.4±11.8	55.5±5.2
Extractable Protein in AD (mg/gVSS)	30.5±10.5	86.3±9.3
Extractable Carbohydrate in AD (mg/gVSS)	32.5±9.6	46.3±9.4
Soluble Ca (mg/L)	86.1±7.4	73.0±4.1
Soluble S (mg/L)	6.8±1.9	4.9±1.3
Soluble Fe (mg/L)	0.11±0.09	0.19±0.07
Particulate Ca (mg/L)	166.0±53.1	445.7±27.6
Particulate S (mg/L)	216.3±42.8	1254.9±381.4
Particulate Fe (mg/L)	193±31.4	2426±213
Extracted TOC from membrane (mg/m^2)	500±37.6	295±20.4
Extracted Ca from membrane (mg/m^2)	321±42.1	95.6±4.7
Extracted S from membrane (mg/m^2)	158±25.5	34.9±7.2
Extracted Fe from membrane (mg/m^2)	54.8±4.3	854±97.3
Attachment of Protein and Carbohydrate on Membrane (CLSM)	Observed	Rarely observed
Thickness of fouling layer (μm)	21±1.7	31±3.6
Citric acid cleaning efficiency (%)	23	75
NaOCl cleaning efficiency (%)	42	11

5.4 Significance

The results obtained in this study provided clear long-term feasibility of operating AnMBR treating municipal wastewater with regard to excellent bioprocess performance and membrane performance by dosing 26.0 mg $FeCl_3$/L sewage. The addition of $FeCl_3$improved the removal efficiencies of COD and BOD_5 by 17.3% and 12.8% due to the coagulation of soluble organic matters, but no significant influence was generated on the removal of TKN and TP because of the reduction of ferric iron to ferrous iron in the anaerobic environment that would modify the nature of the complexes and precipitates that were formed. In addition, $FeCl_3$ dosing did not inhibit the activity of methanogens or reduce the availability of the organic matter in the sewage leading to no significant influence on the methane yield. Even the yields of VSS and FSS were increased by 54.0% and 630.0% by the addition of $FeCl_3$, the overall sludge yields were still less than those associated with aerobic wastewater treatment.

The membrane performance was improved by dosing $FeCl_3$ regarding to substantially reduction in irreversible fouling from 5.7~21.5 kPa to 1.5~8.8 kPa and reversible fouling from 0~2.5 kPa to 2.0~18.8 kPa at a flux of 17 LMH in 90 days. The superior membrane performance can be correlated to the modification of the characteristics of mixed liquor by the addition of $FeCl_3$, such as the shift of particulate size distribution to particulate fraction, the reduction in soluble protein from 56.6 mg/L to 33.7 mg/L, carbohydrate from 99.4 mg/L to 55.5 mg/L, Ca from 86.1 mg/L to 73.0 mg/L and S from 6.8 mg/L to 4.9 mg/L in mixed liquor. The modifications in mixed liquor developed a thicker (31 µm vs 21 µm) and more porous foulant layer in which the mass percentage of inorganic substances increased from 58% to 77% based on the extracted mass weight. The modification of foulant improved the total efficiency of the recovery cleaning from 65% to 86%, especially the efficiency of citric acid cleaning from 23% to 75%.

Therefore, the addition of $FeCl_3$ 26.0mg/L sewage can be concluded as an effective strategy to improve the viability of AnMBR in municipal wastewater treatment by producing good-quality effluent and mitigating the membrane fouling. However, the dosage of $FeCl_3$ on the performance of AnMBR was not investigated. Therefore, Chapter

6 evaluated the dynamic responses of bioprocess and membrane performance of AnMBR to varied $FeCl_3$ dosages.

Chapter 6

Dynamic Characterization of a $FeCl_3$-dosed AnMBR Treating Municipal Wastewater

Key Words: Ferric iron, colloidal matter, membrane fouling, bioavailability

6.1 Introduction

There is growing interest in developing sustainable technologies for wastewater treatment. Anaerobic membrane bioreactors (AnMBR) are of particular interest because the anaerobic process has low energy and nutrients requirements, low sludge production and can generate biogas that can be directly employed as an energy source (Metcalf and Eddy, 2003). In AnMBRs the membrane can completely retain biomass in the bioreactor to maintain long solids retention time (SRT) without prolonging the hydraulic retention time (HRT) (Huang et al., 2011; Smith et al., 2012). However, the application of AnMBRs has been limited due to concerns of membrane fouling which can offset the advantages of AnMBRs.

The addition of $FeCl_3$ to the mixed liquor may improve membrane performance. It has been shown that the addition of $FeCl_3$ can effectively mitigate membrane fouling in aerobic MBR systems (Koseoglu et al., 2008; Ji et al., 2010; Fan et al., 2007; Song et al., 2008; Zhang et al., 2008).In these prior studies the reduction in fouling was attributed to increased particle sizes and lower concentrations of soluble and colloidal materials. However, the interaction of the $FeCl_3$ with components in mixed liquor was not assessed. There is limited information available that describes the transient responses of MBRs, and specifically AnMBRs to $FeCl_3$ addition.

The objective of this study was to dynamically characterize the impact of Fe addition on AnMBR performance. A pilot AnMBR was employed to investigate the influence of $FeCl_3$ dosing on bioprocess and membrane responses when treating municipal wastewater. The results of this study will provide operators of AnMBRs with insight into how these systems will dynamically respond to changes in Fe addition. In addition, the study sought to provide insight into time-dependent processes such as mass transfer of foulants between the mixed liquor and the membrane surface.

6.2 Materials and Methods

A pilot scale AnMBR that was fed with 3 mm screened sewage from the Burlington Skyway Wastewater Treatment Plant (Ontario, Canada) was employed in this study (Figure 3-1). The pilot AnMBR consisted of a550L completely mixed anaerobic digester (AD) and an 80L membrane tank (MT) that held a polyvinylidine fluoride (PVDF) hollow fibre membrane module with a surface area of 5.4 m^2 and a pore size of 0.04µm (GE: ZeeWeed 500). The AD contents were mixed by recirculation of the contents at a flow of 3600 L/h with a positive displacement pump. The AD contents were circulated through the MT using a centrifugal pump that withdrew mixed liquor from the bottom of the AD and pumped it to the bottom of the MT after which it flowed to the top of the AD by overflow. This circulation mixed the MT contents and generated a cross flow velocity (CFV) that would enhance surface shear for membrane fouling control. Biogas produced in the AD was released from the head space of the AD and its production was measured by an electrical gas flow meter. Biogas was recirculated through the MT at a flow of 2.5 cubic feet per minute (equal to 0.786 m^3/h (20ºC and 1 atm)) with a blower (KNF NEUBERGER, PM23820-150.1.2) to reduce membrane fouling.

Throughout the study the temperature of the digester was maintained at 23±1°C by a heat tape that was controlled by a temperature controller which was informed by a temperature sensor in the digester. The pH of the digester was controlled through $NaHCO_3$ addition to maintain a value in the range of 6.7-6.8. Pilot operation and data acquisition were controlled using a programmable logic controller (PLC). The feeding of raw sewage and the wasting of anaerobic digester contents for SRT control were controlled on the basis of the weight of the digester that was monitored by load cells installed at the base of the digester.

The pressures of the headspace in the MT and permeate line were recorded using digital pressure guages. The trans-membrane pressure (TMP) was calculated as the difference between the pressure in the MT and that of the permeate line. To reduce membrane fouling, a discontinuous filtration mode and weekly membrane chemical cleaning were incorporated into the pilot operation. The discontinuous filtration mode consisted of a repeating cycle that had filtration for 8 minutes and relaxation for 2 minutes. The weekly membrane cleaning consisted of backpulsing with 2000mg/L citric acid at 2.9L/min for 4 minutes through the membrane.

Membrane performance was characterized by monitoring the TMP before (TMP(b)) and after (TMP(a)) relaxation. TMP(a) values were considered to be indicative of irreversible fouling that could not be removed by mixed liquor recirculation and biogas sparging. The difference between TMP(b) and TMP(a) values (TMP(b-a)), was considered to result from the presence of reversible foulants that built up on the membrane surface during one filtration cycle but were removed during relaxation.

Wastewater and mixed liquorsamples were collected three times a week from the outlets of the feed pump (upstream of the $FeCl_3$ dosing) and anaerobic reactor, respectively. The samples were analyzed for total suspended solids (TSS), volatile suspended solids (VSS), fixed suspended solids (FSS) and COD. All analyses were conducted according to standard methods (APHA, 2005). The methane concentration in the biogas was measured using a gas chromatograph (Agilent Technologies G2802A). The dewaterability of the mixed liquor was characterized using the capillary suction time (CST) test (Vesilind, 1988).

The sewage and mixed liquor were analyzed for colloidal COD (cCOD) to provide insight into the presence of potential foulants. The 1.5µm-filtered COD was analyzed after centrifuging the sewage or mixed liquor sample at 4000 rpm for 12minutes then filtering the supernatant through a 1.5-µm glassfiber filter. The 0.45µm-filtered COD was analyzed after filtering the 1.5µm-filtered COD sample through a 0.45-µm glassfiber filter. The cCOD was calculated by subtracting0.45µm-filtered COD from 1.5µm-filtered COD (Fan et al., 2006).

Prior to the onset of this study the pilot AnMBR was operated at an HRT of 14.5 hours (Flux of 10LMH) and a SRT of 100 days for 85 days without $FeCl_3$ addition. At the beginning of the study a virgin membrane was installed and hence the first stage of the work was assumed to be at biological steady state as indicated by a stable VSS concentration of 6.5±0.4g/L in the bioreactor. Therefore, the data collected in the first stage of the study was deemed to represent bioprocess steady state and was employed in the subsequent comparison when $FeCl_3$ was added to the influent.

The research was conducted in 4 stages (Figure 6-1) where the Fe dose and the membrane flux were varied. Initially the system was operated without Fe addition (Stage 1) and this was followed by sequential periods of high (Stage 2), intermediate (Stage 3) and high (Stage 4) dosage. The membrane flux was maintained at a low value (10 LMH) until the midpoint of Stage 3 after which it was sequentially ramped up to 17 LMH.

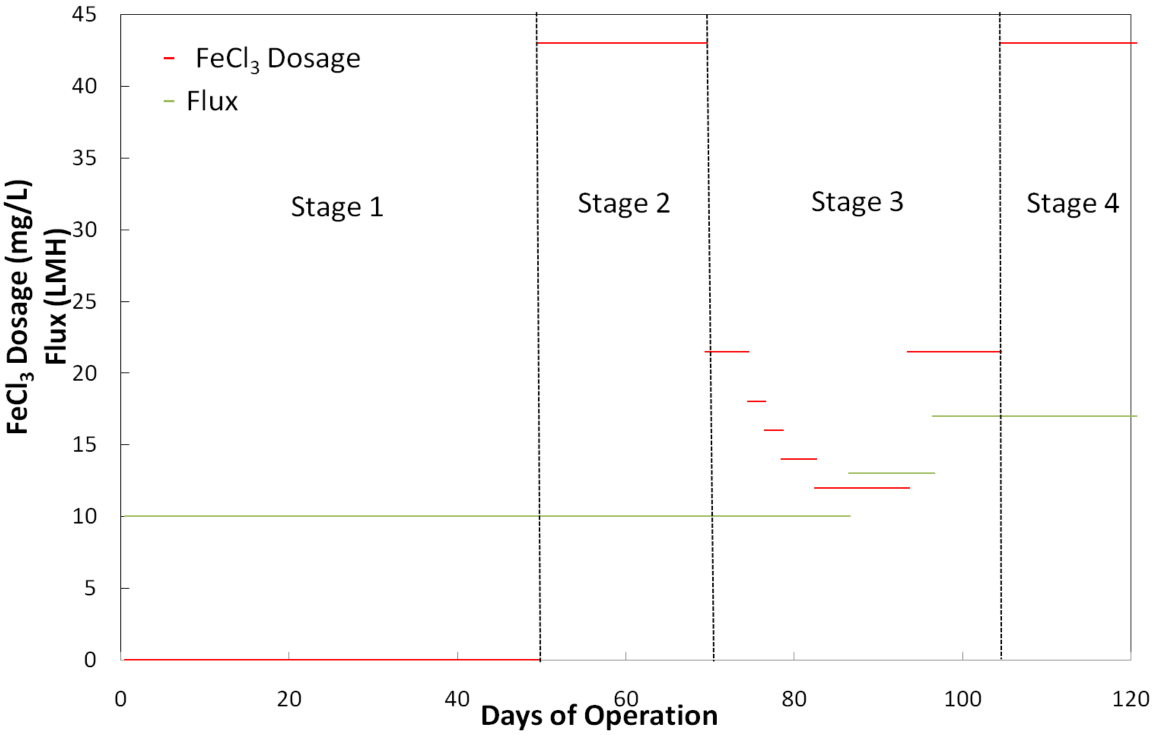


Figure 6-1 Experimental Design

6.3 Results and Discussion

6.3.1 Dynamic Characterization of Bioprocess Performance

The test plan employed a transient approach to characterize the impacts of Fe addition on the AnMBR biological and membrane processes. It was anticipated that this approach would provide operators of AnMBRs with insight into how these systems will dynamically respond to changes in Fe addition. Further, it was anticipated that the study would provide insight into time-dependent processes such as mass transfer of foulants from the mixed liquor to the membrane surface. In order to assist with interpretation of the system dynamics, a general transient model of the AnMBR system was assembled (Equation 6-1) and subsequently employed as a framework to provide dynamic baselines of the responses based on specific assumptions regarding contaminant behaviour. By comparing the baselines predicted by the model with the observed data, the dynamics of the measured responses were interpreted.

$$\frac{dX_{AD}}{dt}V = QX_0 - Q_w X_{AD} \qquad \text{(Equation 6-1)}$$

where$\frac{dX_{AD}}{dt}$ = rate of change of particulate concentration in reactor, g/L/d

V = reactor volume, L

Q = influent flow, L/d

X_0 = concentration of particulate in influent, g/d

Q_w = waste sludge flow, L/d

X_{AD} = concentration of particulate in reactor, g/L

As will be subsequently discussed, Equation 6-1 was employed in several contexts to evaluate hypotheses regarding the role of iron addition in the system. In most cases the model simulations, that employed raw wastewater characteristics (Table 6-1) as inputs, were compared with observed responses in the digester. A review of Table 1 reveals that while there was variability in the raw wastewater characteristics, there were no substantial changes in this stream with time. Hence, it was assumed that the subsequently described responses that were observed in the digester were due to changes in the operating conditions and not due to changes in the wastewater properties.

Table 6-1 Sewage Characteristics

Stage	Total COD (mg/L)	cCOD (mg/L)	VSS (mg/L)	FSS (mg/L)
1	295±64.8	10.3±2.7	102.9±35.7	21.6±10.3
2	262±36.7	15.0±3.8	79.1±15.8	14.5±4.7
3	291±59.3	13.7±4.0	99.4±20.5	28.3±6.4
4	274±29.7	14.7±4.3	92.6±19.7	22.8±5.5

It was hypothesized that the Fe which was dosed into the wastewater would either coagulate organic matter or precipitate in the digester. In either case it would contribute to the FSS present in the digester and hence changes in the FSS concentration in the digester could be employed to evaluate the fate of Fe and to assess the validity of the dynamic modeling approach employed in this study. Figure 6-2 presents the FSS concentrations that were observed in the AnMBR over the duration of the study. From Figure 6-2 it can be observed that during Stage 1 the FSS concentrations were essentially constant with time and this material was attributed to the FSS which were present in the raw wastewater. Upon addition of Fe in Stages 2-4, the FSS concentration increased with time and the rate of increase was a function of the Fe dose.

Equation 6-1 was employed to predict the FSS concentrations during the period of Fe dosing by using the measured FSS concentration in the digester contents as the initial conditions. The integrated form of Equation 6-1 was then applied to each time interval that had a different combination of Fe dose and membrane flux to predict the FSS in the mixed liquor on the assumption that only the added Fe contributed to the FSS. It was anticipated that this approach would yield a conservative estimate of the FSS as it did not account for precipitated inorganic anions. The fraction of the Fe that formed precipitates was not known and hence the model simulations provided a reference point for assessing the fate of Fe.

Figure 6-2 compares the model simulations with the observed FSS concentrations over the duration of the study. From Figure 6-2 it can be observed that the model was able to effectively predict the FSS concentrations over most of the period of Fe dosing. In Stage

2 and 4 the predicted values were somewhat less than the observed values suggesting that there was some formation of inorganic precipitates at the high dose rate. This was less apparent at the intermediate dosages in Stage 3 however the simulation periods in this stage were shorter and hence there was less operational time for the formation of inorganic precipitates to be observed. Overall, it was concluded that the modeling approach employed was valid and hence it was employed to further evaluate the behavior of other particulate species in the AnMBR.

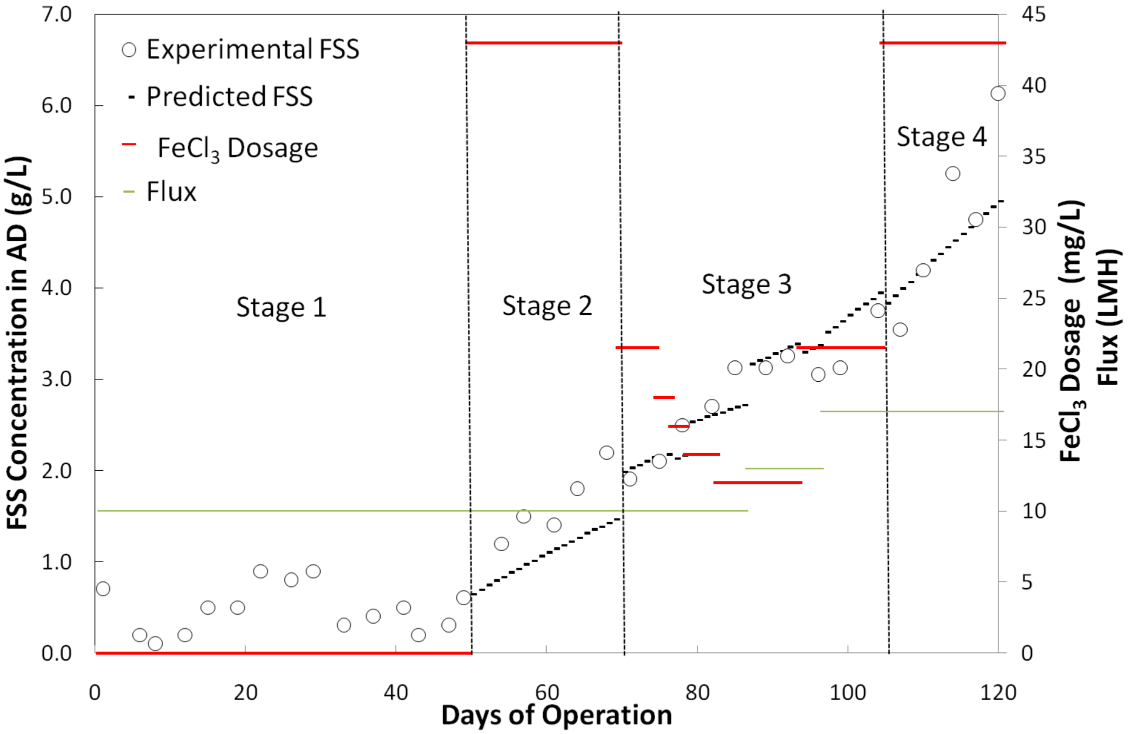


Figure 6-2 Experimental and Predicted FSS in Mixed Liquor

The addition of Fe to AnMBRs has been previously demonstrated to coagulate colloidal matter (Fan et al., 2007; Koseoglu et al., 2008) that is likely responsible for membrane fouling. Hence, the colloidal COD (cCOD) of the mixed liquor was monitored to evaluate the response of the system to $FeCl_3$ addition (Figure 6-3). From Figure 6-3 it can be observed that without Fe addition (Stage 1) the cCOD concentrations in the mixed liquor were in the range of 900-1200 mg/L. Immediately after the start of a high level of Fe dosing in Stage 2 the cCOD concentrations declined significantly to reach approximately 600 mg/L by the end of the stage. When reduced iron dosing was employed in Stage 3 the cCOD concentrations started to gradually increase while the membrane flux was maintained at 10 LMH. When the flux was increased, the cCOD concentrations increased more rapidly despite increases in Fe dosing in Stage 3. Only when a high level of Fe dosing was employed in Stage 4 was the cCOD concentration reduced under high flux operation. The results indicate that cCOD concentrations in the AnMBR were a function of both the Fe dosage and the membrane flux that affected the ratio of HRT to SRT.

It was hypothesized that the cCOD in the mixed liquor would either have entered with the raw wastewater or was generated in the digester by the biological processes. It was however not clear how Fe addition influenced cCOD from these two sources. Equation 6-1 was therefore employed to evaluate the role of Fe addition on cCOD in the system. In this application, simulations were conducted on the assumption that Fe addition would immediately coagulate all of the cCOD in the feed wastewater and that cCOD that was generated in the digester was not impacted. Figure 6-3 presents the results of these simulations in comparison to the observed results. From Figure 6-3 it can be seen that the simulated values in Stages 2 and 4 that had a $FeCl_3$ dosage of 43mg/L declined somewhat slower than the observed values. Hence it would appear that under high dosage conditions the dosed Fe not only coagulated all of the cCOD in the sewage, but also coagulated some of the cCOD that was present in the AD and/or mitigated the cCOD which was generated in the AD.

In Stage 3, that was conducted at lower $FeCl_3$dosages (21 to 12mg/L), the simulations that were conducted on the assumption of complete coagulation of feed cCOD consistently under predicted the observed values. The increase in the observed cCOD values suggested that either some of the feed cCOD was not coagulated or sufficient cCOD was generated in the AD to exceed the coagulation capacity of the Fe addition. To further investigate the contribution of Fe dosing to cCOD removal, additional simulations were conducted in Stage 3 where it was assumed that none of the feed cCOD was coagulated. When these values were considered together with the previously discussed values they formed an envelope of potential responses. From Figure 6-3 it can be seen that the observed values fell within this envelope. Hence, it was concluded that the lower dosages introduced insufficient Fe to coagulate all cCOD in sewage and mitigate cCOD generation. The dosage of $FeCl_3$ can therefore be employed as an operational parameter to control the cCOD in the mixed liquor.

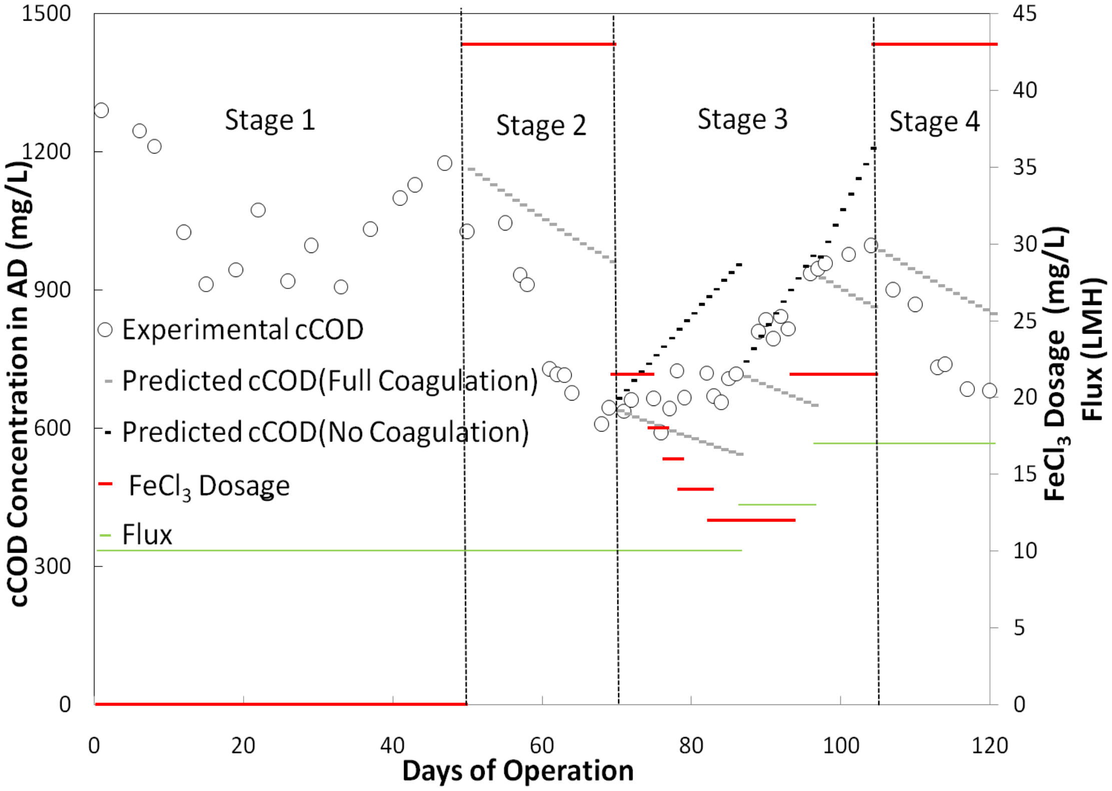


Figure 6-3 Experimental and Modeled cCOD in Mixed Liquor

It was anticipated that $FeCl_3$ would impact on the VSS concentrations in the AnMBR as it was previously demonstrated that cCOD was removed under high dosage conditions. Figure 6-4 presents the observed VSS concentrations over the duration of the testing. From Figure 6-4 it can be seen that in the absence of Fe dosing (Stage 1) the VSS concentrations in the mixed liquor were effectively constant with time. By contrast, the VSS concentrations increased substantially with high Fe dosing in Stages 2 and 4. Under conditions of intermediate Fe dosing (Stage 3) the observed VSS concentrations increased only modestly. Preliminary calculations that were performed to evaluate the potential contribution of coagulated cCOD to the production of VSS in mixed liquor revealed that this could not explain the substantial increases in VSS that were observed in the AnMBR.

An alternate mechanism that was hypothesized for the increased VSS concentrations in the mixed liquor was that Fe addition was rendering normally biodegradable VSS to be non-biodegradable. To investigate this hypothesis Equation 6-1 was employed to simulate the mixed liquor VSS with the assumption that all of the VSS in the feed sewage was non-biodegradable (Figure 6-4). From Figure 6-4 it can been seenthat with the addition of $FeCl_3$ at a dosage of 43mg/L in Stages 2 and 4 the model was able to reasonably simulate the accumulation of VSS in the AnMBR. Hence, the results suggest that the addition of $FeCl_3$ at 43mg/L substantially reduced the biodegradability of VSS entering the AnMBR and it was expected that this would impact upon methane production.

In Stage 3, with reduced $FeCl_3$ dosages (21 to 12mg/L), the simulations that were conducted on the assumption of completely nonbiodegradable VSS in the feed consistently over predicted the observed values. Hence, these results implied that at reduced dosages, there was insufficient Fe interacting with the VSS in sewage to prevent biodegradation of this material. The results indicate that the use of Fe for fouling control should be carefully controlled such that cCOD is coagulated but the biodegradability of the VSS is not inhibited.

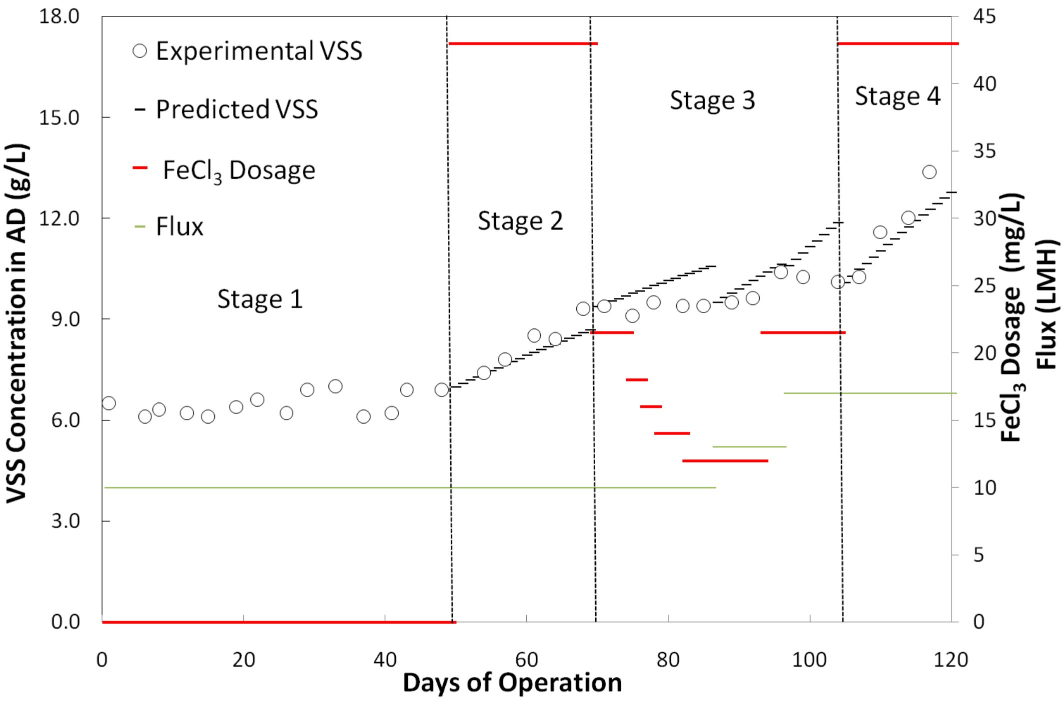


Figure 6-4 Experimental and Predicted VSS in Mixed Liquor

The production of methane is an important factor to consider when assessing the sustainability of AnMBRs as it might be employed to compensate for the energy consumed in AnMBR operation. As previously discussed the addition of Fe appeared to substantially reduce the biodegradability of VSS and it was hypothesized that methane production would be reduced. The impact of $FeCl_3$ addition on the production of methane was therefore investigated. In anaerobic treatment of dilute wastewaters it is important to account for both the gaseous methane in the biogas and the methane dissolved in the permeate as the latter can represent a substantial fraction of the produced methane. In this study the gaseous production was directly measured and the dissolved methane was estimated (Henry's Law) to calculate the daily methane production (as COD) of the system (Figure 6-5). From Figure 6-5 it can be seen that the methane production was 204±13.5gCOD/d in Stage 1 and with the addition of $FeCl_3$ at 43mg/L its production was reduced to approximately 81.0 gCOD/d by the end of Stage 2. Similarly the production of methane decreased from 200.0 to 108.3 gCOD/d during Stage 4.In Stage 3 when $FeCl_3$ dosages were reduced an increase in methane production from 104.5gCOD/d to 200.0gCOD/d was observed. The methane results confirmed the accumulation of VSS and the reduction in its biodegradability due to the interaction with Fe. Therefore, the dosage of $FeCl_3$ should be carefully controlled as it can negatively affect methane production and the economical viability of an AnMBR.

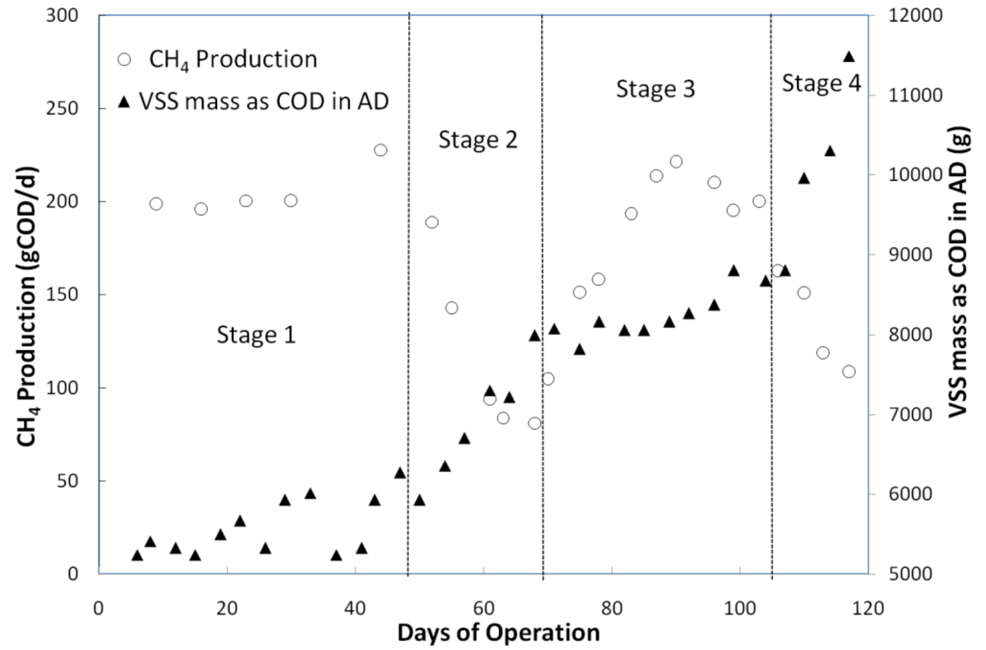


Figure 6-5 Methane Production and VSS Mass in AD

6.3.2 Dynamical Characterization of Membrane Performance

As previously described, the addition of $FeCl_3$ to the AnMBR feed substantially impacted upon the concentrations of cCOD in the AnMBR which was considered to be a membrane foulant. However, fouling may result from either formation of a loosely-attached cake on the surface of the membrane or the development of strongly-attached cake and pore clogging. The former is often assumed to be reversible while the latter is deemed to be irreversible. It was hypothesized that the transient response of the two different fouling mechanisms would differ as the former could be attributed to direct filtration processes while the latter would be more dependent on slower mass transfer processes. Hence, the transient response of reversible and irreversible fouling in the AnMBR to $FeCl_3$ addition was explored.

The impact of $FeCl_3$ dosing on membrane performance was assessed by examining membrane resistances on the basis of the implemented flux values and the observed trans-membrane pressure (TMP) responses. The TMP recovery observed during relaxation (TMP(b-a)) and TMP after relaxation (TMP(a)) were employed to calculate the reversible (RR) and irreversible resistances(IR) respectively (Equation 4-1).

The reversible resistance (RR) was assumed to represent the presence of reversible foulants that was caused by the formation of a loosely-attached cake layer during filtration and were removed by biogas sparging and mixed liquor recirculation during relaxation. From Figure 6-6 it can be observed that without Fe addition (Stage 1) the RR values increased from 2.8 to 8.6×10^{8}m^{-1} in Stage 1. Immediately after the start of a high level of Fe dosing in Stage 2 the RR values declined significantly to reach approximately 0.5×10^{8}m^{-1} by the end of the stage. When reduced iron dosing was employed in Stage 3 the RR stayed constant while the membrane flux was maintained at 10 LMH. When the flux was increased, the RR increased more rapidly despite increases in Fe dosing in Stage 3. Only when a high level of Fe dosing was employed in Stage 4 was the RR reduced under high flux operation. The results indicate that RR in the AnMBR was a function of both the Fe dosage and the membrane flux (ratio of HRT to SRT) that affected the potential foulants in the mixed liquor.

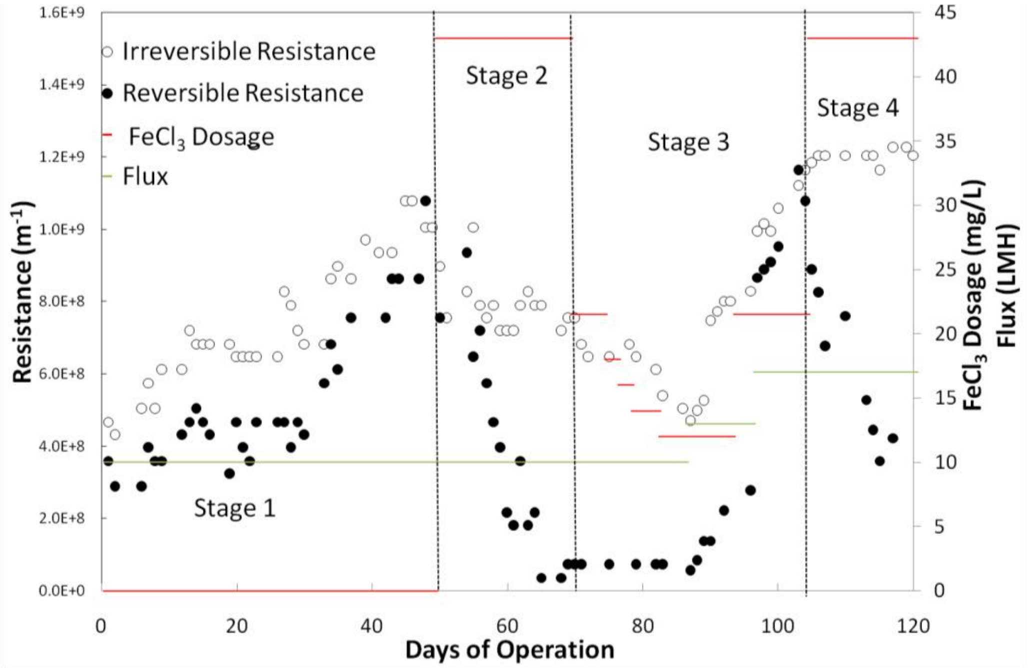


Figure 6-6 Reversible and Irreversible Resistance

As previously discussed, cCOD concentrations in the AnMBR were also a function of both the Fe dosage and the membrane flux. Hence, it was hypothesized that the cCOD was the foulant that directly related to the reversible fouling. To verify this hypothesis, the relationship between RR and cCOD concentration was tested. From Figure 6-7 it can be seen that RR was positively correlated to cCOD which implies that RR was a function of cCOD and the dosage of $FeCl_3$and membrane flux may affect RR by establishing the concentration of colloidal organic matter in the mixed liquor. Hence, the RR responded quickly to operational parameters that immediately affected the cCOD concentration in the mixed liquor.

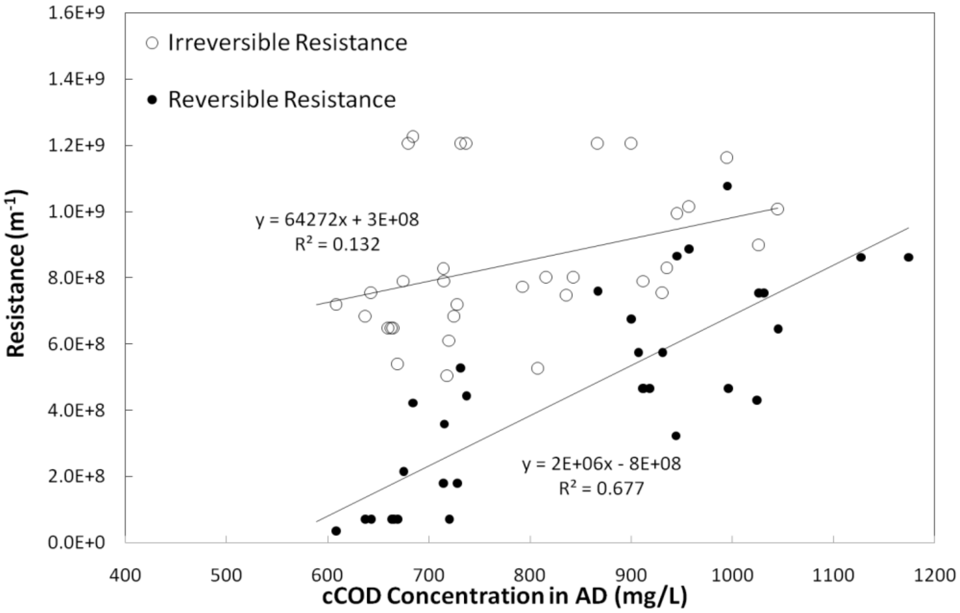


Figure 6-7 Correlation between Colloidal COD and Resistances

A reduction in the tendency of the mixed liquor to cause reversible fouling may also contribute to improved dewaterability of mixed liquor since coagulation of cCOD would increase the particle sizes and hence be easier to dewater. The dewaterability of the mixed liquor was therefore measured by the CST test and the relationship between CST values and RR was examined (Figure 6-8). The results showed a positive linear relationship between the CST and RR (R^2=0.641). Therefore, the mitigated reversible fouling was indicative of improved dewaterability and the CST test may be a viable offline method for assessing the impact of coagulant dosing on reversible fouling in AnMBRs.

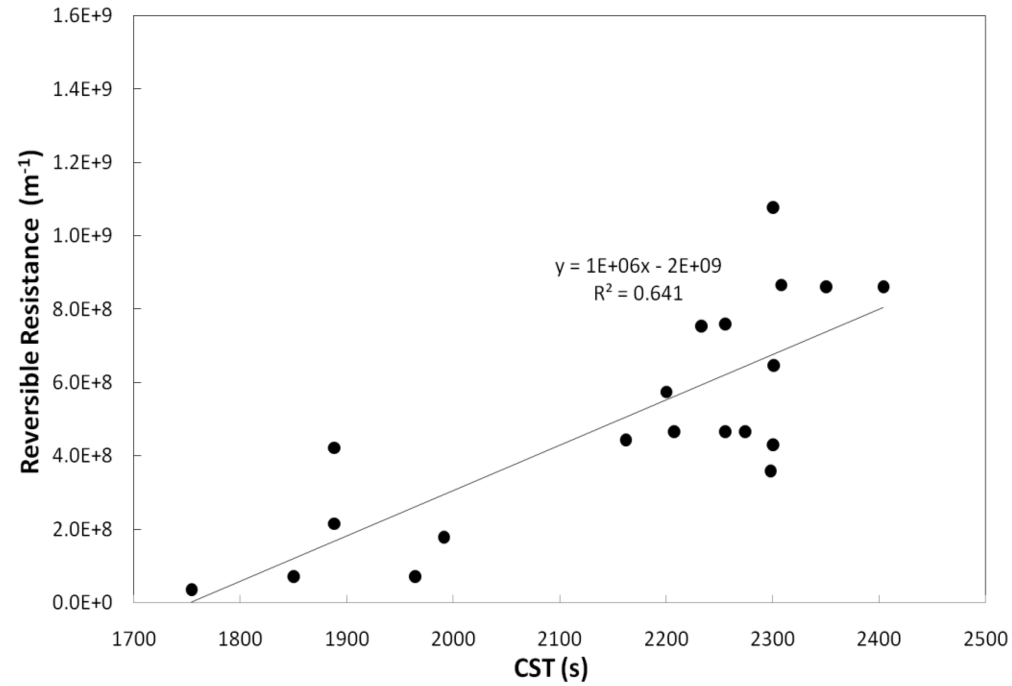


Figure 6-8 Correlation between CST and Reversible Resistance

The irreversible resistance (IR) values were assumed to be indicative of the accumulation of irreversible foulants on the membrane surface due to the formation of either a strongly-attached cake layer or pore blocking. From Figure 6-6 it can be seen that without $FeCl_3$ addition IR values increased from 4.6 to $10.3\times10^{8}m^{-1}$ in Stage 1. In Stage 2 the addition of $FeCl_3$ at 43mg/L resulted in an immediate but slower reduction in IR as compared to RR. Subsequently in Stage 3, while the membrane flux, was maintained at 10 LMH the IR values continued decreasing to a minimum value of $4.7\times10^{8}m^{-1}$ despite the reduced $FeCl_3$ dosage (21 to 12mg/L). The trend in IR values during this period differed from the RR values that remained constant. When the flux was increased, the IR values increased rapidly despite increases in Fe dosing in Stage 3. When a high level of Fe dosing was employed in Stage 4, the IR values stabilized at approximately $12.2\times10^{8}m^{-1}$ under high flux operation. The results indicate that IR in the AnMBR was a function of both the Fe dosage and the membrane flux, but the mechanism by which these factors affected IR may differ from that of RR.

The results indicate that the effects of Fe dosage on IR were due to its impact on cCOD concentration in mixed liquor but that the response was not immediate. Previous studies have demonstrated that irreversible fouling was correlated to cCOD concentration as its presence can contribute to the formation of a strongly attached cake layer and pore blocking (Meng et al., 2007). However, in the current study there was no significant correlation between IR and cCOD concentration (Figure 6-7) in the stages when $FeCl_3$ was added. The lack of correlation of IR with cCOD concentrations may be attributed to the slow mass transfer between the cCOD in mixed liquor and the irreversible foulant layer. Hence an extended time was required for colloidal matter to come in contact with the membrane and to enter the pore structure. This slow process would delay the IR response relative to the changes in the cCOD concentration in the mixed liquor. Therefore, IR responded slower than RR to the changes in cCOD concentration when Fe was added.

The membrane flux would have an impact on the mass transfer of irreversible foulants as it determines the loading of foulants to the membrane surface. The effect of flux on IR was evaluated by comparing the IR in Stage 2 and 4. From Figure 6-6 it can be observed that the high dosage of $FeCl_3$ at 43mg/L had a limited mitigation of IR in Stage 4 as compared with Stage 2, though the cCOD in the mixed liquor was significantly reduced in both stages. The limited mitigation of IR Stage 4 was attributed to the increased flux. An increase in flux from 10 to 17 LMH would enhance foulant loading to the membrane surface and hence in Stage 4 the fouling layer stabilized rather than decreasing as it did in Stage 2 when high dosages of Fe caused a decline in cCOD concentrations. This behavior was consistent with the previous conclusion that the development of irreversible fouling is dependent on slower mass transfer processes.

6.4 Significance

Insights were obtained into physical, biological and membrane responses of a pilot scale anaerobic membrane bioreactor when sequentially operated over a range of dosages of $FeCl_3$ and membrane fluxes. The dynamic response of FSS in the mixed liquor revealed that Fe addition contributed to the production of FSS in the system. The cCOD and VSS responses revealed that the Fe dosage impacted on the extent of cCOD that was coagulated and the biodegradability of fed VSS. The impact of Fe dosage upon biodegradability of VSS was confirmed by the methane production data. Fe dosage should be optimized to balance coagulation of cCOD for fouling control and inhibition of biodegradability of the VSS for methane production.

The dynamic response of reversible fouling to $FeCl_3$ addition was rapid and was attributed to a direct filtration process that was dominated by the cCOD concentration in mixed liquor. The response of irreversible fouling was delayed relative to the IR response and appeared to be controlled by mass transfer of cCOD between the mixed liquor and the irreversible foulant layer. The results suggest thatthe use of Fe addition can immediately control reversible fouling, but it can take long term dosing to mitigate irreversible fouling. Fe addition was less effective at higher flux values that modify the balance between rates at which irreversible foulants accumulate on the membrane.

Chapter 7 Conclusion and Recommendations for Future Research

7.1 Conclusion

The general conclusions are as follows:

This study aimed to reveal the impact of SRT and HRT and the addition of $FeCl_3$ on bioprocess and membrane performance of AnMBRs treating authentic municipal wastewater. The combined testing evaluated a range of HRTs and SRTs and revealed that high quality permeates could be produced over a broad range of operating conditions. Biogas was produced continuously and demonstrated the potential of this technology to generate a value-added product from wastewater treatment.

The SRT was found to be the parameter that could shift the distribution of fed COD mass in AnMBR, thus modifying the mixed liquor characteristics and affecting short-term fouling. However, long-term membrane fouling was control by the residual foulants that resisted recovery cleaning. The addition of $FeCl_3$ at 26mg/L was an effective strategy to mitigate membrane fouling, however, the transient study conducted over a range of dosages revealed that elevated dosages reduced the biodegradability of fed VSS.

The specific conclusions are as follows:

Impact of SRT and HRT on bioprocess performance: An increase of SRT from 40 to 100 days resulted in an enhancement of hydrolysis and subsequent methanogenesis that reduced sludge production and increased methane production. There was no significant influence of HRT on these responses when SRT was held constant. Therefore, extended SRT should be employed in AnMBRs to enhance bioprocess performance. A consistent fraction (~29%) of fed COD mass was not accounted for in the COD mass balance analysis and this was attributed to reduction of sulfate in sewage and oversaturation of dissolved methane in the permeate. This issue needs to be addressed to improve the sustainability of AnMBR in the future.

The hydrolysis, fermentation and aceticlastic methanogenesis models in PetWin were calibrated with the pilot test data. The calibrated model was able to describe steady-state and transient responses over a range of HRTs and SRTs. The calibrated saturation coefficients revealed hydrolysis could be simplified to zero-order kinetics while the fermentation and aceticlastic methanogenesis processes could be simplified to first-order kinetics. The results of this study provides operators of AnMBRs with insight into bioprocess kinetics that could be employed to design full scale AnMBR treating authentic municipal wastewater.

Long-term membrane performance upon varied SRT and recovery cleaning: Short-term fouling was mitigated by a decrease of SRT from 100 to 40 days that resulted in reduced concentrations of TSS concentration and improved dewaterability as indicated by reduction in cCOD concentration and CST. However, the longer term fouling behaviour was not consistent with these parameters, but was consistent with the replacement of fouled membranes with virgin membranes. Therefore, it was concluded that the residual foulants that resisted recovery cleaning appear to have modified membrane properties such as surface charge. The modified properties resulted in more rapid fouling on cleaned membranes than virgin membranes when filtering mixed liquor. Hence, the SRT should be optimized to balance the bioprocess and membrane performance and a new cleaning protocol that could remove more residual foulant should be developed.

Long-term impact of addition of $FeCl_3$ on bioprocess and membrane performance: The addition of $FeCl_3$at 26mg/L improved the removal efficiencies of COD and BOD_5due to the coagulation of soluble organic matter, but no significant influence on the removal of TKN and TP and methane yield were observed. The yields of VSS and FSS were significantly increased by the addition of $FeCl_3$, but the overall sludge yields were still less than those associated with aerobic wastewater treatment.

The irreversible and reversible fouling were significantly mitigated by dosing $FeCl_3$that shifted particulate size distribution to the particulate fraction, reduced soluble proteins, carbohydrates, Ca and S in the mixed liquor. The modifications in the mixed liquor resulted in the development of a thicker and more porous foulant layer that contained more inorganic substances than organic substances based on the extracted mass weight. The modification of foulant improved the total efficiency of the recovery cleaning especially the efficiency of citric acid cleaning. Therefore, the addition of $FeCl_3$26.0mg/L sewage was deemed to be an effective strategy to improve the viability of AnMBR in municipal wastewater treatment by producing good-quality effluent and mitigating the membrane fouling.

Transient characterization of the impact of $FeCl_3$ dosing on bioprocess and membrane performance: The dynamic response of the mixed liquor revealed that Fe addition contributed to the production of FSS in the system and impacted on the extent of cCOD that was coagulated, the biodegradability of fed VSS and the methane production. Hence, Fe dosage should be optimized to balance coagulation of cCOD for fouling control and inhibition of biodegradability of the VSS for methane production.

The dynamic response of reversible and irreversible fouling to $FeCl_3$ addition was different. The response of reversible fouling was rapid and was attributed to a direct filtration process that was dominated by the cCOD concentration in mixed liquor. The response of irreversible fouling was delayed relative to the IR response and appeared to be controlled by mass transfer of cCOD between the mixed liquor and the irreversible foulant layer. The results suggest that the use of Fe addition can immediately control reversible fouling, but it can take long term dosing to mitigate irreversible fouling. Fe addition was less effective at higher flux values that modify the balance between rates at which irreversible foulants accumulate on the membrane.

7.2 Recommendations for Future Research

The following recommendations are suggested for future studies of AnMBR treatment of municipal wastewaters.

The SRT of 40 days was found to achieve superior permeate quality and allowed the membranes to run longer at a sustainable fouling rate. Therefore, this SRT should be considered for future operation of AnMBR. The SRT of 40 days can also act as a baseline from where the further optimization of other operational conditions should be conducted.

The study showed the feasibility of adding FeCl3 to sewage as an effective strategy to control membrane fouling. However, other flux enhancers such as Alum and particle or powdered activated carbons were not tested in this study. Therefore, future studies should systematically investigate the impact of these flux enhancers and their dosage on mixed liquor characteristics and membrane fouling by AnMBR treating municipal wastewater.

This study showed HRTs (8.5 and 12.5 hours) had no significant impact on bioprocess performance in terms of distribution of fed COD mass, but its effect on the membrane was not investigated due to these experiments being conducted on pilot and bench AnMBR respectively. Therefore, there is a need to fully evaluate the effect of HRT on membrane performance. In addition, further reduced HRTs should be tested considering improving the economy of AnMBR.

Biogas sparging and recirculation of the mixed liquor have been proved to be effective strategies to control reversible fouling. Their effect on mitigation of fouling might be enhanced by optimized membrane tank design rather than increased recirculation rate or sparging rate. The currently employed membrane tank had a cross section area that was greater than that of the membrane module and this reduced the shearforces on the membrane. Future studies should focus on optimization of the membrane tank design to enable the generated shearforces to be efficiently contacted with the membrane for fouling mitigation, thus reducing the energy consumption for the operation.

The residual foulants that can resist recovery cleaning by citric acid and NaOCl might have different physicochemical interactions with the membrane and result in subsequent more rapid fouling. However, no test in this study was conducted to achieve direct evidence in this regard. Therefore, future studies should evaluate the properties of cleaned membranes in comparison with the virgin membranes. Furthermore, based on the evidence regarding to cleaned membrane properties, new cleaning protocols should be developed with regards to cleaning chemicals, cleaning duration and frequency.

Colloidal COD had been identified as main component in mixed liquor for membrane fouling. Therefore, there is a need to develop a biological model that can effectively predict its concentration and a filtration model that can employ colloidal COD concentration to predict membrane fouling.

The effect of temperature was not addressed in this study. To expand the application of AnMBR in psychrophilic condition, the impact of temperature on the AnMBR should be evaluated in terms of COD removal, the production of methane (total and dissolved) and the membrane fouling. Furthermore, the other operation conditions such as SRT and HRT should be optimized for operation in psychrophilic condition.

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APPENDICES

A-1. Biosolids Characteristics of AnMBR Treating Municipal Wastewater

The characteristics of biosolids in AnMBR were evaluated in terms of yields of total solids (TS) and volatile solids (VS) based on volume of treated sewage, concentrations of total Kjeldahl nitrogen (TKN), total phosphorus (TP), pathogens (Fecal coliforms and Escherichia coli (E.coli)), and dewaterability. From Table A-1 it can be seen the AnMBR generated TS ranging from 41.1 to 139.9 g/m^3 sewage throughout this study which was less than the sum of TS generated in primary and secondary aerobic treatment (180~270 g/m^3 sewage) (Metcalf and Eddy 2003). In addition, the TS yields in this study were lower or comparable to that in extended aeration process without primary treatment (80~120 g/m^3 sewage), except Phase D.

Table A-1 also showed the VS yield ranged 30.0~90.8 g/m^3 sewage in this study. These values were lower than the typical total VS yield in both primary and secondary aerobic treatment which ranged from 138 to 190 g/m^{3}sewage (Metcalf and Eddy 2003). Even if anaerobic digestion is employed which can reduce VS by 30~45% (Han et al., 1997; Dagnew et al., 2010), the VS yield in AnMBR still have the superiority. Further comparison indicated AnMBR can reach a VS yield even lower or comparable to that in extended aeration process (60~90 g/m^3 sewage) (Metcalf and Eddy 2003). Therefore regarding to yields of TS and VS, the AnMBR are superior to traditional treatment processes and even comparable to the extended aeration when operated at SRT longer than 40 days.

The concentrations of TKN and TP are essential to agricultural application of the biodolids. Table 1 showed the concentrations of TKN and TP in AnMBR biosolids were comparable to those in anaerobically digested municipal biosolids which in the range of 0.5~17.6% and 0.5~14.3% for TKN and TP respectively (US EPA 1984). Therefore, the AnMBR biosolids can compete with anaerobically digested municipal biosolids regarding to the TKN and TP requirement in agricultural application.

The dewaterability of mixed liquor is an essential factor for the efficiency of dewatering processes (e.g., centrifugation, belt filter press and filter press). Hence, it was evaluated in term of capillary suction time (CST). The CST values in all phases were significantly higher than the valuesfor aerobic sludge (5~13s) (Smollen 1986; Ge et al., 2011). In addition the CST values in Phase A-C were generally higher than that for anaerobically digested biosolids (200~800s) (Smollen 1986; Vesilind 1988; Krishnamurthy and Viraraghavan, 2005). However, the addition of Fe and shortened SRT (40 days) in Phase D can improved the dewaterability of AnMBR biosolids to be competitive to that for anaerobically digested biosolids. Therefore the application of membrane to anaerobic digester significantly decreased the dewaterability of biosolids, but Fe addition and SRT at 40 days can overcome this disadvantage to some extent thus ensure the efficiency of dewatering process.

The operational conditions in Phase D may result in the least membrane fouling as it exhibited the highest dewaterability, thus it may holds the most potential in industrial application. Therefore, the pathogen tests (Fecal Coliforms and E. coli) were conducted in Phase D to evaluate its feasibility for agricultural application. From Table 1 it can be seen Fecal coliforms in AnMBR biosolids were less than in typical untreated sludge (10^{10} CFU/L) (US EPA 1979), but were comparable to that in anaerobically digested biosolids ($3*10^5$~$6*10^7$ CFU/L) (US EPA 1979). However, it failed to meet Class B pathogen-reduction criteria ($2*10^6$ CFU/gTS) (US EPA 1999).

Table A-1 also showed another pathogen indicator, E. coli, in AnMBR biosolids. Its occurrence in this study was generally more abundant than in typical raw biosolids ($0.8*10^6$~$1.6*10^6$ CFU/gTS) (Li et al., 1993) and in anaerobically digested biosolids where E.coli can be reduced by 10^3~10^6 CFU/gTS. It also failed to meet the requirement of E. coli (500~1000 CFU/gTS) (Lepeuple et al., 2004; BSI 2005) for the agricultural application. Therefore further treatment is required to remove Fecal coliforms and E. coli from AnMBR biosolids to satisfy the requirement for sequential agriculture application.

Significance: The results obtained in this study indicated that AnMBRs generated less TS and VS than traditional processes. However, the qualities of biosolids can be comparable to or superior to anaerobically digested biosolids in terms of concentration of TKN, TP and pathogen for agricultural application and dewaterability for dewatering process. The results of this study provide valuable insight into the characteristics of biosolids of an AnMBR treating municipal wastewater regarding to the biosolids treatment.

Table A-1 Biosolids Characteristics of AnMBR[a]

Phase	A	B	C	D
SRT/HRT	70d/8.5h	100d/8.5h	70d/8.5h	40d/8.5h
$FeCl_3$ Addition (mg/L Sewage)	0	26	26	26
TS Yield (g/m^3 Sewage)	41.0±5.1	67.4±6.2	109.0±8.8	139.9±3.2
VS Yield (g/m^3 Sewage)	30.0±6.1	38.8±3.8	65.6±7.1	90.8±2.1
TKN(%)[b]	5.5±0.8	5.4±0.4	4.9±0.5	5.7±0.5
TP (%)[b]	1.4±0.1	1.0±0.1	0.82±0.2	0.95±0.07
CST (s)	2655±97	1234±136	1132±140	345±45
Fecal Coliforms	-	-	-	2.2~9.8*10^6CFU/gTS or 4.4~16.6*10^7CFU/L
E.Coli	-	-	-	1.7~8.0*10^6CFU/gTS or 3.4~13.6*10^7CFU/L

a: Results displayed as mean±standard diviation

b: Weight percent in TS

A-2. Short-term Tests on Impact of Biogas Sparging Rates and Temperature on Membrane Fouling

The test showed the increased sparging rate (cubic feet per minute (CFM)) and can significantly mitigate the membrane fouling and this trend appeared to be aggravated with increased temperature. During the tests, the concentration of TSS and cCOD was monitored, no significant difference was found. Hence, it was concluded that the changes in TMP were caused by sparging rates and temperature, not mixed liquor characteristics

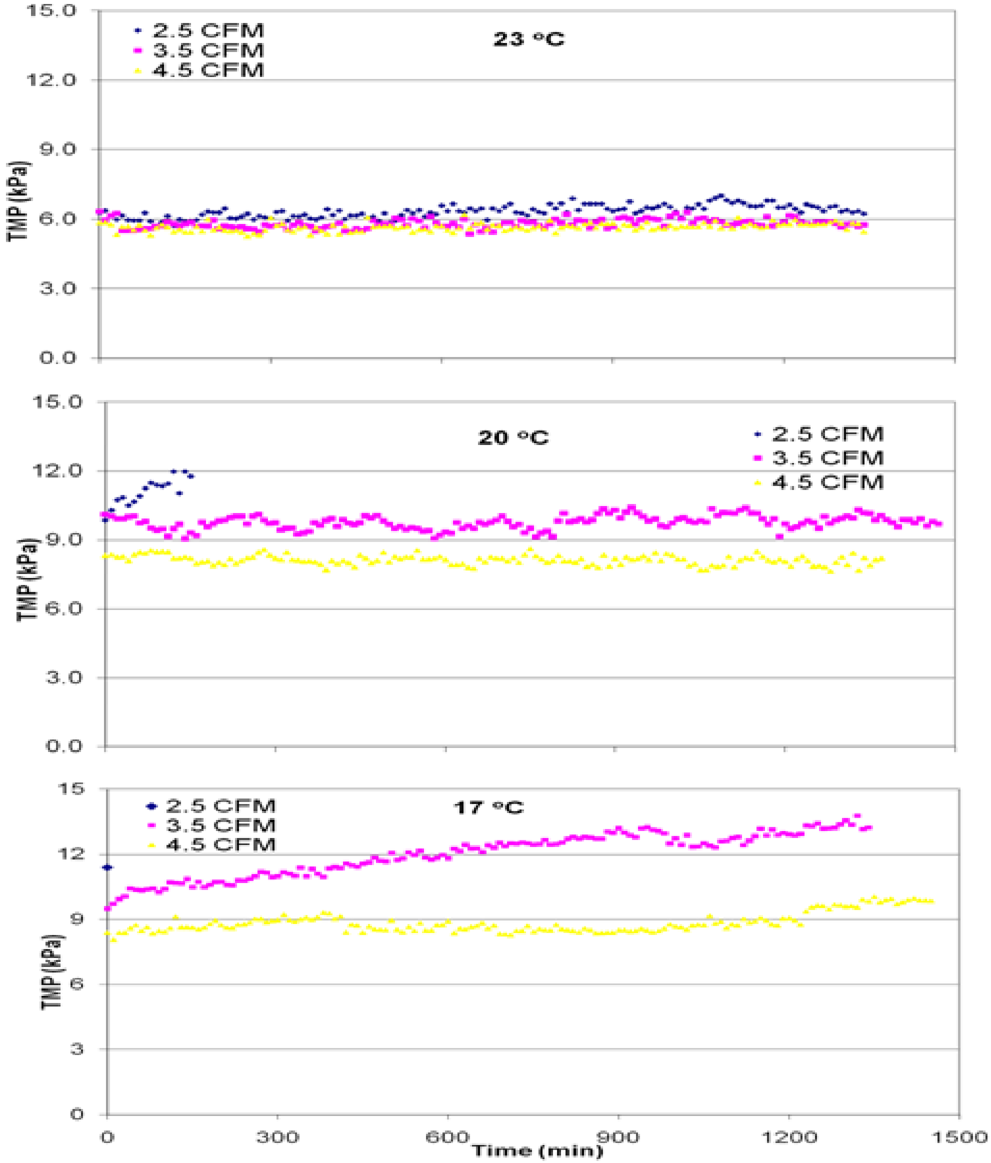

Figure A-1 Sparging Rates and Membrane Fouling

A-3. TMP Profile and Mixed Liquor Characteristics of Bench-scale AnMBR (Associated with Chapter 3)

The fouling behavior on bench AnMBR corresponded to the mixed liquor characteristics such as TSS concentration and dewaterability indicated as cCOD concentration and CST. The overall TMP on bench AnMBR was significant lower than pilot AnMBR despite the identical flux (17LMH). The superior membrane performance might be attributed to low foulants concentrations in mixed liquor at extended HRT and low TMP drop along the fibre in bench AnMBR that resulted in evenly distributed flux along the length of fibre.

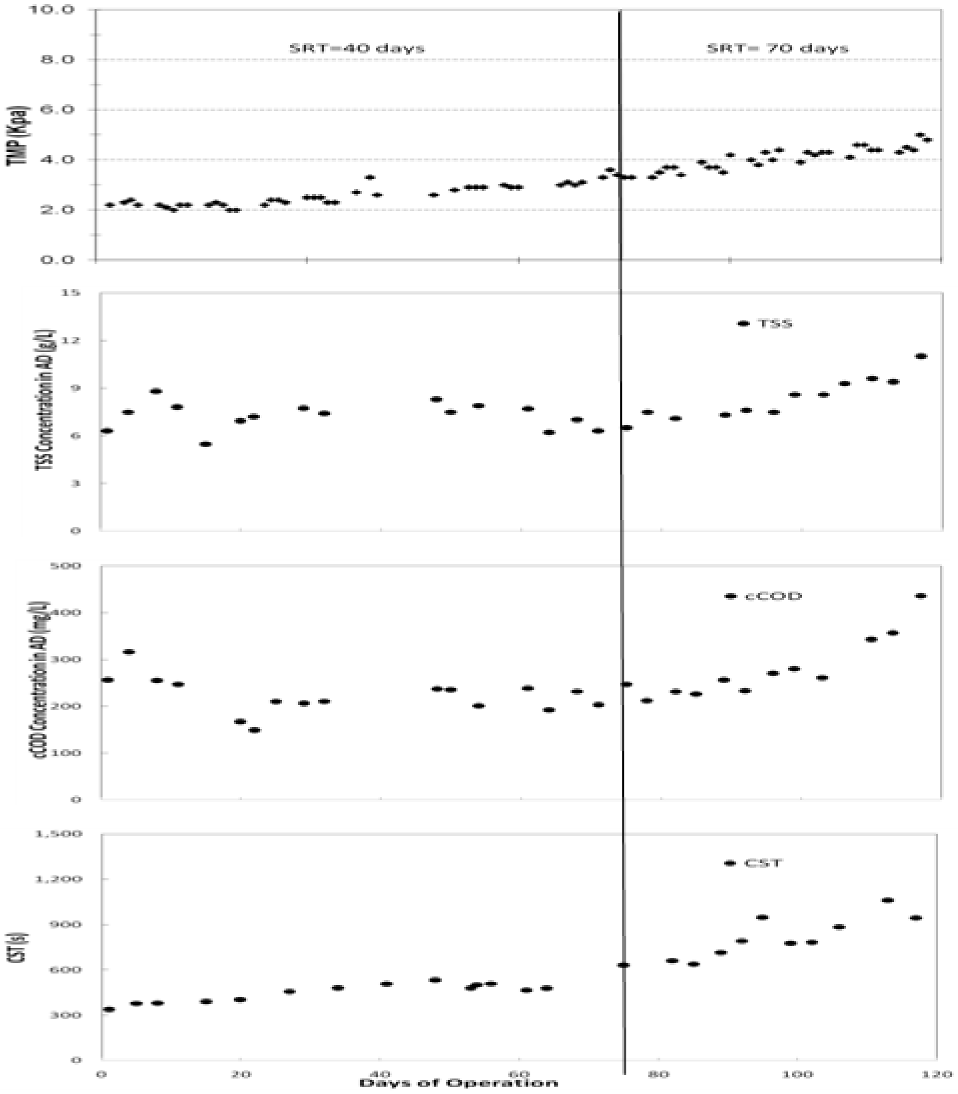

Figure A-2 TMP Profile and Mixed Liquor Characteristics in Bench AnMBR (HRT=12.5h)

A-4. Offline Recovery Cleaning Tests on Loop Apparatus

The offline cleaning study indicated that the use of citric acid and NaOCl resulted in the highest permeability recoveries for the acids and oxidants with values of 31.0% and 30.6% respectively. The chelant EDTA was less effective than either citric acid or NaOCl. In all cases removal efficiencies increased when higher concentrations or longer cleaning periods were employed. For example, the resistance removal efficiencies with 10 mM/L citric acid increased from 18 to 31% when the soaking time was increased from 8 to 16 hours. Increasing the concentration of citric acid from 5 to 10 mM/L with 16 hours of soaking had less of an effect with removal efficiencies of 27 and 31 % respectively. Employing chemical cleanings in series was found to enhance resistance removal efficiency when compared to single applications of individual chemicals. For example, the total resistance removal efficiency with 10 mM/L citric acid followed by 2000mg/L NaOCl reached 53% when the soaking time was 16 hours for both chemicals, while the highest resistance removal efficiencies by the single application of citric acid was 31%. It has been reported that acids and chelants are more efficient to remove organic fouling while oxidants are more efficient for the removal of inorganic fouling (Le-Clech et al., 2006). Therefore chemical cleaning in series can remove both organic and inorganic foulants and result in higher resistance removal efficiency. It is interesting to note that the extent of resistance removal efficiency observed in the bench scale tests was considerably less than that observed when the pilot scale recovery cleaning was conducted. It would appear that the scale of the membrane set-up and the redox condition has an effect on the extent of removal efficiency. Hence, in this case the results of the bench scale testing are useful for comparative studies between cleaners rather than absolute indicators of how larger scale facilities will respond.

Significance: The results of this study provide valuable insight into the cleaning strategies that might be employed to enhance membrane performance in this AnMBR.

Table A-2 Offline Cleaning Results

Chemical	Concentration	Soaking time (h)	Resistance removal (%)
Individual Cleaning			
Citric Acid	10 mM	16	31
		8	17.6
	5 mM	16	27
		8	14
HCl	10 mM	16	13
		8	8.4
	5 mM	16	9.3
		8	7.4
H_2SO_4	10 mM	16	22
		8	18
	5 mM	16	14
		8	10.5
EDTA	10 mM	16	18.1
		8	15.7
	5 mM	16	18
		8	12.2
NaOCl	2000 mg/L	16	30.6
		8	25.3
	1000 mg/L	16	26
		8	22
H_2O_2	2000 mg/L	16	29.7
		8	22.3
	1000 mg/L	16	23.5
		8	20.1
$KMnO_4$	2000 mg/L	16	5.8
		8	3.3
	1000 mg/L	16	3.1
		8	2.8
Sequential Cleaning			
Citric Acid	10 mM	16	53.5
NaOCl	2000 mg/L	16	
NaOCl	2000 mg/L	16	53.7
Citric Acid	10 mM	16	
Citric Acid	10 mM	16	33.9
H_2O_2	2000 mg/L	16	
H_2O_2	2000 mg/L	16	41.3
Citric Acid	10 mM	16	

*Fouled membrane were collected from Pilot AnMBR that operated at a SRT of 70d and HRT of 8.5h for 120 days with addition of $FeCl_3$

A-5. Long-term Membrane Performance of Pilot AnMBR without Addition of $FeCl_3$

The behavior of TMP on pilot AnMBR without $FeCl_3$ addition upon recovery cleaning was consistent with that with $FeCl_3$ addition, however, the extent of fouling was significantly aggravated that resulted in a low operational flux from 12 to 8 LMH.

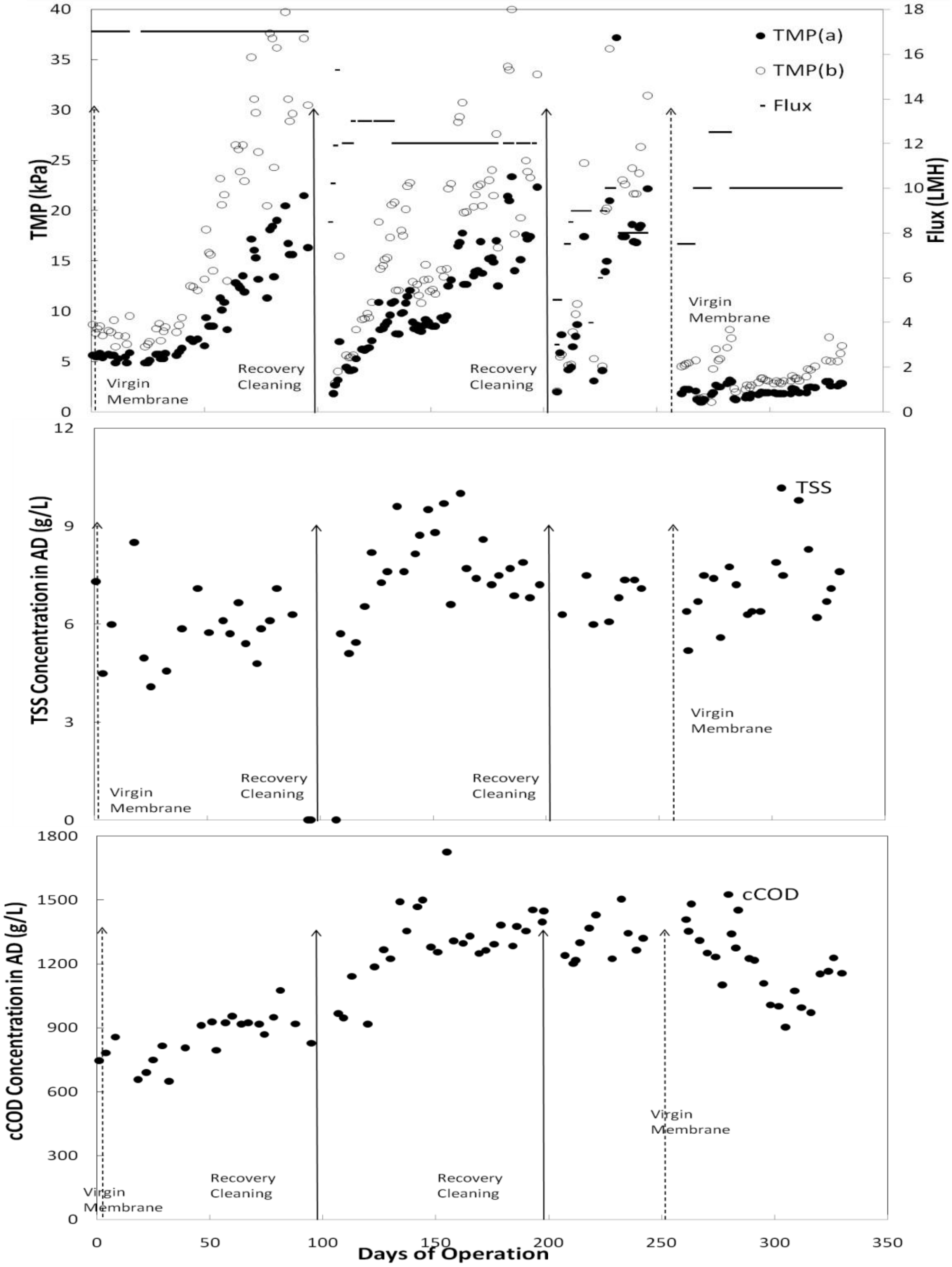

Figure A-3 TMP Profile of Pilot AnMBR without Addition of $FeCl_3$

A-6. SMP and EPS in Pilot AnMBR (Associated with Chapter 4)

The concentration of protein and carbohydrate in SMP corresponded to the concentration of TSS and cCOD that described in Chapter 4. The concentration of protein and carbohydrate in EPS in Phase 3 was significantly higher than Phase 1 and 2 that would enhance the flocculation of particulate and improve the dewaterability which was consistent with CST data.

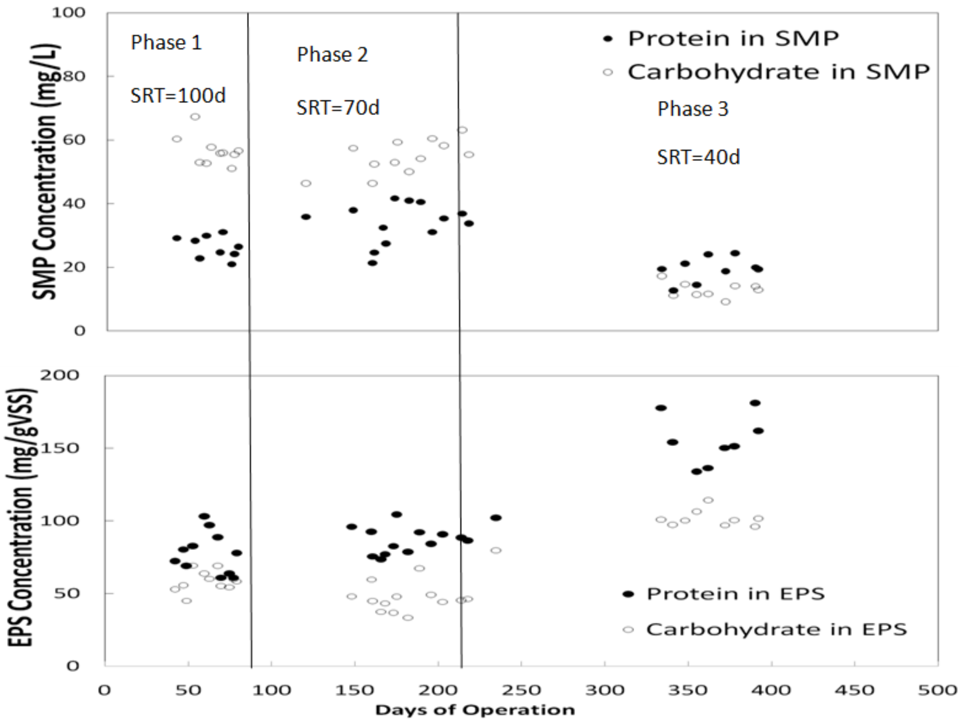

Figure A-4 SMP and EPS Concentration

A-7. Extracted Foulants from Fouled Membrane on Pilot AnMBR (associated with Chapter 4)

Table A-3 Extracted Foulants from Fouled Membrane

	Extracted Foulants (mg/m^2)			
Cleaning order	1st	2nd	3rd	4th
TOC	159	295	353	465
Al	3.3	2.9	4.8	3.6
Ca	65.2	58.4	96.1	86.7
Fe	180	65	854	325
Mg	10.1	8.7	15.8	12.3
S	17.7	16.7	34.9	29.8